"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

S/181/63/005/003/018/046
B102/B180

AUTHOR: Bogdanov, S. V.

TITLE: Experimental criterion of ferroelectricity

PERIODICAL: Fizika tverdogo tela, v. 5, no. 3, 1963, 811-818

TEXT: The author discusses the possibility of classifying ferroelectrics on the basis of specific experimental criteria. Two types are given particular consideration, those with sharp and those with blurred phase transitions. The latter were discovered by G. A. Smolenskiy et al. (FTT 2, 2906, 1960) and show relaxative polarization in a wide temperature range. The phase transition (Curie point or region) and spontaneous, changeable, polarization are common to all ferroelectrics, but the nonpolar (paraelectric) to polar (pyroelectric) phase transition may not be observed with those displaying chemical transformations below the Curie point and, while spontaneous polarization is characteristic of all pyroelectrics, only the ability of changing the sign of P_s being specific for ferroelectrics. It is caused by an applied electric field and indicates the presence of a domain structure which, in its turn, causes the

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nonlinearity of P(E) and ε(E). Ferroelectrics can thus be characterized, below the Curie point, by: a) belonging to the class of pyroelectrics; b) having a domain structure which is c) changed by an electric field; d) hysteresis of P(E) with saturation, P_o and E_{cr} (the points of intersection with the axes) being field-independent; e) nonlinear course of ε(E). Only c) and d) are necessary and sufficient conditions, but even d) is not reliable since saturation is often indistinct and ambiguous. Ferroelectrics with blurred phase transition can be similarly characterized, but with a Curie range in which they show relaxative polarization, i. e. the temperature maxima of ε and tan δ depend not only on the permanent field but also on the variable field frequency, rising with ω. But not even this is a necessary or sufficient condition for this class of ferroelectrics. They can only be classified by the common properties above, together with relaxative polarization, field dependence of the temperature maxima and diffuseness of the structure-sensitive X-ray lines. There are 2 figures.

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

Experimental criterion of ... S/181/63/005/003/018/C46
B102/B180

ASSOCIATION: Fizicheskiy institut im. P. N. Lebedeva AN SSSR, Moskva (Physics Institute imeni P. N. Lebedev AS USSR, Moscow)

SUBMITTED: October 8, 1962

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APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 18949-63 EWT(1)/EWP(q)/EWT(m)/BDS/ES(s)-2 AFFTC/ASD/ESD-3/IJP(C)/
SSD Pt-4 GG/JD

ACCESSION NR: AP3007516 S/0181/63/005/009/2703/2704

AUTHOR: Bogdanov, S. V.; Rassushin, V. A.; Sinkha, D. K.

72
70

TITLE: Relaxation properties of $BaTiO_3$ single crystals containing antimony impurities

SOURCE: Fizika tverdogo tela, v. 5, no. 9, 1963, 2703-2704

TOPIC TAGS: barium titanate relaxation property, single crystal relaxation property, barium titanate single crystal, barium titanate crystal property, barium titanate crystal, barium titanate, relaxation property, barium titanate dielectric property

ABSTRACT: The dielectric constant as a function of temperature was investigated in barium titanate single crystals containing Sb_2O_3 impurities. It was found that 1) the single crystals of barium titanate possess ferroelectric and relaxation properties for certain antimony impurity concentrations; 2) the introduction

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L 18949-63

ACCESSION NR: AP3007516

2

of antimony impurities lowers the Curie point, the effect being well marked at antimony concentrations above 0.01 mol%; and 3) the appearance of a maximum on a curve of dielectric constant versus temperature indicates the presence of relaxation polarization in that temperature region. Dependence of the dielectric constant on temperature was also investigated for temperatures of 120—200C. Orig. art. has: 2 figures.

ASSOCIATION: Fizicheskiy institut im. P. N. Lebedeva AN SSSR, Moscow (Physics Institute, AN SSSR)

SUBMITTED: 06Dec62 DATE ACQ: 14Oct63 ENCL: 00

SUB CODE: PH NO REF SOV: 001 OTHER: 001

Card 2/2

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

KISELEVA, K.V.; BOGDANOV, S.V.

Structure of solid solutions of $SrTiO_3$-$Bi_2O_3 \cdot 3TiO_2$. Fiz. tver. tela 5 no.11:3133-3137 N '63. (MIRA 16:12)

1. Fizicheskiy institut imeni P.N.Lebedeva AN SSSR, Moskva.

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

BOGDANOV, S.V.

Dielectric properties of strontium bismuth titanates. Fiz. tver. tela 5 no.12:3390-3396 D '63. (MIRA 17:2)

1. Fizicheskiy institut imeni Lebedeva AN SSSR, Moskva.

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

BOGDANOV, S.V.; SHIBRYAYEVA, L.S.

Hydroxy derivatives of phenanthrene. Part 3: 1,2-phenanthrenequinone-2-oxime and 3,4-phenathrenequinone-3-oxime. Zhur. ob. khim. 33 no.5:1529-1532 My '63. (MIRA 16:6)

1. Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley.
(Phenanthrenequinone) (Oximes)

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

BOGDANOV, S.V.; SHIBRYAYEVA, L.S.

Hydroxy derivatives of phenanthrene. Part 4: Bisulfite compounds of 4'-sulfonophenylazo-2- and -3-phenanthrols. Zhur. ob. khim. 33 no.5:1532-1536 My '63. (MIRA 16:6)

1. Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley.
(Phenanthrol) (Azo dyes)

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

BOGDANOV, S.V.; SHIBRYAYEVA, L.S.

Hydroxy derivatives of phenanthrene. Part 5: 9.10-Phenanthrenequinone-1,2-furazan and products of its reduction. Zhur.ob.khim. 33 no.6:1978-1979 Je '63. (MIRA 16:7)

1. Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley.

(Phenanthrenequinone) (Furazan)

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

BOGDANOV, S.V.; RASSUSHIN, V.A.; SINKHA, D.K.

Relaxation properties of $BaTiO_3$ single crystals containing antimony. Fiz. tver tela 5 no.9:2703-2704 S '63. (MIRA 16:10)

1. Fizicheskiy institut im. P.N.Lebedeva AN SSSR, Moskva.

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 14846-65 EWT(1)/EWP(e)/EPA(s)-2/EWT(m)/EPF(n)-2/EPA(w)-2/EEC(t)/EWP(t)/EEC(b)-2/EWP(b)/EWA(h) Pab-10/Pt-10/Pu-4/Pl-4/Peb IJP(c)/ASD(a)-5/ASD(m)-3/AS(mp)-2/AFMD(t),
ACCESSION NR: AP4048416 ESD(dp)/ESD(gs)/ S/0181/64/006/011/3372/3377
ESD(t) GG/WD

AUTHORS: Murzin, V. N.; Bogdanov, S. V.; Demeshina, A. I.

TITLE: Dispersion relation and some microscopic characteristics of barium titanate

SOURCE: Fizika tverdogo tela, v. 6, no. 11, 1964, 3372-3377

TOPIC TAGS: barium titanate, dispersion relation, electron polarization, polarizability, dielectric constant

ABSTRACT: The method of W. Cochran (Adv. Phys. v. 8, 387, 1960) is used to analyze the experimental results obtained for $BaTiO_3$ and to derive in explicit form a dispersion relation for the complex dielectric constant of substances with crystal structure of the perovskite type in the cubic state. Allowance is made for the fact that in such crystals the polarization has a complex character, due to the presence of strong local electric fields and to the large

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L 14846-65
ACCESSION NR: AP4048416

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contribution of the electron polarization. In the case of barium titanate, comparison of the calculations with experiment yields estimates for the ion displacements, the total polarizability per unit crystal cell and its ionic components, the values of the local electric fields, and the ion polarizabilities of the atoms. The calculation shows that 65--80% of the total polarization of the crystal is due to electron polarization. "We thank D. G. Sannikov for a discussion of the results of this work." Orig. art. has: 15 formulas and 3 tables.

ASSOCIATION: Fizicheskiy institut im. P. N. Lebedeva AN SSSR (Physics Institute, AN SSSR)

SUBMITTED: 03Dec64 ENCL: 00

SUB CODE: SS NR REF SOV: 007 OTHER: 005

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APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 17125-65 EEC(b)-2/EPF(n)-2/EPA(s)-2/EPA(w)-2/EWA(h)/EWT(1)/EWP(m)/EWG(t)/EWP(b)/EWP(e) Pl-4/Pt-10/Pu-4/Pab-10/Peb AS(mp)-2/SSD(a)/ASD(a)-5/AFWD(t)/ASD(m)-3/ESD(dp)/ESD(c)/ESD(gs)/ESD(t)/IJP(c) GG/WH

ACCESSION NR: AP5000855 S/0181/64/006/012/3585/3593

AUTHOR: Murzin, V. N.; Bogdanov, S. V.; Demeshina, A. I.

TITLE: Transmission and reflection spectra of several titanates in a broad infrared region

SOURCE: Fizika tverdogo tela, v. 6, no. 12, 1964, 3585-3593

TOPIC TAGS: titanate, transmission spectrum, reflection spectrum, ir spectrum, dielectric constant / SVT-227, SVT-802

ABSTRACT: The transmission and reflection spectra of $CaTiO_3$, SVT-227, SVT-802 (solid solutions based on $SrTiO_3$ to which 9.6 and 19.6 mol.% Bi is added), $MgTiO_3Zn_2TiO_4$, $Bi_{2/3}TiO_3$, and barium tetratitanate were measured in the spectral interval 2 -- 1,000μ and in the submillimeter band. The samples were prepared in accordance with the usual ceramic technology. The submillimeter band (2 -- 8 mm) was generated by a klystron. The results have shown that high-frequency normal oscillations are produced in these substances essentially as a result of internal oscillations of the TiO_6 octahedra, while the low-frequency oscillation is connected with the relative dis-

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 17125-65
ACCESSION NR: AP5000655

placement of the Ti and Ba atoms. In all the compounds (except $BaTiO_3$, SVT-202 and SVT-227) the dielectric constant does not depend on the frequency in the range from radio-frequencies up to 500 — 5,000 Gc (the region of infrared resonance). The dielectric constant in this range is therefore due to the oscillations of the crystal-lattice ions. In the case of the polycrystalline $BaTiO_3$ and SVT compounds, a dispersion was observed also at lower frequencies, $\sim 10^9$ cps. The dielectric losses of the polycrystalline $SrTiO_3$, $CaTiO_3$, $MgTiO_3$, $ZnTiO_4$, barium tetratitanate, and $Bi_{2/3}TiO_3$ at microwave frequencies are also completely due to the resonant mechanism connected with the oscillation of their crystal lattices. Orig. art. has: 5 figures, 1 formula and 2 tables.

ASSOCIATION: Fizicheskiy institut im. P. N. Lebedeva AN SSSR, Moscow (Physics Institute AN SSSR)

SUBMITTED: 03Dec63 ENCL: 00

SUB CODE: OP, IC NR REF SOV: 006 OTHER: 004

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APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

ACCESSION NR: AP4030635 S/0048/64/028/004/0636/0642

AUTHOR: Bogdanov, S.V.; Kiseleva, K.V.

TITLE: On the nature of the dielectric properties of $SrTiO_3 \cdot Bi_2O_3 \cdot 3TiO_2$ solid solutions [Report, Symposium on Ferromagnetism and Ferroelectricity held in Leningrad 30 May to 5 June 1963]

SOURCE: AN SSSR. Izv.Ser.fiz., v.28, no.4, 1964, 636-642

TOPIC TAGS: dielectric relaxation, strontium titanate solid solution, bismuth titanate solid solution

ABSTRACT: Solid solutions of up to 9.6% bismuth titanate in strontium titanate were examined by x-ray diffraction at room temperature and liquid nitrogen temperature in search for indications of a phase transition. The investigation was undertaken because of the great difficulties (discussed at some length) encountered in attempting to explain the dielectric relaxation observed in these materials as an effect of a diffuse ferroelectric phase transition. Although the resolution was sufficient to separate structure sensitive lines with a tetrahedral distortion of 0.0011 or a monoclinic or rhombohedral distortion of three minutes of arc, and distortions of one-

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ACCESSION NR: AP4030635

sixth these values could be detected by variations of line width, no deviations from the cubic structure were found. After a further discussion of the difficulties of accounting for the behavior of these materials in a more conventional way, it is concluded that they are representatives of a new class of substances having properties intermediate between those of true ferroelectric materials, and materials showing classic ionic relaxation. The following postulates are adduced to explain the dielectric relaxation of the strontium titanate-bismuth titanate solutions: 1) The dielectric relaxation is due to relaxation of titanium ions within the oxygen octahedra that are distorted by proximity to defects. 2) The concentration of the relaxing quasidipoles is large. 3) The activation energy and dipole moment of a relaxing quasidipole depends on its distance from a defect. 4) The activation energies of the quasidipoles are asymmetrically distributed. The consequences of these postulates are developed, and it is shown (with the aid of plausible assumptions concerning the effects of the dipole-dipole interactions) that they can account for the behavior of the solid solutions. Orig.art.has: 3 figures and 2 tables.

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

ACCESSION NR: AP4030635

ASSOCIATION: Fizicheskiy institut im.P.N.Lebedeva Akademii nauk SSSR (Physical Institute, Academy of Sciences, SSSR)

SUBMITTED: 00 DATE ACQ: 30Apr64 ENCL: 00

SUB CODE: EM NR REF SOV: 011 OTHER: 000

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 25219-65 EWT(1)/EWT(m)/T/EWP(t)/EEC(b)-2/EWP(b) IJP(c) JD

ACCESSION NR: AP5004342 S/0070/65/010/001/0074/0080

AUTHOR: Bogdanov, S. V.; Kiseleva, K. V.; Rassushin, V. A.

TITLE: Effect of bismuth additives on some physical properties of $BaTiO_3$ single crystals

SOURCE: Kristallografiya, v. 10, no. 1, 1965, 74-80

TOPIC TAGS: bismuth additive, barium titanate, bismuth ion behavior

ABSTRACT: The effect of small concentrations of bismuth additive on the structure, dielectric properties, losses, Cury point, and the spontaneous crystallization of $BaTiO_3$ were investigated. It was shown, that two ranges: (1) from 0 to 0.16 atomic % of Bi and above 0.16 atom. % can be separated in the concentration dependency of structural parameters T_k and P_s. The different behavior of the said values in these concentration ranges is linked to different behaviors of bismuth ions in the $BaTiO_3$ lattice. In the second range, relaxation dependencies and tg , related to the electron processes, were disclosed. Probable mechanisms of relaxation processes are also discussed. Orig. art. has: 6 figures and 1 table.

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 25240-65

ACCESSION NR: AP5004342

ASSOCIATION: Fizicheskiy institut im. P. N. Lebedeva (Physics Institute)

SUBMITTED: 12Aug64 ENCL: 00 SUB CODE: IC, SS

NO REF SOV: 010 OTHER: 012

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APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 57031-65 EWT(1)/EWP(e)/EPA(e)-2/EWT(m)/EWP(1)/EPA(w)-2/EEC(t)/EWP(t)/EWP(b)
Pab-10/Pt-7/Pl-4 IJP(c) JD/GG/WH
ACCESSION NR: AP5016113 UR/0048/65/029/006/0896/0900

AUTHOR: Bogdanov, S.V.; Kashtanova, A.M.; Kiseleva, K.V. 61 B

TITLE: Concerning phase transitions in strontium titanate /Report, 4th All-Union Conference on Ferroelectricity, at Rostov-on-the-Don 12-17 Sept 1964./

SOURCE: AN SSSR. Izvestiya.Ser.fizicheskaya,v.29, no.6, 1965,896-900

TOPIC TAGS: single crystal, phase transition, x ray diffraction, double refraction, dielectric constant, strontium compound, titanate

ABSTRACT: The authors have measured the birefringence and dielectric constant of $SrTiO_3$ single crystals at temperatures from 4.2 to 300°K and have examined the diffraction of Fe x-rays by the crystals in order to determine the presence and possible nature of phase transitions in this region. The crystals were grown by the Verneuil technique. Above 118°K the double refraction was small and probably due to strains. Between 112 and 110°K the initial anisotropy of the crystal completely disappeared and the double refraction began to rise rapid-

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L 57035-65

ACCESSION NR: AP5016113

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ly with decreasing temperature. The sudden change in the direfringent properties near 110°K indicates a phase transition corresponding to that found by K.A.Mueller (Arch.sci.10,130,1957) with the electron paramagnetic resonance method. The double refraction ceased to rise with decreasing temperature at 60°K and remained approximately constant from 60° to 20°K. Below 20°K the double refraction suffered large random fluctuations. The sharp bend in the double refraction curve at 60°K indicates the presence of a second phase transition, in agreement with findings of R.S.Krogstad, F.W.Lytle, R.W.Moos and E.B.Moore (Bull. Amer.Phys.Soc.8,470,1963). It is suggested that the fluctuations below 20° are due to a third phase transition; the presence of this transition is also in agreement with the results of Krogstad et al. X-ray diffraction profiles measured at 77°K could not be explained by the frequently assumed tetragonal structure. It is concluded that the structure is pseudomonoclinic with the lattice constants a = c = = 3.8870 Å, b = 3.8988 Å, $\Delta\beta$ = 6'. X-ray diffraction profiles at room temperature revealed a small rhombohedral distortion of the unit cube amounting to two minutes of arc. It is suggested that this distortion may be due to the fact that the crystals were grown at 2000°C. The di-

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L 57035-65
ACCESSION NR: AP5016113

electric constant and loss tangent increased monotonically with decreasing temperature. Since no maxima were found it is concluded that the phase transitions are not ferroelectric transitions. Orig.art. has: 5 figures.

ASSOCIATION: none

SUBMITTED: 00 ENCL: 00 SUB CODE: SS, IC

NR REF SOV: 002 OTHER: 007

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APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 57026-65 EWT(1)/EPA(s)-2/EEC(t)/T/EEC(b)-2 Pt-7/Pi-4/Pl-4 IJP(c) GG

ACCESSION NR: AP5016120 UR/0048/65/029/006/0920/0924

AUTHOR: Murzin, V.N.; Demeshina, A.I.; Bogdanov, S.V.

55
B

TITLE: Vibrational spectra of strontium, barium and calcium titanates /Report, 4th All-Union Conference on Ferroelectricity held in Rostov-on-the-Don 12-18 Sept 1964/

SOURCE: AN SSSR. Izvestiya. Ser.fizicheskaya, v.29, no.6, 1965, 920-924

21

TOPIC TAGS: ferroelectric crystal, barium titanate, calcium inorganic compound, strontium titanate, absorption spectrum, dielectric constant, perovskite structure

ABSTRACT: The infrared transmission and reflection spectra of $CaTiO_3$ were recorded and are compared with the analogous spectra of $SrTiO_3$ and $BaTiO_3$ reported earlier by the authors and by others. The comparison is of interest because all three materials have the perovskite structure but with different symmetries at room temperature. The $CaTiO_3$ transmission spectrum has a doublet with the minimum near 30 microns, and the reflection spectrum has sharper minima than those of

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

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ACCESSION NR: AP5016120

$SrTiO_3$ and $BaTiO_3$. The dielectric constant of $CaTiO_3$ was calculated by the numerical integration method described previously by two of the authors (Fiz.tverdogo tela 6,182,1964). It was found that the degeneracy is partly removed in $CaTiO_3$ and seven resonances were found between 17.9 and 87 microns. The dielectric constants of all three materials were measured at frequencies from 10^3 to 3×10^{14} cycle/sec. The dielectric constants of $SrTiO_3$ and $CaTiO_3$ remained unchanged to about 10^{12} cycle/sec and were determined entirely by lattice vibrations. Additional dielectric dispersion was observed in $BaTiO_3$ near 10^{10} cycle/sec; this is ascribed to domain wall relaxation. The contributions of infrared resonance absorption to the dielectric losses of the three materials were calculated. The dielectric losses of $SrTiO_3$ and $CaTiO_3$ near 10^{10} cycle/sec are due entirely to lattice vibrations. The dispersion equation for the complex dielectric constant of a cubic crystal with the perovskite structure was derived by the method of W.Cochran (Adv.Phys.9,387,1960) in an attempt to elucidate the anomalously high oscillator strength of the low frequency normal vibration. It is concluded that the high oscillator strength is due

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L 57026-65

ACCESSION NR: AP5016120

to induced polarization of the electron shells of the Ti and O ions. Orig.art.has: 6 formulas, 3 figures and 3 tables.

ASSOCIATION: none

SUBMITTED: 00 INCL: 00 SUB CODE: SS,IC

NR REF SOV: 004 OTHER: 005

Card 3/3

APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4"

"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

L 57564-65 EWT(1)/EPA(s)-2/EWT(m)/EEC(t)/T/EWP(t)/EWP(b)/EWA(c) Pt-7/Pl-4 60 59 B
IJP(c) JD/GG

ACCESSION NR: AP5016138 UR/0048/65/029/006/0994/0998

AUTHOR: Bogdanov, S.V.; Kiseleva, K.V.; Matsonashvili, B.N.; Rassushin, V.A.; Sentyurina, N.N.

TITLE: Effect of doping with iron on some physical properties of barium titanate single crystals /Report, 4th All-Union Conference on Ferroelectricity held in Rostov-on-the-Don 12-18 Sept 1964/

SOURCE: AN SSSR.Izvestiya.Ser.fizicheskaya, v.29, no.6, 1965, 994-998

TOPIC TAGS: ferroelectric crystal, barium titanate, doping, iron, crystal structure, phase transition, dielectric constant, electric conductivity, optic absorption

ABSTRACT: The authors have measured the dielectric constant, electrical conductivity and optical transmission of $BaTiO_3$ single crystals containing up to 6 at.% Fe and have investigated the structure of the crystals by x-ray diffraction. At room temperature the structure of crystals containing from 0.48 to 2.6 at.% Fe was tetragonal; crystals containing more than 2.6 at.% Fe were cubic and their lat-

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ACCESSION NR: AP5016138

tice constants were independent of the Fe content. When the temperature was reduced, the (431) reflections from crystals that were cubic at room temperature became broader, while the (222) reflections did not. This broadening was maximum at 243°K, and at 77°K the width of the (431) reflections was practically the same as at room temperature. It is concluded that the structure is tetragonal at 243°K and that a phase transition occurs between 243 and 77°K. The dielectric constants were measured at temperatures from 100 to 530°K. It was found that the Curie point is displaced toward lower temperatures with increasing Fe content. The authors also assert that the dielectric constant maximum corresponding to the 2·m → 3·m transition is displaced toward higher temperatures. Electrical conductivities were measured at temperatures from 100 to 530°K. The plots of the logarithm of the conductivity against the reciprocal of the temperature were straight lines for crystals containing 2.6 at.% or more of Fe and were broken lines for crystals containing 1.84 at.% or less. These curves are analyzed and it is concluded that the Fe impurity atoms form acceptor levels with an ionization energy of 1.5 eV. Optical transmission measurements at

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wavelengths from 0.4 to 2.0 micron showed that the presence of Fe shifts the absorption edge toward longer wavelengths. Three absorption maxima were observed at photon energies of 1.8, 1.5 and 1.1 eV. The 1.8 eV absorption corresponds to ionization of F centers and the 1.5 eV absorption confirms the presence of 1.5 eV acceptor centers. The 1.1 eV absorption is not understood; it is suggested that it may be due to an intra-F center transition. Orig.art.has: 7 formulas and 4 figures.

ASSOCIATION: Fizicheskiy institut im.P.N.Lebedeva Akademii nauk SSSR (Physics Institute, Academy of Sciences of the SSSR)

SUBMITTED: 00 ENCL: 00 SUB CODE: SS, IC

NR REF SOV: 006 OTHER: 018

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L 57561-65 EWT(1)/EPA(s)-2/EWT(m)/EEC(t)/T/EWP(t)/EWP(b)/EWA(c) Pt-7/Pl-4
IJP(c) JD/GG
ACCESSION NR: AP5016139 UR/0048/65/029/006/0999/1000

AUTHOR: Bogdanov, S.V.; Rassushin, V.A.

54
B

TITLE: Regarding the mechanism of appearance of relaxational polarization in barium titanate single crystals doped with antimony /Report, 4th All-Union Conf. on Ferroelectricity held in Rostov-on-the-Don 12-18 Sept 1964/

SOURCE: AN SSSR.Izvestiya.Ser.fizicheskaya,v.29,no.6,1965,999-1000

TOPIC TAGS: ferroelectric crystal, barium titanate, doping, antimony, dielectric constant, relaxation effect

ABSTRACT: The authors and collaborators have previously shown that the dielectric constant of $BaTiO_3$ single crystals containing from 0.3 to 0.6 at.% Sb is frequency dependent at temperatures well above the Curie point and does not follow the Curie-Weiss law (Zh.fiz.tverdogo tela 5,No.9,2703,1963; Kristallografiya 10,74,1965). In order to determine whether the relaxational polarization thus revealed is due to surface barriers at the electrode contacts as was shown by N.P.Bogo-

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roditskiy and L.V.Smirnov (Fiz.tverdogo tela 4,3418,1962) to be the case for rutile, or to polarization of microinhomogenieties distributed throughout the volume of the crystal as discussed by W.A.Weyl and N.A.Terhune (Ceramic Age 62,2,23,1953), the authors have performed the further measurements reported here. The dielectric constants of Sb doped $BaTiO_3$ crystals of different thicknesses were measured at temperatures from 20 to 270°C and at frequencies of 1 and 10 kilocycle/sec. By treating the sample as consisting of three capacitors in series, of which two represent the surface effect and one represents the volume effect, the authors conclude that the capacity will be inversely proportional to the thickness of the sample if it is due to volume effects and that it will be independent of the thickness if it is due to surface effects. The measurements showed that the capacity was approximately inversely proportional to the thickness at temperatures well below the Curie point and that it became approximately independent of thickness at temperatures far above the Curie point. It is concluded that the relaxational polarization is a volume effect at low temperatures and a surface effect at high

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temperatures. In the narrow temperature range from 100 to 120°C the capacity was much less thickness-dependent than at neighboring temperatures on either side of this range. It is suggested that this may be due to the presence in $BaTiO_3$ of a surface layer in which the Curie point is somewhat higher than in the body of the crystal. Orig.art.has: 1 figure.

ASSOCIATION: none

SUBMITTED: 00 ENCL: 00 SUB CODE: SS, IC

NR REF SOV: 006 OTHER: 001

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Structure of the bisulfite compound of nitroso-β-naphthol. The scheme of Bucherer's reaction. S. V. Bogdanov. *J. Gen. Chem.* (U. S. S. R.) 2, 9-22(1932); cf. *C. A.* 23, 2434.—B. concluded that the product (I) of addn. of $NaHSO_3$ to nitroso-β-naphthol (II) has the keto form (III). I is converted to 1,2,4-$C_{10}H_5(NH_2)(OH)SO_3H$ (IV) by boiling with $NaHSO_3$, by treating with SO_2 (Böniger, *Ber.* 27, 23(1894)), or by Zn dust in Na_2SO_3 (Dürwanger, *Diss., Munich* 1912). The mechanism of such a conversion of I to IV is not made clear by these reactions, and is here investigated. IV was prepd. by heating pure I in water with $SnCl_2$ in HCl (or Zn dust and NH_4Cl); this indicates that by the common method of prepn. of the sulfonic acid the sulfonation is caused by the $NaHSO_3$ (primarily combined with II as I) and that the excess of $NaHSO_3$ used in the reaction acts only as a reducing agent. The formula III does not explain the conversion to IV, but becomes clear if the formula V and the scheme $C_6H_4.C(:NOH).CO.CH:CH + NaHSO_3 \longrightarrow VI \longrightarrow V$, in which VI is changed to V by tautomeric rearrangement, are assumed. (Lantz and Mingasson, *C. A.* 25, 5897.) In the detn. of the presence of the CO group in the tautomeric form VI by the action of $NH_2OH.HCl$ on I, there was produced not 1,2,4-naphthoquinone dioxime-$NaHSO_3$ but 1,2,4-$C_{10}H_5(:O)(:NOH)SO_3NH_4$ (VII) (nitroso-Neville-Winter acid) with a good yield (pat. application No. 64,476(1930)). This reaction proves again that the $NaHSO_3$ group in I is in position 4. If the isomeric nitrosonaphthols react with $NaHSO_3$ similarly to II, then the derivs. of α,α-$C_{10}H_5(:NOH)(:O)$ will be represented by the formulas VIII and IX, and those of α,β-$C_{10}H_5(:O)(:NOH)$ by X and XI. Böniger (*l. c.*) obtained 1,2,4-$C_{10}H_5(OH)(NH_2)SO_3H$ by heating α,β-$C_{10}H_6(OH)NO$ with $NaHSO_3$, which corresponds with the formulas X and XI. Vorozhtzov (*C. A.* 10, 2896; 11, 3235) showed that naphthol azo dyes react with $NaHSO_3$ in the quinone-hydrazone form, and he assumed that the addn. of $NaHSO_3$ takes place at the CO group. Of these azo dyes only those react with $NaHSO_3$ which have the azo group in the 1-position and the

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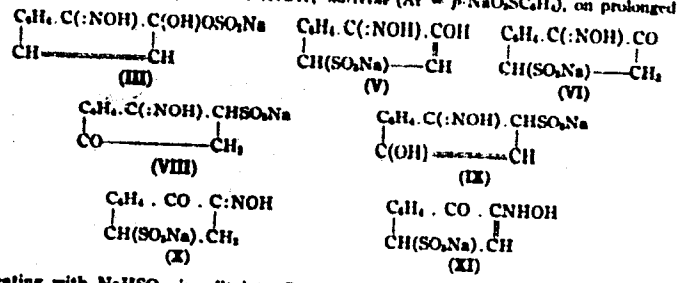
HO group in the 2-position, or the azo group in the 4-position and the HO group in the 1-position, while those with the azo group in the 2-position and the HO group in the 1-position do not react with $NaHSO_3$, these conditions being analogous to nitroso-naphthols. The structure of the bisulfite compds. of azo dyes differs from V only by the substitution of :NNHAr for :NOH; *narceine* (Ar = p-$NaO_3SC_6H_4$), on prolonged



heating with $NaHSO_3$, is split into $C_6H_4(NH_2)SO_3H$ and IV (Bucherer and Stickel, *C. A.* **20**, 195) by analogy with I. In the conversion of naphthols into naphthylamines by heating with NH_4HSO_3 the intermediate products were conceived by Bucherer as sulfonic esters; this was disproved by Vorozhtsov (*C. A.* **18**, 3374) who showed that they are the products of addn. of $NaHSO_3$ to which he ascribed the keto-bisulfite structure. V. and Kasatkin (*C. A.* **23**, 2433) isolated such a product of addn. of 1 mol. $NaHSO_3$ to 2,1-$C_{10}H_6(OH)SO_3Na$ (Tobias acid), while Fuchs (*C. A.* **16**, 2860; **21**, 582) sepd. the bisulfites of 1,2-, 1,4-, 1,5- and 2,5-$C_{10}H_6(OH)_2$. Thus, according to V., Bucherer's reaction may be formulated in the case of the conversion of β-$C_{10}H_7OH$ to β-$C_{10}H_7NH_2$ as follows: β-$C_{10}H_7OH \longrightarrow C_6H_4.CH_2.CO.CH:CH +$

$NH_4HSO_3 \longrightarrow C_6H_4.CH_2.C(OH)(OSO_3NH_4)\ CH:CH + NH_3 - H_2O \longrightarrow$

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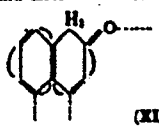
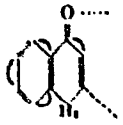
$C_6H_5 \cdot CH_2 \cdot C(NH_2)(OSO_3NH_4) \cdot CH{:}CH - NH_4HSO_4 \longrightarrow C_{10}H_7NH_2$. V. bases the reactivity of naphthols in the keto form on the hypothesis of Thiele: formula XII for β-$C_{10}H_7OH$ and XIII for α-$C_{10}H_7OH$

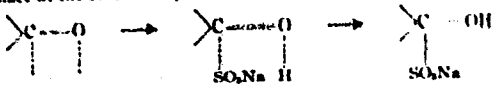


(XII)



(XIII)

In the usual representation of naphthols (and $C_{10}H_8$) there are available 4 partial valencies, while in that of the keto form β-$C_{10}H_7OH$ has 3 and α-$C_{10}H_7OH$ has 2 partial valencies, and from the greater satn. of the keto form V. concludes the possibility of their formation. The addn. of $NaHSO_3$ to the CO group of the ketones and aldehydes must take place at the cost of the partial valencies of the C and O thus:



In the structure of the CO group in the above keto forms of naphthols is found the basic difference from the usual keto group, viz., the absence of the free partial valency at the C bearing the O. A free partial valency in the same nucleus is present only at the C in the 3rd position from the C of the CO, *i.e.*, at the 4-C in β-$C_{10}H_7OH$ and at the 3-C in α-$C_{10}H_7OH$. Thus the addn. of $NaHSO_3$ to naphthols may be represented by the formulas XIV and XV and not by XVI and XVII:

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from AcCl and $AlCl_3$ with II obtained, according to him, 1,2,3,6-$C_6H_3Me(CMe_3)(OMe)Ac$ (IX); this nitrated gave in part I and 1,3,2,4,6-$C_6HMe(OMe)(NO_2)_2Ac$ (X). Because the structure I was conclusively proved by B., it follows that the C_4H_9 group in IX cannot be in the position 6, as this is taken up by the Ac group. Since, however, in the product of nitration of IX is found a considerable amt. of amber musk, as a result of splitting off of the Ac group, therefore the C_4H_9 group in the amber musk (and in II) also cannot be in position 6, *i. e.*, in the *p*-position to the MeO group. Thus is left the only possible structure VIII with the C_4H_9 group in the position 4, and 1,3,4,2,6-$C_6HMe(OMe)(CMe_3)(NO_2)_3$ (XI) for the amber musk. This new formula makes clear why amber musk boils lower than V, and explains without contradiction the results of the work of B. and C. The exptl. data fully support the proposed formulas. *m*-Cresol was nitrated by the method of Staedel and Kolb and Khotinsky and Jacopson (*C. A.* 3, 2947), the isomer 1,3,4-$C_6H_3Me(OH)NO_2$ (XII) was sepd. by steam distn., and converted with Me_2SO_4 to 1,3,4-$C_6H_3Me(OMe)NO_2$ (XIII) (Reisert, *Ber.* 31, 397(1898); Fischer and Rigand, *Ber.* 35, 1259(1902); Khotinsky and Jacopson, *l. c.*); XIII was reduced to 1,3,4-$C_6H_3Me(OMe)NH_2$ (XIV), and converted by the Sandmeyer method to 1,3,4-$C_6H_3Me(OMe)Br$ (XV). A part of XV treated with CO_2 in Et_2O gave 1,3,4-$C_6H_3Me(OMe)COOH$ (XVI) identical with Schall's Me ether of homosalicylic acid (*Ber.* 12, 839(1879)). The bulk of XV was made up into the Mg compd. in Et_2O and treated with *tert*-BuBr producing II identical with that obtained by the Friedel-Crafts synthesis; this when nitrated gave light yellow plates with strong musk odor, m. 85°, which, mixed with various samples of com. amber musk, showed no depression of the m. p. Thus is conclusively proved that the structure of II is VIII and that of amber musk is XI. It also follows that the configuration of B.'s product obtained from II by the action of AcCl and $AlCl_3$ is 1,3,4,6-$C_6H_2Me(OMe)(CMe_3)Ac$ (XVII) and not IX, and that of its mononitro deriv. is either 1,2,3,4,6-(XVIII) or 1,5,3,4,6-$C_6HMe(NO_2)(OMe)(CMe_3)Ac$ (XIX), of which XVIII is most probable because in the nitration of II the NO_2 groups always entered the ring in even positions (2-, 4- or 6-). In addn. to amber musk, III and IV sepd. by B. from the product of nitration of II, Z. and D. isolated also 1,3,4,6-$C_6H_2Me(OMe)(CMe_3)NO_2$ (XX), m. 81-2°, and methyl-*tert*-butyl-*p*-quinone, 2,5,1,4-$C_6H_2Me(CMe_3)(:O)_2$ (XXI), m. 90°, which is the structural analog of thymoquinone and resembles it in every way. The formation of by-products depends on the conditions of nitration and solvents used. The formation of XXI affects the yield of amber musk and imparts to it a disagreeable

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odor. The reaction is common with phenol esters which on nitration become rapidly and intensively colored red, blue or green because of the formation of oxonium salts of quinonoid character (Decker and Solonina, *J. Russ. Phys.-Chem. Soc.* 35, 718, 727, 936 (1905); 37, 120(1905); *Ber.* 36, 725, 2880(1903); 38, 64, 720(1905); Kehrmann, *Ber.* 34, 1623(1901); *C. A.* 14, 1999; K. and Decker, *C. A.* 16, 1227). In the nitration of IX there always appeared an intense blue coloration of the liquid which on heating or dilg. changed to red. The colored product was isolated with $HClO_4$ as the perchlorate in dark blue crystals (Meyer and Gottlieb-Billroth, *C. A.* 14, 1533): $Me(MeO)(Me_2C)C_6H_3N(:O):C_6H_2Me(CMe_3):O(MeClO_4).0.5H_2O$, which treated with water gives the red $Me(MeO)(Me_2C)C_6H_3N(:O):C_6H_2Me(CMe_3):O$ (XXII) (Kehrmann and Decker, *l. c.*; D. and Solonina, *l. c.*). XXII boiled with dil. H_2SO_4 is decompd. into XXI and 2,4,5-$Me(MeO)(Me_2C)C_6H_3NHOH$, or its products of conversion. *Exptl. part.*—VIII was obtained (*a*) in 89% yield from isobutylene and VI by the method of German pat. 184,230, crystals from petroleum ether at −10°, m. 23-4°, b_{10} 224°; (*b*) in 5.1 g. yield when 24 g. XV was added to a mixt. of 2.9 g. Mg shavings and a crystal of I in 40 cc. abs. Et_2O, then refluxed 30 min. in a water bath, poured off from the unreacted Mg, 16.4 g. *tert*-BuBr added, the mixt. cooled with ice water, whereby in 2 min. a violent reaction set in with formation of a ppt., the reaction was completed by refluxing 2 hrs. in a water bath, allowed to stand overnight, then decompd. with ice, the ether layer sepd., washed with NaOH, dried with $CaCl_2$, the Et_2O expelled and distd. *in vacuo*, giving 5 g. VI, b_{10} 62-4°, and VIII, b_{10} 92-4°, m. 21-2° (mixed with VIII, m. 23.5-4°, prepd. by the Friedel-Crafts method it m. 22-3.5°). XIII, m. 60°, b_{10} 153°, formed in 48.5 g. yield when a mixt. of 65 g. of the powd. Na salt of XII (dried at 105°) and 52 cc. Me_2SO_4 in 25 cc. of PhMe was refluxed 2 hrs. at 110-20° in an oil bath, then dild. with 10% NaOH, sepd. and distd. *in vacuo*. XIV, b_{10} 100°, prepd. in 92% yield, when 250 cc. of concd. HCl was slowly added to the mixt. of

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48.5 g. XIII and 90 g. of granulated Sn, then heated 1 hr. in a water bath, 180 g. NaOH in 300 cc. H_2O added, distd. with steam, extd. with Et_2O, dried with KOH, the Et_2O expelled, and distd. *in vacuo*; the picrate is decompd. at 198-9°. XV, b_{11} 107-9°, prepd. in 34.8 g. (68%) yield when a mixt. of 32 g. $Cu(SO_4)_2$, 80 g. NaBr, 51 g. Cu shavings and 25 g. H_2SO_4, d. 1.84, in 185 cc. of H_2O was boiled 30 min., then a diazotized soln. of 33 g. XIV was added in a thin stream to the hot soln., refluxed 1 hr., allowed to stand overnight, steam-distd., extd. with Et_2O, washed with aq. NaOH, sepd., dried with $CaCl_2$, the Et_2O expelled, and twice redistd. *in vacuo*. XVI, m. 103-4°, obtained in 2 g. yield when the Mg compd. from 7.5 g. XV, 0.9 g. Mg shavings and 25 cc. Et_2O were treated 3 hrs. with anhyd. CO_2, then the ppt. decompd. with ice and 15 cc. of 15% HCl, extd. with Et_2O, the Et_2O distd. off, the residue shaken well with Na_2CO_3, the insol. part extd. with Et_2O, the alk. extn. made acid to Congo paper, filtered off, and recrystd. from hot H_2O. XI, m. 84-5°, prepd. when 3.1 g. VIII in 7 g. Ac_2O at −5° was mixed dropwise with agitation with 12.5 g. HNO_3 (d. 1.51), then the mixt. was poured on ice, extd. with Et_2O, washed with aq. Na_2CO_3, dried with $CaCl_2$, the Et_2O expelled, distd. *in vacuo*, the fraction b_{14} 170-205°, was dissolved in 15 g. of hot alc., pptg. a mixt. of 2 types of crystals, which were sepd. by sifting and recrystd. separately from alc., producing plates of XI and yellow needles of IV, m. 101°. XXI, m. 90°, was obtained in 4.5 g. yield by adding 280 g. HNO_3 (d. 1.4) to 20 g. pure VIII in 40 cc. of C_6H_6 with mech. agitation and cooling with ice water; the agitation was continued another 30 min., then dild. with H_2O, the C_6H_6 layer sepd., washed with H_2O, dried with $CaCl_2$, the C_6H_6 distd. off, and the residue distd. *in vacuo*, giving 2 fractions b_{14} 135-45 and 145-70°. The 1st fraction, steam-distd. and recrystd. from alc., produced 4.8 g. XXI, yellow plates with sharp odor, mol. wt. 0.1984 in 21.20 g. of C_6H_6 (K = 50): Δ 0.217°. The 2d fraction recrystd. from hot alc. gave 9 g. XX, m. 81-2°, which nitrated with HNO_3 (d. 1.51), at −5° gave XI and V. 2,5,1,4-$C_6H_3Me(CMe_2)(OH)_2$ (XXIII), m. 122-3°, was prepd. in 0.5 g. yield by refluxing 1 hr. a mixt. of 2.8 g. XXI in 25 cc. C_6H_6 and 8 g. $PhNHNH_2$ in 25 cc. C_6H_6, then the product was washed with 10% HCl, the C_6H_6 distd. off *in vacuo* and recrystd. from $CHCl_3$. Quinhydrone, $C_6H_4O_2.C_6H_4(OH)_2$, m. 116°, was obtained by mixing 1.4 g. XX with 1.4 g. XXIII in little $CHCl_3$, and allowing to crystallize. II, *Ibid.* 472-7. Darzens and Levy (*C. A.* 25, 5408) dispute the structures I for amber musk and 1,2,3-$C_6H_3Me(CMe_2)OMe$ (XXIV) (B., *l. c.*) and VII (Kerkhoff, *C. A.* 23, 1887) for II. By using pure Me_4CCl and little $AlCl_3$ they obtained II, m. 23.4°. From the low m. p. of II they

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conclude that the C_4H_9 group must be in the *p*- and not the *o* position to the OMe group (as in I, XXIV and VII). By the action of the Mg compd. of $1,3,6\text{-}C_6H_3Me(OMe)Br$ (XXV) and Me_3CBr they prepd. $1,3,6\text{-}C_6H_3Me(OMe)CMe_3$ (XXVI), m. 23.4°, identical with that obtained by the Friedel-Crafts synthesis, which produced with HNO_3 the amber musk, m. 85°, and with AcCl the Ac deriv. m. 91° (B., *l. c.*). The strong odor of amber musk is explained by the influence of 2 NO_2 groups in the *o*-positions to the OMe group. The findings of D. and L. are here disputed. In the 1st investigation it was conclusively proved that the *tert*-Bu group in II is in the *o*-position to OMe (Kerkhoff, *l. c.*). The formation of blue oxonium salts in the nitration of II also precludes the *p*-position of the C_4H_9 (Meyer and Gottlieb-Billroth, *l. c.*). II, obtained with *tert* BuCl and $AlCl_3$ and purified by freezing, m. 23-4° and not 23.4°. In order to trace the error, the work of D. and L. was carefully repeated following their inadequate data. The bromo-*m*-cresol used by D. and L. proved to be as claimed $1,3,6\text{-}C_6H_3Me(OH)Br$ (XXVII), this was converted to XXV and then to $1,3,6\text{-}C_6H_3Me(OMe)CO_2H$ (XXVIII), m. 176° (Schall, *l. c.*). From the Mg compd. of XXV in Et_2O and *tert*-BuCl was obtained XXVI different from VIII prepd. by Friedel-Crafts synthesis. VIII b_{16} 94-6° and m. 22-3° while XXVI b_{16} 102-4° and m. 6° (purified by 2 freezings). By nitration of XXVI was obtained $1,3,6,2,4\text{-}C_6HMe(OMe)(CMe_3)(NO_2)_2$ (XXIX), m. 111°, possessing a very faint musk odor, and a mono-nitro deriv., m. 82-3°, with no musk odor and different from XIII with which it gives considerable depression of the m. p., its probable structure being $1,3,4,6\text{-}C_6H_3Me(OMe)(NO_2)CMe_3$ (XXX). The formation of II (VIII) and the amber musk by the method of D. and L. is not clear, neither is the isolation by them in the process of a mono-nitro compd. m. 72°, which could not be obtained in the prepn. of the amber musk and by nitration of XXVI. The assertion that the odor of the amber musk is conditioned by 2 NO_2 groups in *o*-positions to the OMe group is contradicted by the fact that the isomeric musk XXIX smells more faintly than the amber musk XI. *Exptl.*

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part. **XXVII**, m. 61-2° (D. and L. 63°) was obtained in 130 g. yield by adding dropwise with stirring 178 g. Br in 180 g. of 100% AcOH to 120 g. of ice-cold *m*-cresol in 600 g. of 100% AcOH, then pouring into ice water, extg. with Et_2O, washing with H_2O, drying with Na_2SO_4, evapg. the Et_2O, distg. *in vacuo* and recrystg. from petroleum ether. **XXV**, b_{11} 117-9° (D. and L. give b_{11} 112°), was obtained in 115 g. yield when 87 g. Me_2SO_4 was slowly added to 124 g. **XXVII** in 340 cc. of 2 *N* KOH, then 75 of KOH added, refluxed 2 hrs. in a water bath, extd. with Et_2O, dried with Na_2SO_4, the Et_2O evapd. and distd. *in vacuo*. **XXVIII**, m. 170°, prepd. when the Mg compd. (from 20.1 g. of **XXV**, 2.4 g. of Mg shavings, a crystal of I and 50 cc. of Et_2O) was satd. 2.5 hrs. with dry CO_2 with ice-cooling, then decompd. with ice and 10% HCl, filtered and recrystd. from alc. **XXVI**, b_{11} 102-4°, obtained in 12 g. yield when 41.7 g. of *tert*-BuCl was added to the Mg compd

from 10 g. **XXV**, 10.7 g. of Mg, I and 200 cc. of abs. Et_2O, the reaction allowed to subside (2 hrs.), then refluxed 3 hrs. in a water bath, decompd. with ice and 10% HCl, the ether layer sepd., the aq. layer extd. with Et_2O, the 2 exts. combined, dried with $CaCl_2$, the Et_2O expelled, fractionated 7 times *in vacuo*, giving *m*-MeC_6H_4OMe, b_4 57-60°, and **XXVI**, which was cooled with ice, filtered cold, twice frozen out, m. 6°. **XXIX**, m. 111°, obtained in 2.5 g. yield when 40 g. HNO_3 (d. 1.51), and 10 g. **XXVI** in 14 g. Ac_2O were poured separately but at the same time into 9 g. of Ac_2O at −10° with agitation (no blue coloring of the reaction liquid was observed), then poured on ice, filtered off, washed with H_2O, steam-distd. and recrystd. from alc. The alc. mother liquors from **XXIX** were combined, freed from alc., and distd. at 13 mm., the fraction b_4 160-75° was dissolved in alc. and allowed to stand several days at −2-10°, pptg. 0.15 g. of **XXX**, m. 82-3°.

CHAS. BLANC

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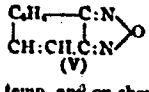
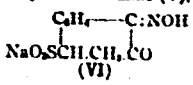
CA

10

Structure of the bisulfite compound of nitroso-β-naphthol. S. V. Bogdanov. *J. Gen. Chem.* (U. S. S. R.) 2, 770-6(1932); cf. *C. A.* 26, 5207.—Previously it was shown that the bisulfite compd. (I) of nitroso-β-naphthol gives with $NH_2OH.HCl$ not the expected 1,2,4-naphthoquinone dioxime-$NaHSO_3$ (II) but 1,2,4-$C_{10}H_4(:O)(:NOH)$-SO_3NH_4 (III). By the neutralization of the HCl of $NH_2OH.HCl$ with AcONa in the reaction there is obtained $C_{10}H_4(:NOH)_2.H_2SO_3$ (IV), which, heated in alk. medium and steam-distd., is converted to the anhydride of 1,2-naphthoquinone dioxime (V), while



(V)



(VI)

at a lower temp. and on shorter heating is formed 1,2-$C_{10}H_6(:NOH)_2$ (VII), which on heating with NaOH is converted to V (Goldschmidt, *Ber.* 17, 801; G. and Schmidt, *Ibid* 17, 209(1884); Kehrmann and Messinger, *Ibid* 23, 2816(1890); Brömme, *Ibid* 21, 391(1888)). V and VII can also be prepd. directly from the reaction mixt. obtained by boiling I with $NH_2OH.HCl$ and AcONa. The easy cleavage of the H_2SO_3 group from IV with alkalies indicates the close similarity of IV to I and that the particle VII may possibly form the basis of the mol. of I; thus by proceeding from the structural formula VI (of the 2 previously proposed for I), the new compd. IV could be considered as identical with II, which was expected in the interaction of I with $NH_2OH.HCl$ in an acid medium. IV, introduced into boiling concd. HCl, produced III, which partly substantiates the previous hypothesis that in the reaction of I with $NH_2OH.HCl$, II is the first intermediate product. *Prepn. of* II.—A mixt. of 11.08 g. I in 150 cc. H_2O, 6.53 g. cryst. AcONa (20% excess) and 3.06 g. $NH_2OH.HCl$ (10% excess) was gently boiled 30 min. (when a sample of the red reaction mixt. produced with NaOH no green ppt. of nitroso-β-naphthol), then filtered, the filtrate evapd. to 25 cc., filtered again, washed with 20 cc. H_2O, cooled with ice, treated with 6 cc. HCl (d. 1.19), let stand 3 hrs., the ppt. filtered off, washed with 15 cc. cold H_2O, dried over H_2SO_4, pwd., refluxed 1 hr. with shaking

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with 175 cc. alc., cooled, filtered and washed with 60 cc. alc., giving 14.15 g. crude II; g. II in 40 cc. H_2O was dissolved with 2.3 g. $NaHCO_3$, filtered, pptd. with 3 cc. HCl (d. .19), filtered again, washed with 4 cc. HCl in 40 cc. H_2O and then with alc. and air-dried, producing 6.6 g. II, pale yellow, microscopic prisms. The alc. ext. from the crude II contained some 1,2,4-$C_6H_3(OH)(:NOH)SO_3H$, V and VII. *Prepn. of* VII.—A soln. of 8.1 g. II in 100 cc. H_2O with 3 g. $NaHCO_3$ was treated with 15 cc. concd. NaOH, then heated to 68°, rapidly cooled and poured into 30 cc. HCl in 200 cc. H_2O, filtered, washed with H_2O and air-dried, yielding 5.21 g. crude VII; it was freed from V when 8.1 g. was dissolved in 350 cc. cold H_2O with 11 cc. NaOH (40° Bé.), filtered, washed, the filtrate pptd. with HCl, filtered again; the yellow needles from a boiling mixt. of 75 cc. alc. and 50 cc. H_2O, m. 152–4° (decompn.) (G. and S., *loc. cit.* 149°; K. and M., *loc. cit.*, 180–1°). *Prepn. of* V.—(1) A mixt. of 1.5 g. II in 35 cc. satd. Na_2CO_3 and 30 cc. alc. was refluxed 1 hr., let cool and filtered, giving 0.65 g. V; (2) a mixt. of 4.60 g. VII in 50 cc. alc., 50 cc. H_2O and 10 cc. NaOH (40° Bé.) was refluxed 2 hrs., then rapidly cooled, filtered, the ppt. washed with a little dil. alc. and then with H_2O, giving 3.84 g. V, colorless crystals from dil. alc., m. 79–9.5°. *Prepn. of* III.—II (8.1 g.) was introduced in small portions with stirring into 160 cc. steadily boiling concd. HCl, then boiled 15 min. longer, the vol. being maintained by adding H_2O, filtered hot, the small brown ppt. in the funnel washed with 50 cc. hot H_2O, the filtrate allowed to stand, the crude III filtered off, dissolved in 25 vols. of H_2O, and recrystd. from dil. alc., yielding 5.26 g. III, which, oxidized with HNO_3, produced 3.77 g. 1,2,4-$C_6H_3(OH)(NO_2)_2$.

CHAS. BLANC

2y2

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CA

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Catalyst for oxidizing toluene. S. V. Bogdanov and N. S. Lemov. Russ. 38,883, Sept. 30, 1934. A catalyst for vapor-phase oxidation of PhMe is prepd. by reduction of higher oxides of V, Mo or their mixt. with metal and acid and distributing the reduction product, or a mixt. of it with unreduced oxide, on a carrier.

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Synthesis of 2,3-dimethoxyaniline. S. Vr. Bogdanov and V. A. Ivanova. *Anilinokrasochnaya Prom.* 4, 7-13 (1934).—The results of the exptl. study of the existing methods of production are discussed. Twenty-one references. Chas. Blanc

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3RD AND 4TH ORDERS

10

Nitroso compounds of the naphthalene series. S. V. Bogdanov, I. I. Levkoev and V. V. Durmashkina. *Azalinokrasochnaya Prom.* 4, 70-6(1934).—The study of the o-aminonaphthols and their derivs. was begun with the production of hydroxynitroso compds. The NO compds. of α- and β-$C_{10}H_7OH$, 2,6- and 2,7-$C_{10}H_6(OH)_2$, 2,4-, 2,5-, 2,6- and 2,7-$HOC_{10}H_6SO_3H$, 2,3,6-, 2,3,7- and 2,5,7-$HOC_{10}H_5(SO_3H)_2$, 1,2-, 1,4- and 1,5-$HOC_{10}H_6SO_3H$, and 1,3,6-, 1,3,8- and 1,4,8-$HOC_{10}H_5(SO_3H)_2$ were prepd. by the common method of acidifying with HCl a soln. or suspension of a compd. mixed with $NaNO_2$. The formation of red or violet by-products with β-naphtholsulfonic acids (Nietzki and Knap, *Ber.* 30, 187) is avoided by carrying on the reaction at 2-5° and introducing HCl below the surface of the liquid. β-Naphtholdisulfonic and α-naphtholsulfonic acids give no colored by-products and can be acidified at 5-8°. 1,3-$HOC_{10}H_6SO_3H$ acts sluggishly, requiring a temp. of 8-10° and 15-20% excess of $NaNO_2$. The nitrosonaphtholsulfonic acids usually form stable ppts. which can be recrystd. from hot H_2O. β-$C_{10}H_7OH$ gives only 1,2-$ONC_{10}H_6OH$, while α-$C_{10}H_7OH$ gives 1,2- and 1,4-$HOC_{10}H_6OH$, the sepn. of which is based on the different solubilities of their bisulfite compds. (cf. Voroshtsov and B., *C. A.* 23, 2434; U. S. S. R. pat. 14,000). The little known 2,4-$HOC_{10}H_6SO_3H$, obtained from 1,2,4-$ClN_2C_{10}H_5(OH)SO_3H$ by reduction with $Sn(ONa)_2$ or Na_2S (cf. Marschalk, *C. A.* 24, 106), produced a new NO compd. with a highly mobile SO_3H group, in which it resembles 1,2-naphthoquinone-4-sulfonic acid. It gives with aq. $PhNH_2$ at room temp. 1,2,4-$ONC_{10}H_5(OH)NHPh$ and on boiling with dil. alkalies 1,2,4-$ONC_{10}H_5(OH)_2$. Some NO derivs. of α-$C_{10}H_7OH$ were prepd. by special methods. B. (*C. A.* 27, 2084; U. S. S. R. pat. 21,130) showed that the bisulfite compd. of 1,2-$ONC_{10}H_6OH$ with aq. $NH_4OH.HCl$ gives 1,2,4-$HOC_{10}H_5(NO)SO_3H$, from which can be prepd. the difficultly obtained 1,2,4-$HOC_{10}H_5(NH_2)SO_3H$. Similarly the bisulfite compds. of 1,2,6- and 1,2,7-$ONC_{10}H_5(OH)SO_3H$ with NH_4OH produced, resp., 1,2,4,6- and 1,2,4,7-$HOC_{10}H_4(NO)(SO_3H)_2$. The reaction evidently is caused by the rearrangement of the NO group and the fixation of the labile bisulfite group as an SO_3H group in position 4. o-Aminonaphtholsulfonic acids with NH_4OH give also only the β-nitroso compds. of α-naphthol derivs. regardless of the original positions of OH and NH_2 groups in the ring. Thus 1,2,4-$H_2NC_{10}H_5(OH)SO_3H$ and 1,2,4-$HOC_{10}H_5(NH_2)SO_3H$ gave 1,2,4-$HOC_{10}H_5(NO)SO_3H$, 1,2,5-$H_2NC_{10}H_5(OH)SO_3H$ and 1,2,5-$HOC_{10}H_5(NH_2)SO_3H$ gave 1,2,5-$HOC_{10}H_5(NO)SO_3H$. Analogously 1,2,6,7- and 1,2,6,8-$H_2NC_{10}H_5(OH)(SO_3H)_2$ gave, resp., 1,2,6,7- and 1,2,6,8-$HOC_{10}H_4(NO)(SO_3H)_2$, and 1,2,7,4-$H_2NC_{10}H_5(OH)SO_3H$ gave 2,1,7,4-$ONC_{10}H_4(OH)SO_3H$. While 1,2,4-$C_{10}H_5(NH_2)SO_3H$ does not react with NH_4OH, 1,2,5-$C_{10}H_5(NH_2)SO_3H$, as well as 1,2,5-$H_2NC_{10}H_5(OH)SO_3H$ and 1,2,5-$HOC_{10}H_5(NH_2)SO_3H$, with 2 mols. of NH_4OH gave 1,2,5-$HOC_{10}H_5(NO)SO_3NH_4$.

Chas. Blanc

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3RD AND 4TH ORDERS

10

C.A

The action of hydroxylamine on certain naphthalene derivatives. S. V. Bogdanov and I. I. Levkoev. *J. Gen. Chem.* (U. S. S. R.) 4, 1353-8(1934); cf. *C. A.* 27, 2684.—A mixt. of 5.54 g. nitroso-β-naphthol bisulfite compd. and 4.8 g. 1,2,4-aminonaphtholsulfonic acid (II) was slowly added to 5 g. $NH_2OH.HCl$ (I) and 1 cc. concd. HCl in 150 cc. boiling H_2O. The boiling was continued for 10 min. On cooling, 10.83 g. of NH_4 2,1,4-nitrosonaphtholsulfonate (III) crystd. Similar treatment of II with I gave 87% of III. With 2,1,4-aminonaphtholsulfonic acid instead of II, the yield of III was approx. the same. No reaction occurred between 1,2,4-naphthalenediaminesulfonic acid and I; while the 1,2,8-isomer formed an unknown nitroso compd., and the 1,2,5-isomer formed NH_4 2,1,5-nitrosonaphtholsulfonate. B. Soyenkoff

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3RD AND 4TH ORDERS

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BC

Action of hydroxylamine on the hydrogen sulphite [illegible] of 1-nitroso-2-naphthol-6- and 7-[illegible] [illegible] and I. I. [illegible] [with V. V. Durmaschkina] (J. Gen. Chem. [illegible]) — $NaHSO_3$ is added to an aq. [illegible] of Na 1-nitroso-2-naphthol-6-sulphonate [illegible] of the latter, when HCl [illegible] HCl [illegible] to yield a ppt. of Na [illegible] (III) (75% yield). (III) is also obtained by the action of HCl on the dioxime of 1 : 2-diketo-1 : 2 : 3 : 4-tetrahydronaphthalene-6 : 6-disulphonic acid, prepared from (I), $NaHSO_3$, and (II) in presence of NaOAc in neutral aq. solution, and converted by NaOH into the Na salt of the dioxime of 1 : 2-naphthaquinone-6-sulphonic acid, the anhydride of which is described. Under analogous conditions, the 7-sulphonic acid corresponding with (I) affords the 4 : 7-disulphonic acid analogue (IV) of (III). The constitutions of (III) and (IV) are established by comparing the products of reduction with the corresponding synthetically prepared aminonaphtholdisulphonic acids. R. T.

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Cu

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2-Naphthol-1-sulfonic acid. S. V. Bogdanov. Russ. 42,[illegible], July 31, 1936. β-Naphthol is treated at a temp. of 130° in an aq. or aq. alc. medium with sulfites in the presence of heavy metal oxides, for example CuO or MnO_2.

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CA

10

Sulfonation and sulfonic acids. S. V. Bogdanov. *Org. Chem. Ind.* (U. S. S. R.) 1, 678-85(1936).—A discussion of the theory and practice of the sulfonation of aromatic compds., with about 70 references. Chas. Blanc

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CO

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Sulfuration with salts of sulfurous acid. I. The Piria reaction. S. V. Bardamov and S. A. Khelfets. *J. Gen. Chem.* (U. S. S. R.) 7, 911-16(1937).—Aromatic NO_2 compds. with sulfides are reduced to sulfaminic (I) and aminosulfonic acids (II), the relative amts. of which, according to Weil and Moser (*C. A.* 16, 3075), remain const. for any nitro compd. To det. the validity of this, B. and Kh. study the reduction of $PhNO_2$ (III) and of *p*-$MeC_6H_4NO_2$ (IV) with $NaHSO_3$ (V), under varied exptl. conditions. The use of neutral V (exactly neutralized with NaOH) retards the rate of reduction. V, contg. excess NaOH (33%), with III, results in even slower reaction, which with IV is completely stopped. In addn., neutral and alk. V with III give secondary products. Neutral V with III gives considerable $PhNHSO_3H$ (VI) (opposed to Weil, Ger. pat. 151,134) and with IV gives not only *p*-$MeC_6H_4NH_2$, but also *p*-$MeC_6H_4NHSO_3H$ (VII) (opposed to Walter, Ger. pat. 109,487). V, neutralized 25%, with III gives 57% VI and with IV 73.7% VII. The ratio of I to II is independent of the reaction time (1-10 hrs.), practically independent of the concn., but is not const. for any one nitro compd., the amt. of II increasing steadily with increased alky. The reaction is postulated to proceed with the intermediate formation of NO and NHOH compds., unstable under the exptl. conditions used. Twelve references. John Livak

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BC

A3

Action of hydroxylamine on certain naphthalene derivatives. S. V. Bogdanov and I. I. Levkoev (J. Gen. Chem. Russ., 1937, 7, 1530—1542).—1-Amino-2-naphthol-6-, -7-, or -8-sulphonic acid and NH_4OH in boiling 1% HCl yield NH_4 2-nitroso-α-naphthol-6-, -7-, or -8-sulphonate. R. T.

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sulfuration with salts of sulfurous acid. II. Simultaneous oxidation of β-naphthol and sodium sulfite. S. V. Bogdanov and V. A. Ivanova. *J. Gen. Chem.* (U. S. S. R.) 7, 2884-93(in English 2894)(1937); cf. C. A. 31, 5777[6].—Oxidation of a mixt. of β-naphthol (I) and Na_2SO_3 (II) in H_2O by means of CuO in an autoclave at 100-180° leads to the formation of 2-naphthol-1-sulfonic acid (III) and products of oxidation of naphthol. Addn. of alkali to the reaction mixt. raises considerably the yield of III, at the expense of the oxidation products. Temp. and the concn. of II have little effect on yield of III. Substitution of MnO_2 for CuO, in a neutral medium, results in complete change of I into III. In a neutral medium CuO changes β-naphthol into β-binaphthol, but alkali retards this reaction. At 130° oxidation of Na_2SO_3 with CuO or MnO_2 leads to the formation of Na_2SO_4. Oxidation of Na_2SO_3 with air at room temp. is retarded by the presence of I. The formation of III can be represented as a reaction between SO_3^{--} and a product of oxidation of I.

S. I. Madorsky

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ca

Hydrazinonaphthalenesulfonic acids. S. V. Bogdanov, M. Ya. Illyukevich and I. M. Daeva-Stepanenko. Russ. 54,285, Dec. 31, 1938. Diazotized aminonaphthalenesulfonic acids are reduced with zinc dust and HCl to which $SnCl_2$ has been added.

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BC

a3

Sulphonation with sulphites. III. Simultaneous oxidation of sodium sulphite and β-naphthol and its derivatives. S. V. Bogdanov and V. A. Ivanova (J. Gen. Chem. Russ., 1935, 5, 1071—1082).—2 : 3-OH·$C_{10}H_6$·CO_2H and aq. Na_2SO_3 heated with MnO_2 at 100° yield 2-hydroxy-1-sulpho-3-naphthoic acid, and 2 : 6-OH·$C_{10}H_6$·CO_2H similarly yields 2 : 1 (6-OH·$C_{10}H_6$·CO_2H)$_2$; the general reaction is: $RH + Na_2SO_3 + O \rightarrow R{\cdot}SO_3Na + NaOH$. At the same time part of the Na_2SO_3 undergoes oxidation to Na_2SO_4 and $Na_2S_2O_6$, but these reactions are independent of that of sulphonation. The sulphonation reaction ceases with time, owing to increasing [NaOH] of the medium. β-Naphtholsulphonic acids accelerate oxidation of Na_2SO_3 by MnO_2, but retard oxidation by O_2. R. T.

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Sulphonation with sulphites. IV. Oxidation of sodium sulphite in presence of β-naphthol-sulphonic acids. (S. V. Bogdanov. (J. Gen. Chem. Russ., 1939, 9, 1145—1147).—Aq. Na β-naphthol-4- or -7-sulphonate or -3 : 6-disulphonate heated at 85° with Na_2SO_3 and MnO_2 yields, respectively, Na β-naphthol-1 : 4- or -1 : 7-di- or -1 : 3 : 6-tri-sulphonate.

R. T.

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Sulphonation by means of sulphites. V. Formation of β-naphtholsulphonic acids. S. V. Bogdanov [with O. J. Novoshilova] (J. Gen. Chem. Russ., [illegible] 1846—1850).—At 85° the ratio $Na_2SO_4 : Na_2S_2O_6$ = 8 : 1 when 0·5M-Na_2SO_3 is heated [illegible] with MnO_2. In presence of β-naphthol[illegible] acids the oxidation is greatly accelerated [illegible] of Na_2SO_4 rises in presence of acids [illegible] sulphonation [2 : 1 : 6-$OH{\cdot}C_{10}H_6(SO_3H)_3$, [illegible] 6-$OH{\cdot}C_{10}H_6(SO_3H)_3$], and falls with acids undergoing further sulphonation in these conditions [2 : 4-, 2 : 6-, and 2 : 7-$OH{\cdot}C_{10}H_6{\cdot}SO_3H$ and 2 : 3 : 6-$OH{\cdot}C_{10}H_5(SO_3H)_3$]. The yields of Na_2SO_4 + sulphonic acid and of $Na_2S_2O_6$ are const. in all cases, amounting to 76—79 and 21—24%, respectively. The ratio $Na_2S_2O_6$: sulphonic acid is variable. R. T.

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1ST AND 2ND ORDERS

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3RD AND 4TH ORDERS

Cl

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Reducing splitting of azo dyes. S. V. Bogdanov. Russ. 56,305, Jan. 31, 1940. The reducing splitting of azo dyes is effected by means of Zn dust activated with Cu in a NaCl soln.

COMMON ELEMENTS

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Derivatives of oleic acid as capillary-active substances. N. M. Kasatkin and S. V. Boglanov. *Org. Chem. Ind.* (U. S. S. R.) 7, 108-9(1940).—Following the general patent procedures $HO(CH_2)_3SO_3H$, $H_2N(CH_2)_2SO_3H$ (taurine) and $MeHN(CH_2)_2SO_3H$ (methyltaurine) were prepd. and condensed with oleic acid to give Igepon A and Igepon T, resp. The solubilities of the detergents in water, dil. acids, inorg. salts and alkalies are tabulated. C. H.

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1ST AND 2ND ORDERS

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2-Chloro- and 2,6-dichloro-4-nitrophenols. S. V. Bogdanov and S. P. Frenkel. Russ. 50,592, Apr. 30, 1941. p-Nitrophenol is treated with gaseous Cl in aq. H_2SO_4 of various concns.

COMMON ELEMENTS

COMMON VARIABLES INDEX

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3RD AND 4TH ORDERS

1ST AND 2ND LETTER

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1ST AND 2ND ORDER

PROCESSES AND PROPERTIES INDEX

Sulfonation with salts of sulfurous acid. VI. Oxidation of sulfite with aromatic nitro compounds. S. V. Bogdanov. *J. Gen. Chem.* (U. S. S. R.) 13, 584-8 (1943)(English summary); cf. C. A. 34, 4007[illegible]-A

mixt. of 27.4 g. *p*-nitrotoluene, 28.8 g. 2-naphthol and 209.1 g. 48.2% Na_2SO_3 in 600 cc. water was stirred for 19 hrs. at 130°, filtered and the filtrate acidified by HCl, after which the sepd. naphthol was extd. with benzene; evapn. of the aq. soln. gave a mixt. of sulfate and Na salts of 2-naphthol-1-sulfonic acid and *p*-toluenesulfamic acid. In a series of expts. it was shown that with increased degree of neutralization of the $NaHSO_3$, the yield of naphthol-sulfonic acid decreases as does the total yield of amines from the nitrotoluene. *m*-$O_2NC_6H_4SO_3H$, as the Na salt (0.05 *M*), and 0.05 *M* 2,3-$HOC_{10}H_6SO_3H$ were dissolved at 80° in aq. NaOH and boiled for 0.5 hr. to yield 2-hydroxy-1-sulfo-3-naphthoic acid as the Na salt in 37% yield (on starting material). It is thus shown that the products of transformation of sulfurous acid, formed during the reaction of Na_2SO_3 with nitro compds., are capable of sulfonating action. In the presence of sulfonating HO compds., the reaction of nitro compds. with sulfite is reduced in its rate. Apparently, sulfamic acids are not an intermediate in the formation of sulfo-sulfamic acids. **VII. Action of sulfite on 1-diazonaphthalene-4-sulfonic acid.** S. V. Bogdanov and M. A. Smorovskii. *Ibid.* 589-92.—It is shown that the diazo group of 1-diazonaphthalene-4-sulfonic acid can be changed into the hydrazine group by Na_2SO_3, with concurrent formation of 1-naphthylhydrazine-4-sulfonic acid and the 2,4-disulfonic acid. The diazo compd. from 15.9 g. 1,4-H_2N-$C_{10}H_6SO_3H$ was washed with water to neutrality and suspended in water, after which it was treated with an alk. soln. of Na_2SO_3 (from the neutralization of 78 g. 35.4% $NaHSO_3$ by 24.15 g. 44% NaOH, followed by 45 g. $NaHCO_3$), stirred for 2 hrs., acidified by HCl and boiled for 1 hr.; on cooling, there was obtained a ppt. of 8 g. mixed *1-naphthylhydrazine-4-sulfonic acid* and the *acid Na salt of 1-naphthylhydrazine-2,4-disulfonic acid*, sepd. by water extn. and treatment with HCl. G. M. Kosolapoff

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Sulfonation with salts of H_2SO_4. VIII. Action of bisulfite on *m*-nitrotoluene. S. V. Bogdanov. *J. Gen. Chem.* (U. S. S. R.) 13, 797–800(1943)(English summary); cf. *C. A.* 39, 609[illegible].—*m*-Nitrotoluene (0.3 mol.), 1.2 mols. $NaHSO_3$ soln., 0.3 mol. NaOH and 750 cc. water were boiled for 5 hrs., the soln. concd. and cooled to yield *Na salt of m-tolylsulfamic acid;* ice cooling sepd. the sulfate, the filtrate being further evapd. to yield more of the sulfamic deriv., with alternate removals of the sulfate. The final yield of Na salt of *m*-tolylsulfamic acid is 30 g., long needles, which heated with mineral acids regenerate *m*-toluidine. The final filtrate concd. to 100 cc. and treated with alc. gave the *di-Na salt of p-sulfo-m-tolylsulfamic acid*, thin plates exceedingly sol. in water; the latter heated with HCl yields *3-aminotoluene-6-sulfonic acid*, rectangular plates, very difficultly sol. in water; *Na salt*, thin prisms, readily sol. in water, which treated with Br water readily yields tribromo-*m*-toluidine, m. 100–1°.

G. M. Kosolapoff

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Sulfonation by salts of sulfurous acid. X. Oxidation of bisulfite by ferric oxide, lead dioxide, and mercuric oxide. S. V. Bogdanov. *J. Gen. Chem.* (U.S.S.R.) 16, 1535-40(1945)(in Russian); cf. *C.A.* 40, 6450ᵍ.—Oxidation of salts of H_2SO_3 by oxides of Fe, Hg, and Pb in the presence of active HO compds. leads to the formation of sulfonic acids, the sulfonating ability of the bisulfite being detd. by the nature of the oxidizing agent. A boiling soln. of 0.05 mole Na 2-hydroxy-3-naphthoate (I) and 0.24 mole $NaHSO_3$, neutralized with 33% NaOH to the extent of ⅓ of available H, in 100 cc. water treated with 0.1 mole fresh $Fe(OH)_3$ and boiled 1 hr. gave 7.61 g. of the starting material, 0.02 g. more being recovered by Et_2O extn. of the acidified and concd. mother liquor, and 0.17 g. 2-naphthol; evapn. of the mother liquor gave 6.8% mixed (approx. 50:50) 1-sulfo-2-hydroxy-3-naphthoic acid (II) and 2-naphthol-1-sulfonic acid (III). I (0.05 mole) and 0.2 mole 5 *N* $NaHSO_3$ neutralized by NaOH to ⅓ available H, in 100 cc. water, treated at 90° with 23.9 g. PbO_2 and boiled 40 min. with stirring, gave 2.87 g. starting material, traces of 2-naphthol, 3.69 g. II, and 0.49 g. III; when the above reaction was repeated with 0.08 mole PbO_2, 0.1 mole Na_2SO_4, and 0.04 mole Na 2-naphthol-6-sulfonic acid, there was obtained 42.5% 2-naphthol-1,6-disulfonic acid. Repetition of the former expt., using 22 g. red HgO, with a 2-hr. boiling period, gave 44.7% mixed sulfonic acids: 4.03 g. II and 4.015 g. III. Sulfonation in the presence of HgO is caused by the formation of intermediate Hg-contg. sulfites, the decompn. of which leads to sulfonic acids or sulfates. An improved method was devised for the prepn. of Na Hg sulfite: 0.1 mole fresh HgO was suspended in 150 cc. water, treated with 0.05 mole 24% NaOH, followed by 0.2 mole 5 *N* $NaHSO_3$; after addn. of 50 cc. water the mixt. was boiled and filtered hot, to yield, on cooling, 25-26 g. air-stable product, $Hg(SO_3Na)_2.H_2O$, which breaks down, on heating with water, to yield Hg, sulfurous acid, and sulfate. Addn. of 10.7 g. of the above salt to 0.05 mole 2-hydroxy-3-naphthoic acid, 0.013 mole Na_2CO_3, and 125 cc. water at 90°, followed by heating to the b.p. 45 min., cooling to 80° and addn. of 1.35 g. Na_2CO_3 and 10.7 g. Hg complex [illegible] 7.82 g. unreacted acid and 13.9% mixed II and III, the 1st being readily isolated as a relatively insol. acid Na salt, which may be converted to a di-Na salt, sta[illegible] at 100° in distinction from the mono-Na salt. Hg Na sulfite (21.3 g.) dissolved in 300 cc. 1% Na_2CO_3 at 85-90°, filtered, and cooled to 15°, then treated with 200 cc. 50% H_2SO_4, gave 11.1 g. finely cryst. colorless product, which is apparently $HgSO_3.HgSO_4.H_2O$, air-stable for several days. Although this product is also capable of the above sulfonation reaction under conditions similar to those used for the Na Hg salt, the yields are very poor.

G. M. Koonlapoff

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Sulfonating by salts of sulfurous acid. XII. Action of some derivatives of sulfurous acid on aniline. S. V. Bogdanov and N. N. Karandasheva (Ivanovsk Chem. Tech. Inst.). *J. Gen. Chem.* (U.S.S.R.) 17, 57-94 (1947)(in Russian); cf. *C.A.* 41, 6330r.—$PhNH_2$ can be sulfonated by $K_2SO_3.2NO$ (confirming Raschig, *Ann.* 241, 232(1887)), $HON(SO_3K)_2$, and $HgNa$ sulfite. An emulsion of 25 cc. $PhNH_2$ in 200 cc. H_2O with a few drops of phenolphthalein and 7 g. $K_2SO_3.2NO$ with a 185° and treated alternately with small portions of $MgSO_4$ and $K_2SO_3.2NO$ (total: 40 g. and 23 g., resp.); then used to ppt. the Mg, the mixt. was filtered, and the filtrate, after extn. of the $PhNH_2$ with C_6H_6, was evapd. to dryness; extn. with hot EtOH gave K phenylsulfamate ($C_6H_5O_3NSK$) as colorless, water-sol. leaflets. Similarly, 100 g. $PhNH_2$ and 100 g. H_2O were treated with 6 g. $K_2SO_3.2NO$ and a drop of phenolphthalein and heated to boiling with stirring; the generated alkali was neutralized with 0.5 *N* HCl, and the mixt. cooled to 85° and treated with 6 g. $K_2SO_3.2NO$; the process of boiling was repeated until a total of 22 g. $K_2SO_3.2NO$ had been used (3.5 hrs.). After working up as above the mixt. contained, as shown by hydrolysis of an aliquot portion with HCl, 1.52 g. $PhNH_2$ which was converted into the sulfo deriv. Repetition of the procedure at 85° gave 1.02 g. $PhNH_2$ in the sulfonated form. 2-Hydroxy-3-naphthoic acid failed to react with $K_2SO_3.2NO$ at 80-90°. When 0.05 mol. Na 2-hydroxy-3-naphthoate, 78.8 cc. (0.4 mol.) Na_2SO_3, and 25.5 cc. 43% NaOH in 200 cc. H_2O were boiled in a H atm. until the air was displaced, then a slow current of NO was passed in for 12 hrs., there was obtained 8.93 g. unreacted acid, while the analysis of the aq. soln. showed that 0.1 g. of the acid had been transformed into 1-sulfo-2-hydroxy-3-naphthoic acid and 0.50 g. into 2-naphthol-1-sulfonic acid; repetition of the above process, using 8.5 cc. 43% NaOH and a 6-hr. treatment with NO, gave 6.32 g. of a mixt. of unreacted acid and 2-naphthol after acidification; the aq. soln. gave 0.59 g. unreacted acid and 0.81 g. 2-naphthol, while the analysis of the aq. soln. showed that 0.22 g. hydroxynaphthoic acid had been transformed into 1-sulfo-2-hydroxy-3-naphthoic acid and 0.85 g. into 2-naphthol-1-sulfonic acid. $PhNH_2$ (50 cc.), 100 cc. H_2O, and 63.5 g. $HON(SO_3K)_2$ were boiled 40 min. with stirring; after addn. of KOH and extn. with C_6H_6, the aq. layer was treated with AcOH to a slightly alk. reaction and filtered; evapn. gave the above described $PhNHSO_3K$; analysis of the aq. soln. by hydrolysis of an aliquot showed that 4.65 g. $PhNH_2$ was sulfonated. $PhNH_2$ (50 cc.), 100 cc. H_2O, 100 g. KOAc, and 63.5 g. $HON(SO_3K)_2$ were boiled 3 hrs. with stirring; after dilu. with H_2O and extn. with benzene, a part of the aq. soln. was hydrolyzed with HCl and gave 0.3 g. $PhNH_2$; the aq. layer absorbed HNO_2 but the soln. failed to give a test for a diazonium compd. $PhNH_2$ (25 cc.), 100 cc. H_2O, and 21.3 g. $HgNaSO_3$ were boiled 2.5 hrs. with stirring; after separn. from Hg, the mixt. was made alk. by NaOH, extd. with C_6H_6, and evapd. to give some Na_2SO_4, followed by Na phenylsulfamate, water-sol. colorless plates ($C_6H_5O_3NSNa.2H_2O$); addn. of EtOH to the concd. mother liquor gave a ppt. of Na sulfate and sulfite, after the removal of which further evapn. gave a mixt. of inorg. salts and very sol. sulfonation products of $PhNH_2$; since the mixt. could not be sepd., it was boiled with HCl and on cooling gave *o*-anilinesulfonic acid as water-sol. hexagonal plates; its Na salt forms water-sol. rhombic and hexagonal plates; its structure was confirmed by diazotization and conversion to *o*-$ClC_6H_4SO_2NH_2$, m. 187-8° (from EtOH).

G. M. Kosolapoff

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BOGDANOV, S. V.

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BOGDANOV, S. V. I MIGACHEVA, I. B. Nekotoryye Proizvodnyye 2-Naftol-4-Sul'fokis-loty. Zhurnal Obshey Khimii, 1949, Vyp. 8. s. 1490-92.

SO: Letopis' Zhurnal'nykh Statey, Vol. 37, 1949

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BOGDANOV, S. V.

PA 2/50T62

USSR/Chemistry - Sulfonation
Sulfuric Acid Salts

Jul 49

"Sulfonation With Salts of Sulfurous Acid. Sulfonation of 1-Naphthylamine and 1-Naphthol," S. V. Bogdanov, G. I. Pavlovskaya, Ivanovo Chem Eng Inst, 3 3/4 pp

"Zhur Obshch Khim" Vol XIX, No 7

Sulfonated 1-naphthylamine with mercuric sodium sulfite to produce 1-naphthylsulfamino acid, 1,2-naphthylaminosulfonic acid, and 1,4-naphthylaminosulfonic acid in a 9:29:62 ratio. Sulfonation of 1-naphthol with manganese sulfite and dioxide or mercuric sodium sulfite proceeded only to a slight degree, main product being 1,4-naphtholsulfonic acid. Submitted 17 Apr 48.

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BOGDANOV, S. V.

"Derivatives of 2-Naphthol-4-sulphonic acid," S. V. Bogdanov and I. B. Migacheva. Zhur. Obshch. Khim., USSR, 1949, 19, 1490-1492. (U.S. Transl. 1493-1495).

Reduction of 1-diazonaphth-2-ol-4-sulphonic acid with $SnCl_2$ in NaOH yields 2 : 4-OH.$C_{16}H_6$.SO Na (I) (83%), as dihydrate and monohydrate in very sol. cryst. forms. $NaNO_8$ and aq. HCl with I produce 1-nitrosonaphth-2-ol-4-sulphonic acid /Na salt, $C_{10}H_4O_5NSNa$ (II)/. Action of NaOH solution on II gives 1 : 2 : 4-NO.$C_{10}H_5$ (OH)$_2$, m.p. 180°, NH_2Ph and p-toluidine with II give, in aq. solution, 1-nitroso-4-anilino-, m.p. 218 degrees, and 1-nitroso-4-p-toluidino-naphth-2-ol, m.p. 197°, respectively.

Ivanovo Chem. Tech. Inst.

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BOGDANOV, S. V. Doc Chem Sci

Dissertation: "Investigation in the Field of Oxidizing Sulfonation." 27/4/50

Inst of Organic Chemistry, Acad Sci USSR

SO Vecheryaya Moskva
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Sulfonation by salts of sulfurous acid. XIV. Scheme of "oxidative" sulfonation. S. V. Bogdanov and I. B. Migacheva (Ivanov Chem. Technol. Inst.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 124-33(1950); cf. C.A. 42, 1386; 44, 1083c.—Among a group of oxidizing agents, including iodine, H_2O_2, K persulfate, $AgNO_3$, $FeCl_3$, and $CuSO_4$ used in conjunction with sulfites, only permanganate and 1,2-naphthoquinone-4-sulfonic acid facilitate formation of sulfonic acids from deriv. of 2-naphthol. The "oxidative" sulfonation is basically similar to ordinary sulfonation by deriv. of SO_3, and the transformation of SO_3 ions to either SO_4 or S_2O_6 probably proceeds via complexes with metal ions; metal ions capable of taking up 2 electrons simultaneously or those taking up only 1 electron sep. the oxidants into 2 classes. Thus, 2-naphthol-4(or 6)-sulfonic acid with Na_2SO_3 and $KMnO_4$ (deficient amt.) gave 14.5-28% (on oxidized sulfite) HO sulfonates; the results with 7-sulfonic acid or 3,6-disulfonic acid were similar. Sulfite with iodine and H_2O_2 at 50° in the presence of 2,7-$HOC_{10}H_6SO_3H$, or with persulfate at 30-85° in the presence of 2-naphthol-4(or 7)-sulfonic acids does not lead to sulfonation products. The use of $AgNO_3$ led to almost complete reduction of the Ag salt and almost no sulfonation, while AgO gave 10% sulfonation; $FeCl_3$ gave 23-39% sulfonation while $CuSO_4$ gave 24-50%.

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Some derivatives of 2-naphthol-4-sulfonic acid. II. Sulfonation of 2-naphthol-4-sulfonic acid. S. V. Bogdanov and I. B. Migacheva. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 1511-13(1951); cf. C.A. 44, 1082f.—Sulfonation of 2,4-$HOC_{10}H_6SO_3H$ by 20% oleum (75 g. per 0.1 mole) 1 hr. at 3-18° yields *2-naphthol-4,8-disulfonic acid*, isolated as the *di-Na salt* (*2.5 H_2O*), prisms (from aq. EtOH), giving a bluish fluorescence in aq. soln.; treatment with HNO_3 gives no color, but $FeCl_3$ gives an intense blue color. Diazo-*m*-nitrobenzene on coupling yields a red-orange dye, orange needles. Addn. of an aq. soln. of diazotized 2,4,8-$H_2NC_{10}H_4(SO_3H)_2$ to hot 10% H_2SO_4 yields a sulfonic acid that is identical with the above, thus proving the structure. Diazotization of 1,2,4,6-$H_2N(HO)C_{10}H_4(SO_3H)_2$ and pptn. of the diazo deriv. by means of $BaCl_2$ from weakly acidified soln., followed by treatment of the ppt. with $SnCl_2$ in alk. soln., and the removal of Ba and Sn ions, gave *2-naphthol-4,6-disulfonic acid*, isolated as the *di-Na salt trihydrate*, thin prisms (from aq. EtOH), giving a bluish fluorescence in aq. soln., turning blue-violet with soda, dirty blue with $FeCl_3$; diazo-*m*-nitrobenzene gives a sol. orange-red dye; HNO_3 gives a yellow color, and the nitroso deriv. can be pptd. by KCl in the form of long needles.

G. M. Kosolapoff

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Naphtho[1,2]furazan-3- and 4-sulfonic acids. S. V. [illegible] I. Karavaev (K. Voroshilov Sci. Research Inst., Moscow). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 1915-18(1951).—*Naphtho[1,2]furazan* (11.8 g.) in 70 ml. 98% H_2SO_4 treated at 20° over 1.5 hrs. with 50 ml. 56% oleum added slowly and the mixt. kept 4 hrs. at 20° gave upon diln. with much H_2O and addn. of 18 g. Na_2CO_3, 75% *Na sulfonate* (I), needles, sol. in H_2O, insol. in EtOH; *Ba salt*, plates slightly sol. in hot H_2O. The *sulfonyl chloride*, m. 171° (from C_6H_6). The product is the *3-sulfonic acid*, since oxidation with dichromate-AcOH gives phthalic acid, and the *4-isomer* (II) (the other possibility) has different properties. I boiled with 66% H_2SO_4 10 hrs. gives 56-9% original naphthofurazan. 1,2-ON(HO)$C_{10}H_5SO_3H$ (as the Na salt) treated with NH_2OH in alk. medium or in the presence of NaOAc, followed by boiling 1 hr. in alk. soln. gave II; *Na salt monohydrate*, needles from aq. EtOH, stable to heating with H_2SO_4; *sulfonyl chloride*, m. 113-13.5°. Reaction with aq. $NH_2OH.HCl$ in aq. medium without base gave yellow *3-nitroso-1-naphthol-4-sulfonic acid*, reduced with $SnCl_2$ to the 2-amino acid, and converted with HNO_3 to 2,4-$(O_2N)_2C_{10}H_5OH$. G. M. Kosolapoff

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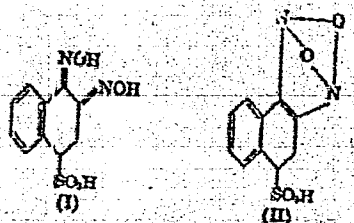
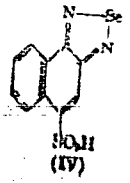
[illegible] thoiuranan. [illegible] Yozoshiloy [illegible] Dyes, Moscow). *Zhur. Obshchei Khim.* 23, 1767-81(1953); cf. *C.A.* 47, 2084.—Refluxing the soln. of the bisulfite compd. of 1,2-$ONC_{10}H_6OH$ with a small excess of NH_2-OH.HCl and NaOAc 0.5 hr. and acidifying the cooled soln. gave 7 g. I. Oxidation of I in acid medium yields a colorless substance which contains N and S. Thus 10.8 g. I and 2.2 g. Na_2CO_3 in 100 ml. H_2O heated with 42.5 ml. 59.4% HNO_3 30 min. at 90-5° yielded 9.8 g. II. II can be obtained directly by treatment of the dry-squeezed paste of 1,2-$ONC_{10}H_6OH$ (from 0.2 mole 2-$C_{10}H_7OH$) with 57.4 g. 38.2% $NaHSO_3$ in 1 part H_2O, filtration, addn. of 38 g. NaOAc and 15.8 g. $NH_2OH.HCl$, boiling 0.5 hr., filtration, dilu. to 200 ml., addn. over 0.5 hr. to 134 ml. 56.8% HNO_3 in 200 ml. H_2O at 65-8°, and heating 15 min. to 90°; the filtered soln. treated with NaCl (20 g./100 ml.) gave 74% HNO_3 ($NaNO_3$+HCl) at 95°, or by H_2O_2 at reflux. The *Na salt of II forms a trihydrate*; it is stable in aq. soln. but on boiling in dil. H_2SO_4 it is cleaved with formation of naphthoiuranan, m. 73°. The Na salt yields the corresponding *Ba salt*, sol. in H_2O, insol. in EtOH; *Ba salt*, $(C_{10}H_6O_4N_2S)_2Ba.5H_2O$, plates, sparingly sol. in cold H_2O, *benzidine salt* (from the Na salt and benzidine-HCl salt), plates sparingly sol. in cold H_2O, insol. in EtOH. To 50.6 g. Na salt of I in 120 ml. H_2O was added 120 ml. NH_4OH, then, gradually 40 g. Zn dust at 33-50°, and the soln. filtered after 7 hrs. at 50° and acidified, yielding 9.1 g. *1,2,4-naphthoquinone-4-sulfonic acid*, (III), which with HNO_3 gave 1,2-naphthoquinone-4-sulfonanilide from $PhNH_2$ with phenanthrenequinone bisulfite adduct. It gave yellow benzophenanthranesulfonic acid. The reduction in NaOH with Zn dust gave the same results. III (7.14 g.) in 25 ml. H_2O treated with 7 g. SeO_2 and the brown soln. treated with 20 ml. 34% NaOH gave 10.27 g. *naphthoselenadiazolesulfonic acid* (IV), isolated as the *Na salt*, $C_{10}H_5O_3N_2SSeNa.1.25H_2O$ (anhyd. after heating to 110°). With PCl_5 this gave the *sulfonyl chloride*, yellow, m. 204.5-5.5° (from PhCl). The III obtained by cleavage of the azo compd. derived from PhN_2Cl and 1,4-$H_2NC_{10}H_5SO_3H$ was precisely the same as the III obtained above (cf. Hammick, *et al.*, *C.A.* 26, 1284.).





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2|2 S.V. Богданов

II. 2-Nitro-1-naphthylamine-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid. S. V. Bogdanov and L. N. Kuroleva. *Ibid* 1761–4.—To 61.9 g. *naphthofurazan-NaHSO₃ adduct* (I) (same as II, preceding abstr.) in 450 ml. H_2O was added 4.5 g. Na_2CO_3, the mixt. rapidly boiled 10 min., cooled, filtered, and the filtrate treated with 20% (by vol.) NaCl, yielding 89.5% *1,2,4-$H_2N(O_2N)C_{10}H_5SO_3H$* (II) in the form of the orange *Na salt*, which washed with H_2O, EtOH, and Et_2O, and the combined filtrate and the residue from the evapn. of the washings heated 2 hr. gave 1.80 g. ppt. (III), the filtrate from which on acidification with HCl gave 6.23 g. yellow ppt. (IV). II *Na salt*, orange plates (from H_2O), was sparingly sol. in EtOH; K salt monohydrate, orange prisms. To 11.6 g. II Na salt in 300 ml. H_2O and 64 ml. HCl was added over 40 min. at 65–90° 18 g. Zn dust and the mixt. stirred 20 min. at 90°, yielding 7.1 g. *1,2,4-$(H_2N)_2C_{10}H_5SO_3H$*. Heating 20 g. II Na salt in 600 ml. 40% H_2SO_4 2 hrs. at 108–12°, cooling, and dilg. with 800 ml. H_2O gave a yellow ppt. which, heated to 90° with dil. NH_4OH, filtered, and washed with hot H_2O, yielded 6.23 g. *2,1-$O_2NC_{10}H_5NH_2$*, m. 142.5–3.0°. II Na salt (5 g.) and 1.31 g. $NaNO_2$ in 100 ml. H_2O added over 0.5 hr. at 1–7° to 10 ml. HCl in 100 ml. H_2O and the suspension of the diazo compd. was stirred 1.5 hrs. (the diazo deriv. forms yellow prisms); this gave a lilac color with 1,8,3,6-$H_2N(HO)C_{10}H_4(SO_3H)_2$, brown with resorcinol, and red-brown with 2,3,6-$HOC_{10}H_3(SO_3H)_2$. The suspension of the diazo compd. was treated over 1 hr. at 20° with 8.5 g. Na_2CO_3 and the orange soln. failed to couple with the above reagents except resorcinol, which gave a lilac color. The filtered soln. acidified with 25 ml. HCl yielded 79.8% *1-diazo-2-naphthol-4-sulfonic acid*, yellow prisms. III extd. with hot H_2O gave a sulfonic acid Na salt contg. 8% Na and giving *1,2,4-$(H_2N)_2C_{10}H_5SO_3H$* on reduction with Zn. The structure of the sulfonic acid is unknown. The H_2O-insol. part of III gave some *naphthofurazan*, m. 74°, and *naphthofurazan*, m. 123.5–4.5° (from MeOH). IV was identified as *1,2,4-$HO(O_2N)C_{10}H_5SO_3Na$*. Refluxing 10 g. II Na salt in 100 ml. 14.1% Na_2CO_3 2 hrs., dilg. and acidifying the cooled soln. gave 88.2% IV, also formed in 90.4% yield when 32 g. Na_2CO_3 in 150 ml. H_2O was treated in 1 hr. with 30.9 g. I in 150 ml. H_2O and the mixt. boiled 2 hrs. (naphthofurazan crystals appear in the reflux condenser), then acidified on cooling. The same reagents mixed at room temp. and then refluxed gave a lower yield of the desired product and greater amts. of the by-products. The *Na salt*, yellow plates, sparingly sol. in EtOH, forms a *monohydrate*. The Na salt (4.4 g.) in 150 ml. H_2O boiled with 150% excess $SnCl_2$ in HCl 20 min. gave 3.22 g. ppt. (the diazo compd. gave red color with resorcinol), which (2.85 g.) was slowly added at 5–10° to 1.3 ml. HNO_3 (d. 1.35) and 3 ml. H_2O, then dild., filtered, and mixed with satd. KCl soln., yielding 2.57 g. *K 1,2-naphthoquinone-4-sulfonate*; addn. of $PhNH_2$ to soln. of the K salt gave red *anilide*, decomp. 257°. The 1,2,4,-$HO(O_2N)C_{10}H_5SO_3H$ is heated to reflux with 1:10 HNO_3 gradually forms *2,4,1-$O_2NC_{10}H_6OH$*, m. 138.5° (from EtOH). Addn. of $NaNO_2$ to the mixt. facilitates the formation of the latter. If the acid is refluxed 7 hrs. with 40% H_2SO_4, *2,1-$O_2NC_{10}H_6OH$*, m. 128.5–9.0° (from MeOH), is formed in good yield. II forms in lower yield from I and aq. Na_2CO_3 on standing at room temp. 18 hrs., but the yields of III and IV tend to rise. The formation of naphthofurazan from I results from the normally expected cleavage. The formation of naphthofurazan may be the result of reduction by the $NaHSO_3$ formed in the reaction.

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BOGDANOV, S.V.; KOROLEVA, I.N.

Research in the field of naphthofuroxan. Part 2. 2-nitro-1-naphthylamine-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid. Zhur.ob.khim.23 no. 10:1761-1764 O '53. (MLRA 6:11)

1. Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley im. K.Ye.Voroshilova. (Sulfonic acids)

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Naphtho[1,2]furazan series. II. Nitration and chlorination of naphtho[1,2]furazan. S. V. Bordanov and S. V. Petrov (K. E. Voroshilov S.-I. [illegible] Intermediates and Dyes, Moscow). Zhur. Obshchei Khim. 24, 1954, 1[illegible]; cf. C.A. 46, 7090d; Green and Rowe, C.A. 12, 670.—Passage of NH_3 at 68–1° into 1-ONC_6H_4OH in aq. NH_4OH gave 75% 1,2-$ONC_6H_4NH_2$, oxidized with 5% NaOCl (20% excess) at 0–5° in 10% NaOH to 88% naphtho[1,2]-furazan (C.A. numbering) (I), m. 70°. To 10 g. I in 100 ml. conc'd. H_2SO_4 was added 3.0 ml. 95% HNO_3 in 15 ml. conc'd. H_2SO_4 over 40–75 min. at −2° to 0°, and the mixt. stirred 4 hrs. at 0°, then treated with ice (until the acid concn. reached 30%), yielding 15.7 g. nitration product; in later expts. either the theoretical amt. or a 2% excess of HNO_3 was used. The washed nitration product was stirred 0.5 hr. with 7.5% NaOH and filtered; after 3 such treatments the product was light brown and m. 132–55°; crystn. from EtOH gave a colorless product, m. 138–41°. Reduction of this with $SnCl_2$-HCl gave 83.2% amino analog; cast-iron chips and HCl gave an 85.6% yield, while aq. alc. Na_2S gave, from 81.5 g. nitro deriv., about 60.8 g. amino deriv., besides some 14% acid-insol. material, m. 190–220°. The amino deriv. prepd. as above, m. 132–60°, failed to be purified by crystn.; 17.52 g. (prepd. by the sulfide method) refluxed with 2.1 l. 4% HCl, filtered, and the filtrate cooled, yielded the HCl salt of an NH_2 deriv. [free base m. 150–60° (crude), m. 161–21.5° (from HCl)], of a compd. identified as the 8-amino deriv. of I. The filtrate from the above HCl salt treated with NH_4OH yielded the yellow 6-amino isomer, m. 208.3–3.7° (from EtOH), whose HCl salt forms short prisms. In all there was obtained 56.1% 8- and 24.3% 6-

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amino deriv. of I, with same 1.25 g. unresolved mixt. The 8-amino deriv. (4.62 g.) in 25 ml. concd. H_2SO_4 diazotized at −1° with 2.08 g. $NaNO_2$ in 25 ml. H_2SO_4, stored 3 hrs., diluted with ice, treated with urea to remove N oxides, and poured into a hot (70–80°) soln. of 8 g. Cu_2Cl_2 in 120 ml. concd. HCl and 40 ml. H_2O yielded an orange ppt. of a Cu complex, which, twice refluxed 1 hr. with 10% HCl, gave 4.83 g. 8-Cl deriv. of I, colorless, m. 132.7–3.2° (from dil. EtOH). If the dil. diazo soln. (above) is poured into hot 50% H_2SO_4, it gives the *8-HO deriv.* of I, colorless, m. 217.5–18° (from dil. EtOH), which with Me_2SO_4 in NaOH forms the *8-MeO ether*, m. 129.8–30.2° (from dil. EtOH), while Ac_2O gives the *5-acetate*, m. 137–7.4° (from dil. EtOH). Analogously, 6-nitro deriv. of I gave a good yield of the *6-Cl compd.*, m. 129.2–30.8° (from dil. EtOH); *6-HO compd.*, yellow, m. 220.6–1.1° (from dil. EtOH); *6-MeO analog*, yellowish, m. 159.1–9.5° (from EtOH). To 4.62 g. 6-amino deriv. of I in 35 ml. concd. H_2SO_4 was added at 3–4° 2.10 g. $NaNO_2$ in 25 ml. H_2SO_4, the mixt. stirred 4 hrs., diluted with 270 g. ice, treated with urea, poured over a period of 5 min. into a SO_2-satd. mixt. of 38 ml. concd. H_2SO_4, 400 ml. H_2O, and 46.5 g. fresh Gattermann Cu paste, the mixt. filtered after 1 hr., and the solid heated to 95° with Na_2CO_3, filtered, treated with 7 ml. 30% H_2O_2, stirred 2 hrs., treated with MnO_2 to destroy the peroxide, filtered, and evapd., yielding 5.3 g. *Na salt*, needles with 2.5 H_2O, of the 6-HO_3S deriv. of I, which with PCl_5 gave the corresponding *sulfonyl chloride*, m. 116.5–17.2°; *amide*, m. 235.8–6.3° (from EtOH). The diazo paste from 97.8 g. 2,5-$H_2NC_6H_3SO_3H$ added in 35 min. to 505 ml. hot 20% H_2SO_4, and the mixt. neutralized with $Ba(OH)_2$, filtered, treated with Na-

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CO_2, filtered, and evapd. yielded 61% *2,5-HOC₁-H₄SO₃Na·4H₂O*, hexagonal plates, converted in the conventional manner 1,2,5-ON(HO)$C_{10}H_4SO_3Na$, 34.7 g. of which treated in 100 ml. H_2O with 27 ml. 43.8% NaOH and 73 ml. H_2O, then with 14 g. $HONH_2.HCl$, kept 1 hr. at 20°, and boiled 20 min. yielded on cooling 28.9 g. *Na salt*, needles with *2.5H₂O*, of the 6-HO_2S deriv. of I this gave the *sulfonyl chloride*, m. 118-18.3°, and *sulfonamide*, m. 236-6.3°, identical with the above described specimens. Passage of Cl into 13.6 g. I and 0.14 g. powd. Fe 1 hr. at 78-80° gave a solid mass which was treated with dil. Na_2CO_3, heated to boiling, cooled, filtered, and the ppt., m. 113-31°, taken up in 159 ml. hot AcOH and cooled, yielding 9.05 g. *4-Cl deriv.* of I, augmented by careful diln. of the soln.; further diln. gave 1.30 g. I. Pure *4-Cl deriv.* of I, m. 144.2-4.8° (from EtOH or AcOH), also formed in 86.5% yield from 2.99 g. Na salt of the 4-HO_2S deriv. of I in 100 ml. hot H_2O and 5.6 ml. concd. HCl was treated over 3 hrs. with 1.47 g. KOCl in 20 ml. H_2O. Analogously the Na salt of the 5-HO_2S compd. gave 91.7% 5-Cl deriv. of I, m. 96.8-7.1° (from EtOH).

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BOGDANOV, S. V.

Naphthofuroxan series. III. 1,2-Naphthoquinone-4-sulfonic acid dioxime. S. V. Bogdanov and I. N. Koroleva (K. E. Voroshilov Sci., Research Inst. Org. Intermed. and Dyes, Moscow). *Zhur. Obshchei Khim.* 24, 1994-8(1954); cf. *C.A.* 48, 13658a.—To 34.4 g. Na salt of the bisulfite adduct of naphthofuroxan suspended in 175 ml. H_2O was added at 5° 28.6 ml. 46.7% NaOH and the mixt. kept 2 hrs. at 5° and 18 hrs. at room temp. and filtered yielding 0.4 g. mixed naphthofuroxan, m. 124-5.5°, and naphthofurazan, m. 76-8°. The filtrate treated in the cold with 45 ml. 35.4% HCl dild. with 100 ml. H_2O gave SO_2 and a ppt. of 72.3-5.0% Na 1,2-naphthoquinone-4-sulfonate dioxime, $C_{10}H_7N_2NaO_5S$ (I), while the filtrate after addn. of AcONa and concn. gave *naphthofurazan-4-sulfonic acid*, whose *chloride*, m. 112.5-13.5°. The yield of I declines in an expt. of shorter duration and in one employing smaller amt. of NaOH. I yields orange solns. in alkalies, giving violet color in the presence of Fe, which may be green initially if the product is contaminated with 2-nitroso-1-naphthol-4-sulfonic acid. Pure I, yellow, is obtained as the *trihydrate* (from H_2O); the H_2O is not lost even at 110°, while at 120-30° decompn. occurs. The corresponding *K salt* is less sol., forms orange-yellow prisms and is isolated as monohydrate. *Ag salt* forms yellow needles, decompd. by hot H_2O. *Benzidine salt*, $C_{22}H_{18}O_{10}N_6S_2 \cdot 2H_2O$, is also decompd. in hot H_2O. I (34.4 g.) in 300 ml. H_2O was treated with 9 ml. 35.4% HCl and refluxed 2 hrs. yielding 75% *Na 2-nitroso-1-naphthol-4-sulfonate*, yellow needles (from H_2O), which gave green color with Fe. Heated with Zn and a trace of AcOH it gave a colorless soln., which turned blue; acidification gave a red color and addn. of alkali gave a green color.

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Reduction with Sn-HCl gave 2-amino-1-naphthol-4-sulfonic acid, which oxidized with HNO_3 gave 2,4-dinitro-1-naphthol, m. 138.5° (decompn.). I (12.77 g.) in 40 ml. H_2O was treated with 6.55 g. NaOH in 18 ml. H_2O, kept 1 hr. at 15° and refluxed 15 min., yielding on cooling 87% *Na 1,2-naphtho(3',4')furoxan-4-sulfonate* (II), colorless prisms, isolated as *hemihydrate*, which does not lose its H_2O even at 100°; the *$PhNH_3$ salt*, $C_{16}H_{12}O_4N_2S$, plates, decompn. 277°; *sulfonyl chloride*, m. 112.5-13.5° (from C_6H_6). The same product is obtained on 12 hrs. refluxing of I with Ac_2O. If 10.33 g. I in 75 ml. H_2O is treated at 30° with 8.6 ml. 46.7% NaOH and refluxed 2 hrs. there is obtained 6.99 g. II, while the filtrate gave 0.73 g. 2-nitro-1-naphthol-4-sulfonic acid on acidification. Keeping 20 g. I in 100 ml. H_2O and 52 ml. 55.8% HNO_3 1 hr. at 90° and 15 min. at 100° gave 14 g. *1,2-naphthofuroxan-4-sulfonic acid* in the form of its *Na salt*, while the filtrate on neutralization gave a further amount bringing the yield to 90.8%; the Na salt is sparingly sol. and is anhyd. Reduction of I with $SnCl_2$-HCl at reflux (10 min.) gave *1,2-naphthylenediamine-4-sulfonic acid*, prisms; oxidation with HNO_3 gave 1,2-naphthoquinone-4-sulfonic acid, while reaction with phenanthrenequinone $NaHSO_3$ adduct gave 10,11-benzophenanthrazine-sulfonic acid, yellow needles. If the above reduction is run with $SnCl_2$ and Zn dust, the same product is formed. To refluxing soln. of 5.76 g. I in 320 ml. H_2O acidified with 11.2 ml. 35.5% HCl was added over 1 hr. 2.94 g. $KClO_3$ in 50 ml. H_2O and the mixt. refluxed 1 hr. and cooled, gave 3.38 g. *4-chloro-1,2-naphthofuroxan*, m. 140.2-40.8° (from EtOH).

G. M. Kosolapoff

S. V. Bogdanov
I. N. Kotoleva

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The bisulfite compound of 1-naphthol. 7-Nitro-1-naphthol. N. N. Karandashova and S. V. Bogdanov (K. E. Voroshilov Sci. Research Inst. Org. Intermed. and Dyes. Moscow). Zhur. Obshchei Khim. 25, 1152-6(1955).— [illegible] 2-naphthol acid with $NaHSO_3$ [illegible]

[illegible] Refluxing 21 g. Na 1-hydroxy-2-naphthoate and 286 g. [illegible] soln. of $NaHSO_3$ 3 hrs. gave 48.6% 1-$C_{10}H_7OH$, m. 95.3-5.5°, which separates on cooling. Further cooling gave 4.65 g. residue unreacted acid. If the refluxing extends to 23 hrs. there is formed a slight ppt. of inorg. salts and the soln. on dilu. to 500 ml. yielded 1.75 g. 1-$C_{10}H_7OH$. The filtrate on acidification and extn. with Et_2O, followed by washing the ext. with Na_2CO_3, then with NaOH, gave 0.13 g. initial acid from the soda soln. and 0.73 g. 1-$C_{10}H_7OH$ from NaOH soln. Evapn. of the aq. soln. to 300 ml. and addn. of 40% NaOH to decompose the $NaHSO_3$ adduct gave, on heating and acidification with HCl, 75.7% 1-$C_{10}H_7OH$. Refluxing 10.5 g. Na 1-hydroxy-2-naphthoate with 143 g. 36.3% soln. of $NaHSO_3$ 23 hrs., followed by removal of unreacted acid as described above, partial neutralization with Na_2CO_3 and concn. to 150 ml. gave 8.73 g. 1-$C_{10}H_7OH.NaHSO_3.H_2O$; rhombic plates or needles (from dil. EtOH). This heated with $(NH_4)HSO_3$ and concd. NH_4OH 20 hrs. at 60° 48.4% 1-$C_{10}H_7NH_2$; if NH_4HSO_3 is omitted, the yield is 12%. The $NaHSO_3$ complex (53.2 g.) added at 3-5° to 300 ml. concd. H_2SO_4 and the soln. treated at −2° over 1.5 hrs. [illegible]

[illegible] from AcOH [illegible]

$(CH_2Cl)_2$, gave about 15 g. 7-nitro-1-naphthol, yellow, m. 213.8-14.5° (oxidation with $KMnO_4$ gave 4-nitrophthalic acid, m. 161-1.5°; reduction with Fe-dil. HCl gave 7-amino-1-naphthol, decomp. 154.5-5°; N-Ac deriv., decomp. 220-1°). The $(CH_2Cl)_2$ sol. isomer was purified by crystallization from H_2O and $(CH_2Cl)_2$, yielding about 3 g. 5-nitro-1-naphthol, yellow, m. 171.5-2°, which is more sol. than the 7-nitro isomer. The same was formed by the reduction of 1,5-$C_{10}H_6(NO_2)_2$ with Na_2S-$(NH_4)_2SO_4$, diazotization and hydrolytic treatment. Also in J. Gen. Chem. U.S.S.R. 25, 1105-7(1955)(Engl. translation). G. M. Kosolapoff.

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Naphthofuroxan series. IV. Derivatives of 1,2-naphthoquinone dioxime-6-sulfonic acid. S. V. Bogdanov and I. N. Koroleva (K. E. Voroshilov Inst. Org. Intermediates and Dyes, Moscow). *Zhur. Obshchei Khim.* 26, 243-6; *J. Gen. Chem. U.S.S.R.* 26, 259-62(1956); cf. *C.A.* 50, 10715d.—The bisulfite compd. (I) of 1,2-naphthoquinone dioxime-6-sulfonic acid from 0.07 mole 1-nitroso-8-naphthol-6-sulfonic acid, was added in 2 hrs. to 181 g. 24.5% HNO_3 at 65-70° and kept ½ hr. at 95° yielding on neutralization and concn. 12 g. crude product, which extd. with hot MeOH gave 7.2 g. *di-Na 1,2-naphthoquinone dioxime-4,6-disulfonate*, needles or prisms (from MeOH or aq. EtOH); also formed from I and aq. $NaNO_2$ added to warm dil. HCl. The Na salt (II) of the bisulfite adduct of 1,2-naphthofuroxan-6-sulfonic acid (22.3 g.) in 125 ml. 1% Na_2CO_3 was heated, then chilled rapidly and the soln. treated with 27 g. NaCl and 40 ml. EtOH, yielding 74% *di-Na 8-nitro-1-naphthylamine-4,6-disulfonate*, yellow needles (from aq. EtOH); diazo coupling with resorcinol gave a red color, with 1-amino-8-naphthol-3,6-disulfonic acid a lilac color, and with 2-naphthol-3,6-disulfonic acid a red ppt. II (10 g.) in 100 ml. 12.5% Na_2CO_3 was refluxed 2 hrs., yielding on cooling and acidification, *di-Na 2-nitro-1-naphthol-4,6-disulfonate*, yellow pyramids (contg. 4.25 moles H_2O) (from aq. EtOH). II kept with 15% NaOH 20 hrs. gave on acidification 94.5% *1,2-naphthoquinone dioxime-4,6-disulfonic acid*, isolated as the *di-Na salt* (III) (with 3.5 mol. H_2O; from aq. EtOH), yellowish prisms. The latter (10.5 g.) refluxed 2 hrs. with dil. HCl gave *2-nitroso-1-naphthol-4,6-disulfonic acid*, isolated as the *di-Na salt dihydrate*, yellow needles (from aq. EtOH), while refluxing III with 5% KOH 8 hrs. gave 52% *1,2-naphthofuroxan-4,6-disulfonic acid*, isolated as the *di-Na salt* (3.5 mol. H_2O), colorless needles (from aq. EtOH). III refluxed 10 min. with 1:2 HNO_3 gave 79.5% *1,2-naphthofuroxan-4,6-disulfonic acid*, isolated as the *di-Na salt tetrahydrate*, colorless needles

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BOGDANOV, S.V., KOROLEVA, I.N.

(from aq. EtOH). V. Sulfonation and chlorination of naphthofuroxan. *Zhur. Obshchei Khim.* 26, 264-7; *J. Gen. Chem. U.S.S.R.* 26, 281-4(1956)(Engl. translation).--Crude 1,2-naphthoquinone dioxime (15.23 g.) in 110 ml. 7.7% KOH was added in 0.5 hr. to 150 ml. 22.5% HNO_3 at 65-70° and kept 15 min. at 90°, yielding a ppt. of 76.0% *1,2-naphthofuroxan* (I), m. 124-5° (from EtOH). I (7.44 g.) in 28 ml. concd. H_2SO_4 was treated in 0.5 hr. at 20° with 6.4 ml. 62% oleum and kept 3 hrs.; after addn. of ice, neutralization with chalk, filtration and cooling, there was obtained a ppt. of Ca 1,2-naphthofuroxan-3-sulfonate; this with Na_2CO_3 gave the corresponding *Na salt*, plates (from H_2O), in 53.2% yield; the corresponding *sulfonylchloride*, m. 221° (from CCl_4). Reduction of the acid with Zn dust in HCl in the presence of $SnCl_2$ gave *1,2-naphthylenediamine-3-sulfonic acid*, needles. This with SeO_2 (cf. *C.A.* 48, 13057*b*) gave *1,2-naphthoselena diazole-3-sulfonic acid*, isolated as the *Na salt*, plates (from H_2O); the *sulfonylchloride*, decomp. 230° (from PhCl). The same Na salt and chloride were prepd. by coupling of 1-naphthylamine-3-sulfonic acid with *p*-$O_2NC_6H_4N_2Cl$ and cleavage of the azo deriv. with Zn dust in 4% NaCl in the presence of $CuSO_4$. I (23.3 g.) in 200 ml. 95.5% H_2SO_4 chlorinated at 25° 2 hrs. until 4.4 g. wt. gain was reached; treatment with ice gave 30.8% *3-chloro-1,2-naphthofuroxan*, m. 145.5-6.5° (from CCl_4), which formed in moderate yield from I in hot 3.3% HCl on treatment 3 hrs. with $KClO_3$.

G. M. Kosolapoff

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BOGDANOV, S.V.; KOROLEVA, I.N.

Study of the naphthofuroxan series. Part 5. Sulfonation and chlorination of naphthofuroxan. Zhur.ob.khim. 26 no.1:264-267 Ja '56. (MLRA 9:5)

1. Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i kresiteley imeni K.Ye. Voroshilova.
(Naphthofuroxan)

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1,2-Naphthol[1',4']furoxan series. VI. Bisulfite compound of 6-nitro-1,2-naphthol[1',4']furoxan and its derivatives. S. V. Bogdanov and N. I. Zil'berman (K. E. Voroshilov Research Institute, Intermed. and Dyes, Moscow). *Zhur. Obshchei Khim.* 26, 2071-6(1956); cf. C.A. 26, 693-50, 13884d.—To 15.3 g. K salt of the bisulfite complex of 1,2-naphthofuroxan in 94 ml. 100% H_2SO_4 was added at −2° in 1 hr. 3.32 g. 97.8% HNO_3 in 20 ml. H_2SO_4; after 2 hrs. the mixt. was treated with ice and left 12-14 hrs. yielding a ppt. of the *K salt* (I) of the *bisulfite complex of 6-nitro-1,2-naphthofuroxan*, recrystd. from H_2O in 65-70% yield.

I refluxed briefly with 1% K_2CO_3 gave, on cooling, orange plates and yellow needles and [illegible] H_2O left behind an unknown [illegible] yellow needles, while the cooled filtrate gave 32 [illegible] *dinitro-1-naphthylamine-4-sulfonic acid* in the form of its *K salt* (II), orange prisms; the mother liquor after evapn. gave 20% *K salt of 6-nitro-1,2-naphthofurazan-4-sulfonic acid*. II treated with $NaNO_2$ in cold H_2SO_4 gave a diazonium soln. which gave a red-violet dye with 2-naphthol-3,6-disulfonic acid (III), and a brown color with resorcinol; the diazonium soln. with ice treatment yielded *6-nitro-1-diazo-2-naphthol-4-sulfonic acid* which gives a violet color with resorcinol but does not couple with III; the diazo deriv. was repptd. from Na_2CO_3 soln. and treated as per Ruggli's method (*C.A.* 24, 2125) yielding *O,N-dibenzoyl-6-amino-2-naphthol*, m. 233.5°. II heated 3.5 hrs. with 40% H_2SO_4 at 110° gave *2,6-dinitro-1-naphthylamine*, decomp. 300.2°, which diazotized in H_2SO_4 and treated with ice gave a ppt. of *6-nitro-1-diazo-2-naphthol*, which boiled with Cu_2O in EtOH gave *6-nitro-2-naphthol*, m. 158.2-9°. II refluxed 2 hrs. with 13% K_2CO_3 gave on

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Bogdanov, S. V. & Zil'berman,

acidification 2,6-dinitro-1-naphthol-4-sulfonic acid as the mono-K salt, yellow prisms, forming a sesquihydrate, which heated to boiling with dil. HNO_3 0.5 hr. gave 2,4,6-trinitro-1-naphthol, yellow, decomp. 157°. I treated as in Boganby, et al., (C. A. 49, 13077f) gave 51.2% 6-nitro-1,2-naphthoquinone-4-sulfonic acid dioxide, isolated as the K salt, yellow prisms; on boiling with 1% HCl it yields apparently the K salt of 6-nitro-1,2-naphthofuroxan-4-sulfonic acid, isolated as the trihydrate, colorless prisms. Oxidation of the K salt of the dioxime deriv. (IV) above, similarly gave 81.3% K salt of 6-nitro-1,2-naphthofuroxan-4-sulfonic acid, colorless prisms, spondgly sol. in hot H_2O. IV refluxed with aq. KOH 15 min. after 1 hr. at 10° gave on cooling 92.5% K 6-nitro-1,2-naphthofuroxan-4-sulfonate (V), colorless prisms. This treated as in (C. A. 49, 4[illegible]) gave 4-chloro-6-nitro-1,2-naphthofuroxan, m. 166.7–7°. V reduced with $SnCl_2$-HCl gave 65% 6-amino-1,2-naphthofuroxan-4-sulfonic acid, colorless needles, which on diazotization reacts with III giving an orange-red color, and with resorcinol, a yellow-brown color. The diazotized substance refluxed with EtOH, then treated with HCl and KOCl, gave 4-chloro-1,2-naphthofuroxan, m. 93.4–4.7°.

G. M. Kosolapoff

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f. Bisulfite compounds of 4-nitroso-1-naphthol and 1-naphthol. S. V. Sogdanov and N. N. Karandasheva (K. E. Voroshilov Sci. Research Inst. Org. Intermediates and Dyes, Moscow). Zhur. Obshchei Khim. 26, 3365-8(1956); cf. C.A. 50, 3365f.—Keeping 21 g. 4-nitroso-1-naphthol (I) with 50 g. 37% $NaHSO_3$ in 45 ml. H_2O 8 hrs. at 20°, letting the mixt. stand 18 hrs., filtering off a slight ppt., and adding NaCl, gave 35 g. I $NaHSO_3$ compd., formulated as *Na 2,3-dihydro-1,4-naphthoquinone-3-sulfonate 4-oxime*, colorless plates, destroyed by 9% NaOH in the cold. It formed a *monohydrate*, which loses H_2O at 100°, and decompd. at 110°. Refluxed with $NH_2OH.HCl$ and NaOAc 1 hr. in H_2O it gave I and *$NaHSO_3$ adduct* (II) of *1,4-naphthoquinone dioxime*, colorless plates, stable to 9% NaOH in the cold but destroyed by 13% NaOH in 24 hrs.; on acidification its soln. turned yellow and on repeated addn. of NaOH and acids it lost SO_2 and yielded I. II (2 g.) in 5 ml. 38.7% NaOH and 25 ml. H_2O was briefly refluxed, cooled, and added to 15 ml. 34.4% HCl in 50 ml. H_2O, yielding SO_2 and 0.88 g. *1,4-naphthoquinone dioxime*, decomp. 217°; *di-Ac deriv.*, m. 167.5-8°. Refluxing 28.8 g. 1-$C_{10}H_7OH$, 602 g. 34.6% $NaHSO_3$, and 1-3 ml. MeOH with periodic passage of SO_2 28 hrs. gave on acidification with 200 ml. 34.4% HCl and air blowing at 20-60°, followed by extn. with Et_2O 9.4-11.8% 1-$C_{10}H_7OH$, while the aq. soln. of the bisulfite complex on neutralization with Na_2CO_3 and concn., gave on addn. of NaCl 86.7-90% bisulfite complex, formulated as *1,2,3,4-tetrahydro-1-oxonaphthalene-3-sulfonate* (III), isolated as the *Na salt*, which treated with $NH_2OH.HCl$ and NaOAc gave in 22 hrs. 94.7% *corresponding monoxime*, isolated as the *Na sulfonate* (IV). IV does not lose SO_2 in 37% NaOH but

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Sv. Begdanov and N. N. Karandashev

boiled after acidification, made alk. and reacidified, it loses SO_2 and yields 1-C_6H_4OH; IV Na salt decomp. 140-50°. IV *Na salt* was converted to the *Ba salt*, isolated as the *tetrahydrate*, $C_6H_4O_4N_2S_2Ba.4H_2O$, hexagonal plates, sparingly sol. in H_2O, which loses H_2O at 110°. III and semicarbazide·HCl, with NaOAc, gave after 18 hrs. 97.1% the corresponding *semicarbazone*, prisms of *trihydrate* being isolated; this loses H_2O at 110°; the anhyd. product is very hygroscopic. Thus, I bisulfite complex treated with NH_2OH yields the bisulfite complex of 1,4-naphthoquinone dioxime, which in alkali loses the sulfite group and forms 1,4-naphthoquinone dioxime, while in acid medium it is hydrolyzed to bisulfite complex of I. G. M. Kosolapoff

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Distr: 4E4j

Structure of the bisulfite compound of 1-naphthol. S. V. Bordonov. *Khim. Nauka i Prom.* 2, 134(1957).—Reduction of the bisulfite addn. product of 1-naphthol with Zn and dil. AcOH at 90° yields a mixt. of 1,2-dihydronaphthalene-2-sulfonic acid (I), 1,2,3,4-tetrahydronaphthalene-2-sulfonic acid (II), and o-$C_6H_4.CH_2.CH(SO_3H).CH_2.C(OH).C:CH.CH(SO_3H).CH_2.C_6H_4$-o (III). I can be hydrolyzed to naphthalene and H_2SO_3; reaction with Br H_2O produces 1-hydroxy-2-3-bromo-1,2,3,4-tetrahydronaphthalene-2-sulfonic acid. II with 10% NaOH yields naphthalene-2-sulfonic acid. III produces under identical conditions 1,1-binaphthyl.

V. S. Mihajlov

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Nauchno-issledovatel'skyy institut organicheskikh poluproduktov i krasiteley im K. Ye. Voroshilova.

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BOGDANOV, S.V.; GORELIK, M.V.

Bisulfite compounds of oxy-derivatives of anthracene. Khim. nauka i prom. 3 no.2:279-280 '58. (MIRA 11:6)

1. Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley im. K.Ye.Voroshilova.
(Anthracene) (Sulfites)

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

AUTHOR: Bogdanov, S. V. 79-28-5-47/69

TITLE: Reduction of a Bisulfite Compound of 1-Naphthol (Vosstanovleniye bisul'fitnogo soyedineniya 1-naftola) I. 1,2-Dihydronaphthalene-2-Sulfo Acid (I. 1,2-Digidronaftalin-2-sul'fokislota)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5, pp. 1324-1327 (USSR)

ABSTRACT: As was noticed (ref 1) the bisulfite compound of 1-naphthol behaves toward hydroxylamine and semicarbazide like a ketone and converts to the oxime and semicarbazone of the bi-sulfite compound. For this reason the formula 1-oxo-1,2,3,4-tetrahydronaphthalene-3-sulfo acid (formula I) was suggested for this compound. According to data in publications the reduction of 1-oxo-1,2,3,4,-tetrahydro-naphthalene leads to 1-oxo-1,2,3,4-tetrahydronaphthalene and to 1,1'-dioxy-1,1'-ditetralyl. In the reaction of 1-naphthol with bisulfite, besides the bisulfite compound of naphthol, also 1,2- and 1,4-naphtholsulfo acids form. It was of interest to investigate also the behaviour of the bisulfite compound of 1-naphthol toward the reducing agents. The

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Reduction of a Bisulfite Compound of 1-Naphthol. 79-28-5-47/69
I. 1,2-Dihydronaphthalene-2-Sulfo Acid

results showed that this compound on the action of zinc in diluted acetic acid in the presence of copper sulfate converts to a mixture of reduction products from which the sodium salt of the 1,2-dihydronaphthalene-2-sulfo acid (II) was isolated. 1,2 dihydronaphthalene-2-sulfo acid is cleft into alkali liquors and mineral acids in naphthalene and sulfurous acid, and on the action of bromine water, converts to 4-oxy-3-bromo-1,2,3,4-tetrahydronaphthalene-2-sulfo-acid. The latter in acidous medium yields naphthalene and -2-bromonaphthalene, and in alkaline medium naphthalene-2-sulfo acid. The formation of the 1,2-dihydronaphthalene-2-sulfo acid in the reduction of the bisulfite compound of 1-naphthol proves the proposed structure of the latter, i. e. formula I. There are 5 references, 3 of which are Soviet.

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Reduction of a Bisulfite Compound of 1-Naphthol. 79-28-5-47/69
I. 1,2-Dihydronaphthalene-2-Sulfo Acid

ASSOCIATION: Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley (Scientific Research Institute for Organic Intermediate Products and Dyes)

SUBMITTED: April 22, 1957

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

AUTHOR: Bogdanov, S. V. 79-28-5-48/69

TITLE: Reduction of the Bisulfite Compound of 1-Naphthol and of Its Oxime II. (Vosstanovleniye bisul'fitnogo soyedineniya 1-naftola i yego oksima. II)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5, pp. 1328-1332 (USSR)

ABSTRACT: Not long ago (ref 1) it was noticed that in the reduction of the bisulfite compound of 1-naphthol with zinc in acetic acid a reaction mixture forms from which the 1,2-dihydronaphthalene-2-sulfo acid was isolated (formula I). The deposit produced from the reaction solution by addition of sodium chloride contained 76,5 % sodium salt of the compound (I) and a considerable amount of sodium salt of the sulfo acid, which reacted neither with iodine nor with bromine water and which was resistant to alkali liquors and acids. This salt was separated from compound (I) by fractional crystallization of water and by boiling with a 1% soda lye. This compound is a tetrahydronaphthalenesulfo acid, which on the dehydration with sulfur converts to naphthalene-2-sulfo acid and is, as must be assumed, a

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Reduction of the Bisulfite Compound of 1-Naphthol and of Its Oxime. II. 79-28-5-48/69

salt of the 1,2,3,4-tetrahydronaphthalene-2-sulfo acid (II) (yield more than 11 %). Its formation takes place by immediate reduction of the bisulfite compound, as compound I) is not subject to the action of zinc and acetic acid. In the reduction of the bisulfite compound of 1-naphthol with zinc and acetic acid besides compounds (I) and (II) the 1-oxy-1,2,3,4-tetrahydro)-(3',4'-dihydro-)-1,1'-dinaphthyl-3,3'-disulfo acid (III) is also formed, which can as well be obtained with hydrochloric acid in the place of acetic acid. The same compound converts to 1,1-dinaphthyl on heating with sodium hydroxide of sulfuric acid. In the reduction of the oxime of the bisulfite compound of naphthol with zinc and acetic acid the 1-amino-1,2,3,4-tetrahydro-naphthalene-3-sulfo acid (V) results. The direction of the bisulfite compound of 1-naphthol and of its oxime corresponds to the reduction course of 1-oxo-1,2,3,4-tetrahydronaphthalene and of its oxime and thus proves th[illegible]arlier proposed structure formulae of the bisulfite compound and of its oxime. There are 3 references, 2 of which are Soviet.

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Reduction of the Bisulfite Compound of 1-Naphthol and of Its Oxime, II. 79-28-2-48/69

ASSOCIATION: Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i kresiteley (Scientific Research Institute for Organic Intermediate Products and Dyes)

SUBMITTED: April 22, 1957

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KOROLEV, A.I., otv.red.; VUL'FSON, N.S., zam.otv.red.; BOGDANOV, S.V., red.; DOKUNIKHIN, N.S., red.; MASLENNIKOVA, Ye.V., red.; FODIMAN, I.V., red.; KHOMSKIY, I.G., red.; ZETKIN, V.I., red.; SHPAK, Ye.G., tekhn.red.

[Organic intermediate products and dyes; collected articles] Organicheskie poluprodukty i krasiteli; sbornik statei. Moskva, Gos.nauchno-tekhn.izd-vo khim.lit-ry. No.1. 1959. 238 p. (MIRA 13:7)

1. Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley.

(Dyes and dyeing) (Aromatic compounds)

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"APPROVED FOR RELEASE: 06/09/2000 CIA-RDP86-00513R000205820019-4

AUTHORS: Bogdanov, S. V., Gorelik, M. V. SOV/79-29-1-30/74

TITLE: Investigations in the Field of the Oxy-Derivatives of Anthracene (Issledovaniye v oblasti oksiproizvodnykh antra-~~tsena)~~ I. Bisulfite Compounds of the 1-Anthrol and 4-Nitroso-1-Anthrol (I. Bisul'fitnyye soyedineniya 1-antrola i 4-nitrozo-1-antrola)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 1, pp 136-139 (USSR)

ABSTRACT: The investigation of the properties of the bisulfite compounds of 1-naphthol and 4-nitroso-1-naphthol (Refs 1, 2) made it possible to describe their structure with the formulae (I) and (II). In the present paper the affiliation products of the bisulfite to the 1-anthrol and 4-nitroso-1-anthrol are investigated. This affiliation takes place on the treatment of the 1-anthrol with boiling sodium bisulfite solution (Ref 3). The product $C_{14}H_{10}OH.NaHSO_3.3H_2O$ obtained by the authors is stable in neutral and acid medium but is decomposed into sulfite and 1-anthrol in alkaline medium. In the reaction with hydroxylamine, semicarbazide or phenylhydrazine in acetic acid it is converted accordingly into the oxime, semicarbazone,

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SOV/79-29-1-30/74

Investigations in the Field of the Oxy-Derivatives of Anthracene. I. Bisulfite Compounds of the 1-Anthrol and 4-Nitroso-1-Anthrol

phenylhydrazone of the bisulfite compound of 1-anthrol. This indicates the presence of a carbonyl group and the formula (III). The formulae of the oxime, semicarbazone, phenylhydrazone are presented in the formulae (IV) a, b. The bisulfite compound of 4-nitroso-1-anthrol was obtained by the reaction of 4-nitroso-1-anthrol with dissolved sodium bisulfite in the presence of pyridine. Without pyridine the yield decreased from 82 to 6%. Alkali liquors readily split off a sulfite molecule from the bisulfite compound. With hydroxylamine hydrochloride in the presence of sodium acetate the bisulfite compound of 1,4-anthraquinone dioxime is formed from it. The transition of the bisulfite compound of 4-nitroso-1-anthrol into the bisulfite compound of 1,4-anthraquinone dioxime indicates the affiliation of the bisulfite molecule to the carbon-carbon double bond (V and VI), yet not to the carbonyl group. It may be concluded from these results that the bisulfite compounds of anthrol and of 4-nitroso-1-anthrol resemble by their structure the corresponding derivatives of the naphthalene series. There are 5 references, 4 of which are Soviet.

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Investigations in the Field of the Oxy-Derivatives of Anthracene. I. Bisulfite Compounds of the 1-Anthrol and 4-Nitroso-1-Anthrol SOV/79-29-1-30/74

ASSOCIATION: Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley (Scientific Research Institute of Organic Intermediate Products and Dyes)

SUBMITTED: November 25, 1957

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AUTHORS: Bogdanov, S. V., Gorelik, M. V. SOV/79-29-1-31/74

TITLE: Investigation in the Field of the Oxy-Derivatives of Anthracene (Issledovaniye v oblasti oksiproizvodnykh antratsena) II. The Bisulfite Compound of the 1-Nitroso-2-Anthrol (II. Bisul'fitnoye soyedineniye 1-nitrozo-2-antrola)

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ABSTRACT: As previously shown by Bogdanov (Ref 1), the bisulfite compound of 1-nitroso-2-naphthol is converted by hydroxylamine into the bisulfite compound of the 1,2-naphthoquinone dioxime which, on its part, is capable of different transformations. It suggested itself to synthesize also the bisulfite compound of 1-nitroso-2-anthrol and to investigate whether in the anthracene series also reactions take place which are characteristic of the bisulfite compound of 1-nitroso-2-naphthol and its derivatives. On acidification of the bisulfite solution of 1-nitroso-2-anthrol Fieser obtained the 1-amino-2-anthrol-4-sulfonic acid in small yield (Ref 2), but he did not succeed in separating the bisulfite compound. The authors were able to obtain the bisulfite compound of 1-nitroso-2-anthrol in a 90% yield, by allowing the double quantity of sodium bisulfite to act in 1-nitroso-2-anthrol in the presence.

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of pyridine. This treatment considerably increased the yield, as was previously seen with the 4-nitroso-1-anthrol (Ref 3), and part of the product was separated in the form of a pyridine salt. This bisulfite compound is unstable in alkaline medium only, where it decomposes quantitatively into bisulfite and 1-nitroso-2-anthrol. On the reduction of this compound with sulfurous acid or tin chloride the 1-amino-2-anthrol-4-sulfonic acid is formed, in the reaction with hydroxylamine the bisulfite compound of 1,2-anthraquinone dioxime. The former transformation shows that the sulfo group in the bisulfite compound of 1-nitroso-2-anthrol is in position 4, and the latter indicates the presence of a carbonyl group. On the basis of these facts the structure (I) may be assigned to the bisulfite compound of 1-nitroso-2-anthrol. Compound (II) is converted, according to conditions, in alkaline medium into the 1,2-anthraquinone dioxime (III), the bisulfite compound of 1,2-anthra-(3',4')-furazan (IV) or the 1,2-anthra-(3',4')-furazan (V). The two figures show the absorption spectra of the compounds to be compared. There are 2 figures and

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