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ACCESSION NR: AT4016598 S/2556/63/000/034/0020/0028

AUTHOR: Shemyakin, M. M.

TITLE: More on the pattern of arrangement of certain lunar craters

SOURCE: Vsesoyuznoye astronomo-geodezicheskoye obshchestvo. Byulleten', no. 34, 1963, 20-28

TOPIC TAGS: astronomy, moon, lunar crater, lunar crater distribution

ABSTRACT: Despite the apparent chaotic distribution of lunar craters certain of them are arranged in a pattern which can be expressed mathematically. Certain craters are arranged in chains and the features forming the chain lie on a smooth curve, to a considerable extent close to the arc of a circle. The area of the craters in the chain changes regularly or is identical. In certain cases this regularity is close to a geometric progression and can be expressed by the formula $d_n = 2\ d_{n+1}$. There are three principal cases: a) diameters of craters decrease and their change can be expressed as a smooth curve; b) in part of the chain diameters decrease, but in part of the chain diameters remain constant; c) diameters of the craters in the chain are identical. Examples are shown in Enclosure. The distance between the centers of all craters in the chain for the most part changes in conformity to the change in diameters of the craters. The chains have been

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formed by craters which are both ancient and youthful in selenographic terms. Craters of a different age may occur in the same chain. Orig. art. has: 5 formulas, 7 figures and 1 table.

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SUBMITTED: 00 DATE ACQ: 24Feb64 ENCL: 02

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SHEMYAKIN, M.M.

Aid to amateurs in constructing telescopes. Talk 1.
Zem. i vsel. 1 no.4:79-81 Jl-Ag '65.

(MIRA 18:12)

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SHEMYAKIN, M.P.

For amateurs constructing telescopes. Talk 2. Polishing the main telescope mirror. Zem.i vsel. 1 no.5:79-91 S-O '65. (MIRA 18:11)

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Brown vat dyes M. A. Ilinskii and M. M. Shemyakin. *Anilinokrasochnaya Prom.* 3, 253-7(1933).—A systematic survey was undertaken of the foreign patents for production of various brown vat dyes with a view of selecting the best suitable dyes and methods for domestic production. Chas. Blanc

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Acidimetric method for determination of phenol in the melt. M. M. Shemyakin. *Anilinokrasochnaya Prom.* 3, 403-4(1933). Rhodes, Jahnes and Bivans (*C. A.* 21, 3049) studied the production of phenol by fusing Na benzenesulfonate with NaOH and recommended an acidimetric method for detg. the phenol in the melt. A ppt. of $C_6H_3Br_3OH$ was formed in an aliquot part of the aq. ext., which was filtered off, dissolved in a measured vol. of 0.05 *N* NaOH and the excess titrated with 0.05 *N* HCl. Detailed directions are given for carrying out a similar procedure which has been found more accurate than any other method. Stress is laid upon the treatment of the neutralized soln. with Br_2 at 0°, removal of excess Br_2 with $Na_2S_2O_3$, washing the ppt. with satd. NaCl soln. and finally with alc. and the use of considerable NaCl in the final soln. of the ppt. in NaOH. Chas. Blanc

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Formation of phenol by fusion of sodium benzene sulfonate with sodium hydroxide. R. K. Eikhman, M. M. Shemyakin and V. N. Vozhdaeva. *Anilinokrasochnaya Prom.* 4, 461-72(1934).—A crit. review of the literature and exptl. study of the process led to the following conclusions. The formation of phenolic by-products and the process of resinification are closely related, beginning after a fusion of over 1-1.5 hrs. up to 315°, or over 30-45 min. up to 330°, or over 7-15 min. up to 350°. At temps. below 330° and 30-45 min. heating, the yield of actually sepd. PhOH is 90%, or 92% by the acidimetric method. A more prolonged heating results in poorer yields of PhOH and a greater yield of the by-products. The optimum conditions of heating are 15-30 min. at 320-30°, viz., at 320-5° and 15 min. 94% PhOH (sepd.) or 96% PhOH (acidimetry), and at 330-5° and 0-3 min. 94.9 and 96% PhOH, resp. Thus no resinification and formation of phenolic by-products takes place, which is further substantiated by the closeness of the results obtained in the detn. of PhOH by the sepn. and acidimetric methods. The resp. values for melts obtained at 340-5° and 45 min. are 85.5 and 95.5% PhOH. Melts obtained at 350° and 15 min. contain 88% PhOH and not 95% as claimed by Rhods. The iodo- and bromometric methods of analysis of PhOH in melts give inaccurate results, because some of the Br or I reacts with the by-products and resinous matter. The identified by-products are: resorcinol, p-HOC_6H_4Ph and (o-HOC_6H_4)$_2$. Chas. Blanc

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Formation of phenol by fusion of sodium benzenesulfonate with sodium hydroxide. II. R. K. Elkhman, M. M. Shemyakin and V. N. Vozhdaeva. *Anilinokrasochnaya Prom.* 4, 523-31(1934); cf. *C. A.* 29, 1076[9].—The influence of by-products and impurities on the yield of PhOH was studied by alk. fusion of pure $PhSO_3Na$ with the addn. of these products at 320-5° for 15 min. The addn. of a mixt. of Na_2SO_4, NaCl and Na_2CO_3 showed that Na_2SO_4 up to 10% practically does not affect the yield of PhOH; NaCl up to 4% gradually decreases it from 93-4% to 85.6%, while a further addn. of NaCl improves the yield. The addn. of Na_2CO_3 counteracts the neg. action of NaCl and increases the yield of PhOH at a rate of 1.5-2% for every 2% of Na_2CO_3 added to 94% PhOH with 8% Na_2CO_3. The addn. of 0.5 and 1.5% Fe reduces the yield of PhOH to 89 and 87.5%, resp., and that of 0.5 and 1.5% Fe_2O_3 to 90.5 and 89%. Contrary to general opinion $NaClO_3$ (a common impurity in the electrolytic NaOH) affects the yield of PhOH very moderately, viz., to 92% with 0.5 and 89% with 1.5% $NaClO_3$. It oxidizes primarily the Na_2SO_3, increasing the Na_2SO_4 in the melt from 3-4% to 15-18%. The reduction of PhOH yield is caused here by the formation of phenolic by-products, which is related to the increase of Na_2S from 2-3% to 5-6%. With Ph_2SO_3 the combined content of Na_2SO_3 and Na_2S in the melt is reduced to 87-8%, which indicates a neg. action on the main reaction. The relatively high yield of PhOH (90-1% with 1-3% Ph_2SO_3) is derived in part from the decompn. of Ph_2SO_3 into PhOH with 98% yield and Ph_2 (Otto, *Ber.* 19, 2425(1886)). The only phenolic by-product isolated from the distn. residue of the melt was 1% Ph_2O, m. 54-6°, b. 275° (Hongschmid, *Monatsh.* 22, 506(1901)) and probably some Ph_3. m-$C_6H_4(SO_3Na)_2$ (I) sharply decreases the yield of PhOH to 80 and 81% with 1 and 3% I, resp. The decreased content of Na_2SO_3-Na_2S (85-6%) in the melt shows that I activates the formation of by-products. Special expts. showed that the addn. of 1% resorcinol to the melt reduces the yield of PhOH to 85%, which indicates that the adverse effect of I in the main reaction is partly caused by the decompn. of I with the formation of 25-30% resorcinol. The addn. of 2 and 4% Na_2S reduces the PhOH yield to 87 and 76%, resp., with the formation of Ph_2, m. 76° (Fittig, *Ann.* 121, 364), and 1-2% PhSH, b. 172-3° (Stenhouse, *Ann.* 49, 248). The difference of 7% PhOH between the detn. by sepn. and acidimetry shows an excessive formation of phenolic by-products, of which o- and p-HOC_6H_4Ph were isolated. The adverse action of Na_2SO_3 becomes pronounced after the addn. of 13% Na_2SO_3 with the reduction of the PhOH yield to 87% and the formation of resorcinol, o- and p-HOC_6H_4Ph and $(o\text{-}HOC_6H_4)_2$. The addn. of 5 and 15% PhONa (added to NaOH) reduces the PhOH yield to 88 and 80%, resp., and that of 10, 20 and 30% of a melt from a previous run to 89, 88 and 86% PhOH. Increasing the autoclaving from 1.5 to 4 hrs. reduces the PhOH yield by 5-6%. In all expts. only c. p. or purified products were used.

Chas. Blanc

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Aldehydo acids and aldo enol lactones. I. The possibility of condensation of aconic acid with aldehydes and ketones. M. M. Shemyakin and I. A. Red'kin. *J. Gen. Chem. U. S. S. R.* 9, 442-6 (1939). It is planned to synthesize relatively simple compds. contg. the essential group of the cardiac glucosides and study them pharmacologically. Aconic acid (I) is used so that H_2O-sol. salts can be obtained. When I is heated for 1 hr. at 100.5° with excess BzH, *n*-$NO_2C_6H_4CHO$ or furfural in the presence of 5 drops of EtNH catalyst, it gives 14.5% [illegible] (n. 201.2°), 18.5% *m-nitrobenzalaconic acid*, darkens to 200° but does not melt, or 41% furfuralaconic acid, darkens to 200° without melting, resp. All these compds. are insol. in H_2O but dissolve without change in cold alkali, and all form Ag mirrors. I does not condense with ketones. **II. The synthesis of α-hydroxy-β-phenyl-γ-aldo enol lactone 3-hydroxy-4-phenylfuran-2-one.** M. M. Shemyakin. *Ibid.* 484-90. When $PhCH_2CHO$ (I) is heated with $HOCH(OEt)CO_2Et$ (II) and Ac_2O at 140.5° for 20 hrs., it gives 29.5% *Et β-formyl-β-phenylacrylate* (III), b_2 110-14° (*semicarbazone*, n. 167°), and 13% *acetyl α-hydroxy-β-phenyl-γ-aldo-enol lactone* (IV), m. 140.1°. The first step in this reaction is the elimination of EtOH between I and II with formation of the intermediate $HOCH(CO_2Et)CH(CHO)Ph$, which then decomps. in 2 directions to give III and IV. Hydrolysis of III with 5% HCl gives *β-formyl-β-phenylacrylic acid* (V), m. 161.2°. When IV is hydrolyzed with 10% HCl, the lactone ring is opened and V is also formed. The reaction between I and II can be used to synthesize aldo-enol lactones with substituents on the β-C atom, but it is not general, since when $PhCH_2CHOCOMe$ replaces I in the reaction, action is slight and no identifiable products can be isolated. **III. Some specific peculiarities of γ-aldo enol lactones and unsaturated aldehydo acids.** *Ibid.* 491-5. Compds. of this type do not add Br to the double bond of the lactone ring or to one adjacent to it. Their reactivity in many reactions is very great, however. Thus, acetyl-α-hydroxy-β-phenyl-γ-aldo-enol lactone and β-formyl-β-phenylacrylic acid or its Et ester, when heated for 2-3 min. at 80-90° with 2-4% NaOH give a dibasic acid, $C_{14}H_{10}O_6$, m. 195.6° on slow heating and 206.8° on rapid heating. Me ester, m. 198.9°. It is probably a new truxinic acid. H. M. Leicester

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Ketones. I. Condensation of ketones with cyanoacetic acid. M. M. Shemyakin and D. M. Trakhtenberg. *Compt. rend. acad. sci. U. R. S. S.* 24, 763-7(1939) (in English); cf. *C. A.* 34, 887. When cyclopentanone, cyclohexanone, Me_2CO, MeEtCO and α-hydrindone (I) are condensed with 2-3 times the required amt. of $CNCH_2CO_2H$ (II) and piperidine at 100-15° for 2 hrs., 70-90% of the corresponding nitriles is obtained. No intermediate cyano acid appears in the product. The condensation reaction probably precedes the decarboxylation. In alicyclic compds., the double bond appears in the ring; in aliphatic compds., it is in the position -C CHCN. MePhCO and Ph_2CO do not react with II. The compd. from I and II in 68-70% instead of 18% as Ingold and Thorpe (*C. A.* 13, 1211) report for α-hydrindenylacetonitrile. Since the new compd. gives no α-hydrindone on oxidation and does not add Br, it is probably the normal compd. and the compd. of I. and T. is hydrindenylidene-acetonitrile.

H. M. Leicester

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Aldehydo acids and aldo-enol lactones. IV. Specific transformations of certain aldehydo acids and γ-aldo-enol lactones in an alkali medium M. M. Shemyakin. *Compt. rend. acad. sci. U. R. S. S.* 24, 768-72 (1939) (in English); cf. *C. A.* 34, 89[1].—In continuing previous research, the transformation of certain aldehydo acids and γ-aldo-enol lactones in contact with alkalies leading to a dicarboxylic acid was examd. more closely. The acids so produced are of particular interest for stereochemistry. Five of them are truxillic acids, the remaining 6 truxinic acids, 2 of the latter being *new*, viz.: (1) m. 196°, empirical formula $C_{18}H_{16}O_4$. Isomerization into a known truxinic acid proved it to be 1 of the diphenylcyclobutanedicarboxylic acids so far unknown; (2) m. 245°. Some particulars about the truxinic acid, m. 196°, prepd. in the previous paper and its derivs. conclude the article. 7 references. A. H. Kruppe

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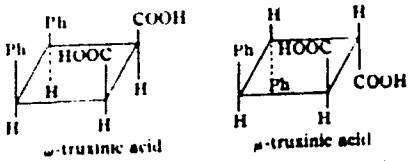
Spatial structure of two new diphenylcyclobutanedicarboxylic acids μ- and ω-truxinic acids. M. M. Shemyakin. *Compt. rend. acad. sci. U. R. S. S.* 29, 199-201 (1940) (in English).—The monoanilide of μ-truxinic acid undergoes no change when heated even up to 270°, while the monoanilide of ω-truxinic acid splits out water even at 108-110°, going over to the corresponding phenylimide, m. 177-9°. Also, the monoanilide of the μ-acid undergoes no change even when heated to boiling with 10% HCl for 2-3 hrs., whereas the mono-



ω-truxinic acid μ-truxinic acid

anilide of the ω acid under such conditions is easily converted to the corresponding phenylimide, which is very stable to acids. From these considerations S. concludes that of the 2 structures possible (all other structures having been assigned to other truxinic acids) ω-truxinic acid, m. 196°, has the *trans* structure while ω-truxinic acid, m. 245°, has both carboxyl groups in a *cis* position with respect to each other. S. also reports these syntheses: *Monochloride of ω-truxinic acid*, m. 130°: 1 g. of the acid is boiled for 10 min. with 10 cc. $SOCl_2$ and the ppt. recrystd. twice from ligroin with bone carbon, 0.65 g. being obtained. *Monoanilide*: to 0.75 g. of the monochloride in 30 cc. dry benzene, 0.75 cc. of aniline in 5 cc. benzene were added. Excess aniline was pptd. by HCl and filtered off and the benzene distd. off. The remaining oil crystd. completely, when ether was added, in long fibrous needles (yield 0.7 g.), m. 108-11° (decompn.), above which temp. the product solidifies again and m. 199-214°.

Rebecca Yablonsky

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Properties of μ-truxinic acid. M. M. Shemyakin. *Compt. rend. acad. sci. U. R. S. S.* 29, 212-5(1940)(in English). The 2 carboxyl groups of μ-truxinic acid (I), m. 190°, which is the trans isomer, differ from each other in their degree of dissocn. and in their behavior toward certain reagents. E. g., with alkalies as 0.1 N NaOH, Na_2CO_3, etc., only 1 carboxyl group is neutralized, with formation of the mono-Na salt. The 2nd carboxyl group can be neutralized only with an excess of alkali. When I is boiled with $SOCl_2$, only the monochloride, insol. in a cold, alk. soln., is produced, not the dichloride. μ-Truxinic acid forms 2 Me esters, both insol. in a cold, alk. soln. The ester m. 190° is thought to be the mono-Me ester although this was not proved conclusively by org. analysis, while the ester m. 183° is believed to be the di-Me ester. Isomerizat. on of I or its derivs. to the cis form, ω-truxinic acid, or its derivs., takes place readily. I forms no cyclic anhydride, does not react when boiled with HOAc and is insol. in water but rather easily sol. in ether and glacial HOAc. Rebecca Yablonsky

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Condensation of bromoacetaldehyde with malonic acid. N. S. Vul'fson and M. M. Shemyakin. *Compt. rend. acad. sci. U. R. S. S.* 29, 206-7(1940)(in English). To 10 g. of malonic acid, 5 cc. of piperidine was added. Heat was evolved. When the mixt. began to cool, 1[illegible] g. of $BrCH_2CHO$ was added. After 24 hrs. the reaction mixt. was heated for 2 hrs. in an oil bath at 105-15°, when CO_2 and water were given off. The mixt. was poured into 250 cc. of 5% H_2SO_4 and the flaky ppt. (about 1 g.) was filtered off and washed with ether. The product was assigned the structure of a [illegible] lactonic acid, $BrCH_2CH_2CH(CO_2H)_2COO$. The proof of its [illegible] rested on the behavior of the product toward alk. hydrol. There should be and there was a break in the compd. and formation of $BrCH_2CHO$ and malonic acid, which actually were recovered, the latter as Ba malonate. The product was insol. in water, alc. and benzene and very slightly sol. in ether.

Rebecca Yablonsky

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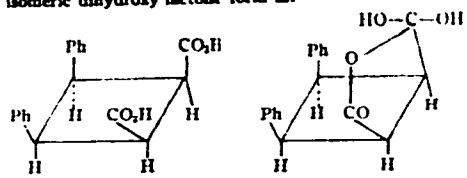
Structure of ω-truxinic acid. M. M. [illegible]rmyakin. *J. Gen. Chem.* (U. S. S. R.) 11, 219-24(1941); cf. *C. A.* 35, 3978[2], 3979[3].—From the anomalous behavior of ω-truxinic acid toward certain reagents, for instance, from the fact that only 1 carboxyl group is neutralized with 0.1 *N* NaOH, Na_2CO_3, etc., the 2nd carboxyl group being neutralized only on boiling with alkali, and from the fact that on boiling with $SOCl_2$ only the monochloride, insol. in alkali, and not the dichloride is formed, it is concluded that ω-truxinic acid is present not in form I but in the isomeric dihydroxy lactone form II.



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Heterocyclic ketones. M. M. Shemyakin and E. I. El'kina. *J. Gen. Chem.* (U. S. S. R.) 11, 319-52(1941). *N*-Methyl-2-pyridone (I) reacts easily in cold Et_2O with $(COCl)_2$ to give *2,2-dichloro-N-methyldihydropyridine* (II), which is very hygroscopic and easily regenerates I with H_2O. II reacts with $H_2NCHMe(CH_2)_3NEt_2$ to give *(4-diethylamino-1-methylbutylimino)-N-methyldihydropyridine*, whose *$AuCl_3$-HCl salt*, m. 128-9°. Similarly, II and *p*-$NH_2C_6H_4SO_2NH_2$ give the *amide* of *(p-sulfophenylimino)-N-methyldihydropyridine*, m. 245-6°. *$AuCl_3$-HCl salt*, m. 177-8°. With H_2O this regenerates I. The dichlorides cannot be isolated in this way from ketones in which no group is substituted on the ring N. H. M. Leicester

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"[illegible] Hydrolysis [illegible] Isosaccharides. I. [illegible] Hydrolysis [illegible] [illegible]." By I. A. [illegible] and [illegible] Sadykin. (p 1157)

[illegible] (Zhurnal Obshchei Khimii, 1951, Vol 11, No. 1)

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[illegible] Ind. Dib.Dl[illegible] Control [illegible] Gas [illegible] Pipelines." by [illegible] and [illegible] . (p 1163)

SO: Journal of Technical Physics (Zhurnal Tekhnicheskoi Fiziki) 1951, Vol 21, No. 10

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[illegible] V. Dedoublement hydrolytique des [illegible] taux [illegible] acides [illegible]." By I. A. [illegible] (p 1175)

[illegible] Chemistry (Zhurnal [illegible] 1/1, Vol 11, [illegible]

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[illegible]

"[illegible] Heterocyclic Ketones. II. Alkylation of Heterocyclic Ketones," [illegible] Lab Org. Chem. All-Union Inst. Exp. Med., Moscow, [illegible].

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[illegible]

"The Structure of [illegible] and their [illegible] [illegible]," Zhur. Obs. [illegible] Khim., 1[illegible], No. [illegible], [illegible]. Lab. [illegible] Chem., All-Union Inst. [illegible] and [illegible] ~~Soch.~~ [illegible] Inst., -1[illegible] -.

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"[illegible] in the [illegible] of Heterocyclic [illegible]. [illegible] A, [illegible] of [illegible]-Heterocyclic Compounds," [illegible], 13, No. [illegible], 1[illegible]. [illegible] Textile Inst., [illegible].

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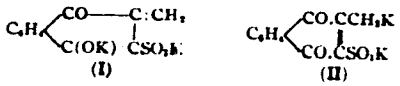
Vitamin "K" group II. Tautomeric and oxi[illegible] reduction transformations of 2-methyl-1,4-naph[illegible] none and its derivatives. L. A. Shukina, Yu. B. S[illegible] and M. M. Shemyakin. *J. Gen. Chem.* (U. S. S. R.) 13, 327-30 (1943) (English summary); cf. *C. A.* 38, 572[illegible]; Fieser, *et al.*, *C. A.* 35, 4065[illegible].—The authors investigated some properties of 2-methyl-1,4-naphthoquinone and related compds. The quinone on prolonged boiling with water yields phthalic anhydride and a deep violet, cryst. solid (does not m. 35[illegible]° (from AcOH)). Boiling with 10% KOH leads to similar results with a greater amt. of the violet product. Boiling with concd. HCl leads only to the violet solid, with only traces of phthalic acid. K 2-methyl-1,4-naphthoquinone-3-sulfonate (20 g.) boiled for [illegible] hrs. with 2 l. H_2O and cooled, yields the *quinhydrone* which is filtered off (3.4 g., m. 243-4° (from water)), while evapn. of the water soln. yields 0.8 g. phthalic anhydride. The K sulfonate (5 g.) was stirred with 55 cc. of 25% KOH for 4-5 min. and immediately filtered; the filtrate rapidly deposited the *enolate* (I), which was filtered off and dried after washing with EtOH and Me_2CO. I (5 g.) in 20 cc. water rapidly darkens and precipitates the quinhydrone described above (1.8 g.) and phthalic acid; 5 g. of the enolate are shaken with 100 cc. 25% KOH for 2 hrs. and filtered; on standing there occurs



(I)

(II)

crystn. of 0.5 g. of an orange-red compd. (II). The mother liquor on acidification yields the original K sulfonate.

G. M. Kosolapoff

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CA

11E

The vitamin K group. III. The biological action of vitamin K and of its synthetic analogs. M. M. Shemyakin, I. A. Shukina and Yu. B. Shvetsov. *J. Gen. Chem.* (U. S. S. R.) 13, 398-402(1943)(English summary); cf. C. A. 38, 572[1]. —After consideration of known data on the biol. activity of the vitamin K group, the authors believe that vitamin K and its analogs are provitamins, while the actual vitamin K carrier is phthalic acid, which is probably formed from vitamin K and its analogs in the course of operation of the oxidation-reduction system. **IV. Structure of the products of reaction of 1,4-naphthoquinones with bisulfites of alkali metals.** D. A. Bochvar and M. M. Shemyakin. *Ibid.* 467-76(English summary).—The authors studied the reaction between 1,4-naphthoquinones with alkali bisulfites. Soln. of 4 g. 92% $KHSO_3$ in 10 cc. water was added to 6 g. 2-methyl-1,4-naphthoquinone-3-sulfonic acid (as K salt) suspended in 10 cc. water at 40-5°. There was formed a white ppt. of $C_{11}H_{10}O_3SK.KHSO_3$ (55%), which is crystd. from hot water and is readily sol. in water. On heating it suffers partial dissociation and its soln. treated with $BaCl_2$ yields a ppt., sol. in HCl. K_2CO_3 or KOH cause rapid decompn. of the complex, whereas d.l. HCl effects decompn. rapidly only on warming, with formation of a red-violet ppt. Treated with H_2O_2, this complex adds a mol. of O, indicating its probable structure as a complex equil. mixt. of the component salts. The oxidized (bisulfate) complex crystallizes readily from EtOH as large needles and yields $BaSO_4$ on treatment with $BaCl_2$ only extremely slowly. Aqueous pastes of 2-methyl-1,4-naphthoquinone treated with a soln. of $KHSO_3$ at 40-5°, after filtration and evapn., gave 51% of a complex, $C_{11}H_8O_2.KHSO_3.H_2O$. For practical use, it is advised that 2 mols. of $KHSO_3$ or $NaHSO_3$ be used and the soln. evapd. to dryness, without sepn. of excess bisulfite. The complex can be crystd. from water or EtOH. $BaCl_2$ causes slow pptn. of Ba sulfite, heating with HCl yields SO_2 and a deep-violet ppt.; strong alkali ppts. the quinone instantly; Cl leads only to traces of K 2-methyl-1,4-naphthoquinone-3-sulfonate (I). The bisulfite complex of the I on treatment with various quinones rapidly ppts. I.

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1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

Ca

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No 7-8

Ketone series III. Condensation of the esters of keto acids and diketones with cyanoacetic acid. M. M. Shemyakin and D. M. Trakhtenberg. *J. Gen. Chem.* (U. S. S. R.) 13, 552-6(1943)(English summary); cf. C. A. 38, 3218[1]. It is shown that esters of aliphatic β- and γ-keto acids and alicyclic and aliphatic β-diketones can condense with $NCCH_2CO_2Et$, analogously to aliphatic and alicyclic monoketones, with formation of the corresponding unsatd. nitriles. Introduction of a Ph radical adjacent to the CO group hinders this reaction in mono- and diketones, *p*-quinones are also incapable of condensation. $AcCH_2CO_2Et$ (10 g.), 15 g. $NCCH_2CO_2H$ (I) and 10 cc. piperidine heated for 3 hrs. at 100-10°, then at 120-5° for 0.5 hr., gave 2 g. $NCCH_2CMeCH_2CO_2Et$, b_{12} 116-18°. Et levulinate (5 g.), 0.75 g. I and 8.1 g. piperidine heated for 2.5 hrs. at 110-15°, then for 0.5 hr. at 120°, gave 1.5 g. $NCCH_2CMeCH_2CH_2CO_2Et$, b_{12} 136-40°. Dimedone (2 g.), 5 g. I and 7 cc. piperidine heated to 110-15° for 3 hrs. gave the dinitrile $C_{12}H_{14}N_2$, m. 89-90° (dil. EtOH). Phloroglucinol (4 g.), 6.2 g. I and 8 cc. piperidine heated for 2 hrs. at 115-25° gave 1.1 g. pink solid, m. 143-5° (decompn.), having the compn. C 50.1%, H 6.6% and N 12.1%; its structure has not been established. CH_3Ac_2 (4.3 g.), 15.7 g. I and 19.6 cc. piperidine heated for 3 hrs. at 110-15° gave 1.5 g. of a yellow liquid, b_{12} 58-60°, contg. 22.7% N. Ethoxyacetylacetone (10 g.), 25 g. I and 22 cc. piperidine heated for 3.5 hrs. at 115-25° gave 1.5 g. of a product, b_{12} 58-60°, contg. 21.45% N. Similar reaction with quinone yielded only hydroquinone.

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Ca

1ST AND 2ND ORDERS — PROCESSES AND PROPERTIES INDEX — 3RD AND 4TH ORDERS

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β-Lactones and β-lactonoacids. III. Condensation of citral with malonic acid. N. S. Vul'fson and M. M. Shemyakin. *J. Gen. Chem.* (U. S. S. R.) 13, 436-47 (1943) (English summary). cf. C. A. 37, 610[9]. Malonic acid (20 g.), 30 g. citral and 3 cc. glacial AcOH are treated with 3 cc. piperidine, heated on a water bath for 1.5 hr. when the mass solidifies. After washing with [illegible] the solid is crystd. from 60% alc., to yield 19 g. (40%) [illegible] *dilactone of citrylidenemalonic acid*, $Me_2C.CH(CH_2)_2C$ [illegible] O - CO (Me.CH_2.CH.CH.CO.O), (I), m. 186.7°. The mother liquors yield *citrylidenecetic acid*, b_{15} 165-75° (decomp.). I (1 g.), heated to soln. with 4 cc. 10 N NaOH, heated for 2-3 min. and acidified by dil. H_2SO_4, yields 0.50 g. $Me_2C.CH.CH_2CH_2CMe(OH)CH_2CH.CH(CO_2H).CO.O$, m. 113-14° (after extn. with hot benzene); the evapd. benzene extract yields 0.1 g. $Me_2C.CH.CH_2CH_2CMe(OH)CH_2.CH.CH_2.CO.O$ (II), m. 120-0.5°; a soln. of the Na salt of the above acid, on acidification, yields the mixt. of the acid and the above lactone, indicating fairly ready decarboxylation; the Ag salt of the acid appears to have an appreciable water soly., while AcCl leads to loss of some CO_2 and yields I. I boiled with 10 N NaOH and acidified, yields 57% II, which, treated with slight excess of 0.1 N NaOH, acidified by HNO_3 and treated with $AgNO_3$, gave $Me_2C.CH.CH_2CH_2CMe(OH)CH_2CH.CH.CO_2Ag$. II is not affected by Ac_2O in pyridine at about 100°, while AcCl yields 47.5% $Me_2C.CH.CH_2CH_2CMe(OAc)CH_2.CH.CH_2.CO.O$, m. 117-18° (from benzene). Oxidation of II by alk. $KMnO_4$ yielded $(CO_2H)_2$, while no HCO_2H was detected, thus indicating the presence of the β-lactone ring. IV. **The rate of opening of the β-lactone ring.** M. M. Shemyakin and N. S. Vul'fson. *Ibid.* 448-50 (English summary). The authors studied the rate of ring opening of the lactones $Me_2C.CH(CO_2H).CO.O$ and $PhCH.CH(CO_2H).CO.O$ at various temps. The results, presented in tabular and graphical form, show that the ring opening of β-lactones is a 1st-order reaction. There are indications that the hydrolysis in alk. medium leads to unsatd. acids and that the hydrolysis reaction is a tautomeric one. For the 2 lactones tried (above) the activation energy of hydrolysis was found to be 19,323 and 22,832 cal., resp. G. M. Kosolapoff

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[illegible]

"[illegible] in the [illegible] "[illegible]", [illegible]. [illegible] of Reaction. Products [illegible] 1, [illegible] [illegible] [illegible]," [illegible], [illegible] [illegible], [illegible] [illegible] [illegible] Inst., [illegible].

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SHEMYAKIN, M. M.

"Investigation of B-Lactones and B-Lactono-Acids. IV. Study of the Reaction Rate of the Cleavage of the Lactone Ring." Shemyakin, M. M. and Vulfson, N. S. (p. 455)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1943, Volume 13, no. 6.

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[illegible], N. .

"[illegible] of Vitamin A. [illegible] of the [illegible] Action of Vitamin A and of Its Synthetic Analogs," [illegible], 40, No. 4, [illegible]. All-Union Inst. [illegible] Vitamin. [illegible]

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PROCESSES AND PROPERTIES INDEX

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Glucosides of sulfonamides. S. I. Lure and M. M. Shemyakin. *J. Gen. Chem.* (U.S.S.R.) 14, 935–40(1944) (English summary).—Sulfapyridine (10 g.), 17 g. glucose and 0.1 g. fused $CaCl_2$ are refluxed with 200 cc. abs. EtOH for 1–1.5 hrs. until soln. occurs, 0.5 g. activated charcoal is added, the mixt. is filtered, and the filtrate evapd. to dryness in vacuo; the residue is treated with 100 cc. Et_2O and the ppt. is filtered off to give 96% *diglucoside* of *2-sulfapyridine*, as a white powder readily sol. in water and hot EtOH. *Similar products* were formed with *sulfomethylthiazole* (I) and *sulfaguanidine*. The biol. action of these diglucosides is analogous to that of the original sulfonamides. In the case of the deriv. of I, however, it was found that appreciable activity against cholera and cholerlike organisms (*Vibrio cholerae*) exists. All of the above diglucosides are readily hydrolyzed in weak acids.

O. M. Kosolapoff

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[illegible], . .

"Experimental Study Of The Mechanism Underlying The Biological Action Of Quinones Of The Vitamin K Type," Dok. AN, 45, No. 4, 1944. Lab. for the Chem. of Vitamins, All-Union Inst. of Experimental Med., c1944-.

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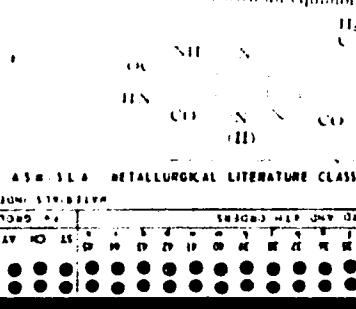
The synthesis of di- and triaminophthalides. M. E. Kurilo and M. M. Shemyakin, *J. Gen. Chem.* (U.S.S.R.) 15, 701-10 (1945) (English summary). 4-Nitrophthalimide (100 g.), 225 g. Zn dust, 350 cc. 20% NaOH, and 1 g. $CuSO_4$ in 50 cc. water were mixed with ice-cooling and the mixt. was stirred for 30 min., after which water was added and the NH_3 formed in the reaction was removed by steam distn. The soln. was filtered and acidified with HCl to Congo red to yield 44% *5-aminophthalide*, m. 193-4° (from water). 5-Acetamidophthalide (60 g.) and 7.3 g. (d. 1.84) concd. H_2SO_4 were treated at −10° with a mixt. of 19.8 g. HNO_3 (d. 1.52) and 80 cc. concd. H_2SO_4 (d. 1.84), kept at −5 to −8° for 30 min., for 2 hrs. at −3° to −2°, and then poured on ice; the resulting paste was stirred with 300 cc. hot alc. and filtered; the residual product was 25.8%, *5-acetamido-6-nitrophthalide* (I), m. 206.8° (from AcOH). Hydrolysis by 10% HCl gave *5-amino-6-nitrophthalide*, m. 252-3° (from AcOH), while diazotization of the latter in H_2SO_4 and treatment with boiling EtOH gave *6-nitrophthalide*, m. 141-3° (from EtOH). Reduction of the nitroamino compd. with Zn dust in HCl with mild warming gave *5,6-diaminophthalide*, m. 275°, which, heated with an equimol. amt. of alloxan



(II)

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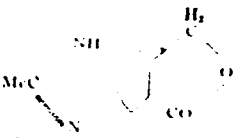
PROPERTIES NOTE



from 70% MeOH, m. 82-3°, [illegible] (2 H.O), $C_{10}H_{10}$, and has the compn. C_8H_6O. I, when titrated with $BaOH$ in $CHCl_3$, consumes 2 atoms O at 0°, indicating the presence of 2 double bonds which are present in isolated posi-

in AcOH by H in the presence of Pd gave a colorless product which appeared to be III. 5-Aminophthalide (35 g.) in 210 g. concd. H_2SO_4 was treated, after cooling to −15°, with a mixt. of 16.5 cc. HNO_3 (d. 1.4) and 57 cc. concd. H_2SO_4. After stirring for 20 min., the mixt. was poured on ice, and the resulting paste, treated with 30-40 cc. EtOH, yielded pure *4,6-dinitro-5-aminophthalide*, m. 207° (from $CHCl_3$). Reduction of this with Zn dust in 10% HCl gave a crude triamino deriv., m. 224°, which was dissolved in warm dil. HCl, and, on cooling, gave the *HCl salt* of the pure *4,5,6-triaminophthalide* (no m.p. given), while addn. of NH_3 to the filtrate gave the by-product, *nitrotriaminophthalide*, m. 230-1°. Condensation of the triamine with alloxan in water with gentle heating gave the *corresponding alloxazine*, m. 305° (from pyridine), while the use of the triamine HCl salt gave the *corresponding HCl salt*, m. 360°.

G. M. Kosolapoff

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SHEMYAKIN, M. M.

Compounds with quinoid structures. 1. The mechanism of the reaction of p-quinones with alkali bisulfates. D. A. Bochvar, A. S. Gnarnyshev, and M. M. Shemyakin (Moscow Textile Inst.). J. Gen. Chem. (U.S.S.R.) 15, 444-57(1945); cf. C.A. 39, 3325[2].--- $KHSO_3$ and K 1,4-naphthoquinone-2-sulfonate (I) form a cryst. complex which gives a green color with $FeCl_3$, couples with diazobenzenesulfonic acid, reacts with more I to form the quinhydrone deriv., decolorizes a dil. fuchsin solu., and gives with Cl a deep yellow solu. from which I can be recovered. Boiling the complex with H_2O converts it to an addn. compd. which shows none of these reactions. The analogous complexes of 1,4-naphthoquinone and K 2-methyl-1,4-naphthoquinone-3-sulfonate give similar reactions. These facts confirm the proposed mechanism in which $KHSO_3$ reacts with quinones to form an oxonium salt which rearranges to the complex. The complex has 4 resonance forms, 3 quinoid and 1 benzenoid. The complex may break down to form the hydroquinone, the initial quinone, and a bisulfate, or in another way to give a hydroquinone sulfonate. The structure of the quinones and the exptl. conditions det. the relative concns. of the different forms of the complex, and this in turn determines the direction of the decompn. H. M. Leicester

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1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

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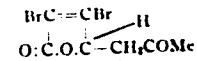
Structure of aldehyde acids and their tautomeric transformations. II. Structure and tautomeric transformations of bromomucic acid. E. I. Vinogradova and M. M. Shemyakin. *J. Gen. Chem.* (U.S.S.R.) 16, [illegible] (1946); cf. *C.A.* 38, 962[3]. Further confirmation was obtained for hypotheses advanced in part I of this series as to the structure of aldehyde acids. Bromomucic acid (I) was found to have, in cryst. state, the structure of a HO lactone; in this solid state it is *3,4-dibromo-5-hydroxy-2,5-dihydro-2-furanone* and reacts in this form under conditions which do not favor tautomerization; in the other form, *α,β-dibromo-β-formylacrylic acid*, it can react only under suitable conditions and in the presence of proper catalysts. I (m. 123–4°) (2.58 g.) in 4 cc. abs. EtOH was mixed at 5° with 1.44 g. sulfanilamide in 55 cc. EtOH to yield $C_{10}H_8SN_2Br_4$, which decomps. 186° and has a free CO_2H group. Condensation of I with AcPh in dil. alc. NaOH gave, on standing, a primary product, *PhCOCH:CHCBr:CBrCO₂Na*, which with acid gave *5-phenacyl-3,3-dibromo-2,5-dihydro-2-furanone*, m. 168°. I (5.16 g.) and 3 g. Me_2CO in 350 cc. water, treated with 12 cc. 10% NaOH and allowed to stand 10 hrs. at 5°, gave, on acidification with HCl, a condensate of 2 moles I with Me_2CO, $O:C(:O)CBr:CBr:CH(CH_2)_2CO$, m. 102–3° (from EtOH); the mother liquor was made alk. with Na_2CO_3 to yield *5-acetonyl-3,4-dibromo-2,5-dihydro-2-*



furanone which m. 90–1° (from EtOH); *p-nitrophenylhydrazone* m. 83–5°. Heating 2 g. I with 5 cc. Me_2CO and 13 cc. Ac_2O 8 hrs. on a steam bath gave *5-acetoxy-3,4-dibromo-2,5-dihydro-2-furanone*, m. 54–5° (from EtOH). 5-Methyl-3,4-dibromo-2,5-dihydro-2-furanone was prepd. in 50% yield according to Simonis, *et al.* (*Ber.* 38, 3983 (1905)); this compd. failed to react with MeMgI, however, one of its Br atoms was found to be rather reactive and on standing in the cold with $PhNH_2$ in EtOH soln. for 10 days gave the *aniline deriv.*, $C_{11}H_{10}O_2NBr$, m. 119–21° (from benzene-ligroin). G. M. Kosolapoff

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PROCESSES AND PROPERTIES INDEX

CA

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Synthesis of dimethoxy derivatives of salicylic acid and the so-called steric hindrance. B. M. Bogoslovskii, M. M. Shemyakin, and A. S. Chernyshev. *J. Gen. Chem.* (U.S.S.R.) 16, 1135-6(1946)(in Russian). 2,3-Dimethoxy-6-aminobenzoic acid (9.85 g.) in 10 cc. concd. H_2SO_4 and 50 cc. warm water was cooled to 0° and treated with 3.6 g. $NaNO_2$ in 25 cc. water; the diazo soln. was stable at room temp. for several hrs. Decompn. by heating to 60° for several hrs. led to much tar formation; it was possible to isolate from the tar by hot-water extn. 2-3% *5,6-dimethoxysalicylic acid*, m. 77-9° (from H_2O). Attempts to prep. the isomeric 3,4-dimethoxysalicylic acid analogously failed, apparently because of steric hindrance effects.

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Mechanism of the reaction of phenylmagnesium bromide with bromomucic acid. [illegible] Vinogradova and M. M. Shemyakin. [illegible] (U.S.S.R.) 10, [illegible] (1946) (in Russian). PhMgBr (from 3.84 g. Mg and 25.1 g. PhBr) was filtered and treated with ice cooling with 10 g. bromomucic acid in 50 cc. Et_2O; the ppt. was sepd., washed with Et_2O, and decompd. with ice and dil. H_2SO_4 to yield 0.9% [illegible] (from EtOH), and [illegible] (from water). Repetition of the above using a 50% excess Mg without filtration gave [illegible]%. The same result being obtained when the Mg was added to the reaction mixt. just prior to hydrolysis and allowed to dissolve in the acidic hydrolysis soln. [illegible] and Na salts of I were prepd. conventionally; *p-bromophenacyl ester* m. 127° (from EtOH). Heating I with 1:1 H_2SO_4 2 hrs. on a steam bath gave the *lactone*, m. 151.3° (from EtOH), while boiling with 20% NaOH converts I into $PhCOCHPhCH_2CO_2H$, m. 162° (from EtOH); *p-bromophenacyl ester*, m. 108.9°; the use of 40% NaOH (10 hrs.) gave BzOH and hydrocinnamic acid. The Grignard reaction appears to consist of the following stages: PhMgBr forms a salt of bromomucic acid, a 2nd PhMgBr mol. reacts with the CHO group of the latter, a 3rd PhMgBr mol. adds to the double bond, then 2 mols. PhMgBr remove the 2 Br atoms. G. M. Kosolapoff.

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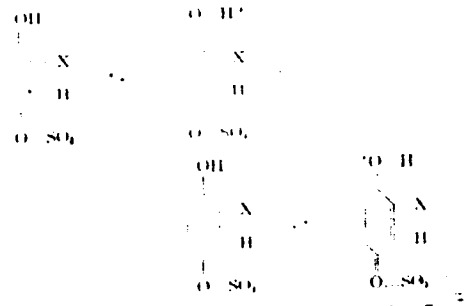
Vitamin K group. V. Structure of the products of the reaction of 2-methyl-1,4-naphthoquinone with alkali bisulfites. D. A. Bochvar and M. M. Shenyakin (Moscow Textile Inst.). *J. Gen. Chem.* (U.S.S.R.) 16, 2033-42 (1946) (in Russian), cf. C. A. 41, 747g. Cryst. adducts of alk. bisulfites to 2-methyl-1,4-naphthoquinone (I) are assigned the structure of *2,3-dihydro-2-methyl-4-oxo-1-naphthol-3-sulfonates*, which exist in aq. soln. in equil. with the 1,4-dihydroxy-type ionic structure and with resonant forms (4) of the 1,4 ionic structures of the HO.... O-SO_3 type. The $NaHSO_3$ adduct was prepd. analogously to the K salt (*C.A.* 38, 3325[2]). Neither the Na nor the K salt give a green-blue color with $FeCl_3$; they do not react with diazobenzenesulfonic acid; they do not decolorize dil. fuchsin solns.; addn. of satd. K_2CO_3 leads to quant. pptn. of I, and treatment of aq. solns. of the adducts with Cl causes no reaction. The adduct of I (3.1 g.) in 20 cc. H_2O was treated with 2.9 g. K 2-methyl-1,4-naphthoquinone-3-sulfonate (II), heated to 60-70° 10 min., with stirring, cooled, filtered, and the ppt. extd. with 20 cc. hot Me_2CO; the insol. material (0.04 g.) was pure I. The adduct (7 g.) in 25 cc. H_2O, 3.2 g. semicarbazide-HCl, and 4 g. NaOAc.$3H_2O$, allowed to stand at 10° 24 hrs., yielded 7 g. *semicarbazone*, $C_{13}H_{12}O_5N_3SNa.H_2O$, colorless, sol. in H_2O, insol. in EtOH. On boiling in H_2O this rapidly changes to I semicarbazone. The adduct of I (2 g.) in 8 cc. H_2O was refluxed 0.5 hr. (about 0.03 g. I ppts.) and the cooled soln., after addn. of 15 cc. satd. KCl soln., was treated with Cl until the brown-violet ppt. of the quinhydrone became light yellow; the ppt. after washing with satd. KCl, H_2O, and Me_2CO, was 0.18 g. II. I (3.4 g.) in 60 cc. EtOH (d. 0.85), treated below 15° with 2.4 g. $KHSO_3$ in 8 cc. H_2O, stirred 0.5 hr., let stand 1.5 hrs., filtered, and dild. with Et_2O, gave a small yellowish ppt., which was discarded, and the clear soln. after further diln. with Et_2O and rubbing gave 1.75 g. colorless solid which was a mixt. of I-bisulfite complex with I-$KHSO_3$ adduct and gave a blue green color with $FeCl_3$ (typical of *p*-quinone complexes only). The complex in aq. soln. gradually isomerizes into the adduct, losing the capacity for $FeCl_3$ reaction; this is hastened by catalytic amts. of mineral acids. Because of ready isomerization it was impossible to isolate the complex without admixts. of the adduct. The complex is assumed to represent the resonant structural forms



G. M. Kosolapoff

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

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Cd

18

Hydrolytic cleavage of C bonds. VI. Hydrolytic cleavage of substituted diphenylethylenes (stilbenes). M. M. Shemyakin and N. I. Oranskii. *J. Gen. Chem.* (U. S. S. R.) 13, 175-83(1943)(English summary); cf. *C. A.* 37, 4053⁷.—2,4-Dinitrostilbene was boiled with 15% KOH with slow distn. of the products and gradual addn. of H_2O to maintain the KOH concn. The distn. products included BzH and NH_3, while the residue contained BzOH, as well as a dark solid which did not m. 270°. The NH_3 formation is due to a secondary process of reaction of 2,4-dinitrotoluene which is one of the intermediate products of hydrolysis. The latter compd. treated as above gave a dark residue, identical apparently with that formed from the stilbene, as well as NH_3. Use of more dil. KOH led to the same results but required longer boiling. 2,2',4-Trinitrostilbene hydrolyzed as above yielded NH_3, o-$O_2NC_6H_4CHO$ and o-$O_2NC_6H_4CO_2H$, but the reaction required 4-6 hrs. with 30% KOH (a lower concn. tried needed an even longer reaction time), while 60% KOH led to fairly rapid reaction. 2,2',4,4'-Tetranitrostilbene boiled with 40% KOH gave NH_3, m-$C_6H_4(NO_2)_2$, 2,4-$(O_2N)_2C_6H_3CHO$ and HCO_2H; 20% KOH is totally ineffective. 4,4'-Dinitrostilbene boiled with 40% KOH gave p-nitrotoluene, p-$O_2NC_6H_4CO_2H$; 20% KOH is almost ineffective. Di-Na 4,4-dinitro-2,2'-stilbenedisulfonate boiled with 45% KOH yielded 4,2-$O_2N(HO_3S)$-$C_6H_3CO_2H$ and HCO_2H; the 2nd product, 2,5-Me(O_2N)-$C_6H_3SO_3H$, could not be isolated as it underwent resinification and many other reactions under the exptl. conditions. Stilbene boiled with 30% KOH gave BzOH in minute amounts only, which were increased somewhat by heating in an autoclave to 160-5°. G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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[illegible]

"Oxidation of the [illegible] with Selenium Dioxide. I. Oxidation of the [illegible]." by [illegible] Sultanov, V.M. [illegible] and [illegible] (p. [illegible])

: [illegible], p. 12

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

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USSR/Vitamins Mar 1947
Chemistry - Vitamins

"Advances in the Chemistry of Vitamins and Their Inactivators in Recent Years," M. M. Shemyakin, 35 pp

"Uspekhi Khimii" Vol XVI, No 3

Comprehensive review, with a nine-page bibliography of work in this field chiefly since 1943. Discusses the various vitamin complexes separately, giving structural diagrams.

10T45

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

CA

Sulfanilamide derivatives of glutaconaldehyde. S. I. Lur'e and M. M. Shemyakin. *J. Gen. Chem.* (U.S.S.R.) 17, 1356-8(1947)(in Russian). 1,5-Bis(phenylmethylamino)-1,3-pentadien-5-ylidene chloride (4.5 g.) (prepd according to Zincke, *Ann.* **330**, 361(1903); **338**, 107 (1905)) in 45 cc. MeOH was carefully heated with a little 20% Na_2CO_3; dilu. with 50 cc. H_2O, neutralization with AcOH, and rapid addn of 4.5 g. sulfanilamide in 30 cc. 6% HCl gave, after 24 hrs. standing, an unspecified amt. of $PhMeNCH:CHCH:CHCH:\overset{+}{N}H(Cl)C_6H_4SO_2NH_2$, m. 144-6° (from MeOH-$Et_2O$). Similarly, *sulfapyridine* gave the correspondng pyridine *analog*, orange powder (from MeOH-Et_2O) neither the yield nor m.p. are given. *Sulfamethylthiazole* gave the corresponding *deriv.*, brick-red (from MeOH-Et_2O), no yield or m.p. given. 1-(2,4-Dinitroanilino)-1,3-pentadien-5-al (5 g.) (prepd. according to Z., *loc. cit.*) in 20 cc. AcOH and 20 cc. concd. HCl boiled 3-5 min., cooled, dild. with 75 cc. cold H_2O, the pptd. 2,4-dinitroaniline filtered off, and the filtrate treated with 10 g. sulfanilamide in 70 cc. 6% HCl gave after 24 hrs. standing $H_2NSO_2C_6H_4NHCH:CHCH:CHCH:\overset{+}{N}H(Cl)C_6H_4SO_2NH_2$, decomp. 170° (from MeOH-$CHCl_3$), deep violet. Similarly, *sulfamethylthiazole* gave the corresponding *deriv.*, red-green (from MeOH-$CHCl_3$), no m.p. given. G. M. K.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

USSR/Chemistry -1,4-Naphthoquinone Jan 1948
Chemistry - Hydrazine

"Research in the Field of Compounds of Quinoid Structure: II, Reaction of Some Bisulfite Derivatives of P-Naphthoquinone With Substituted Hydrazines," D. A. Bochvar, Ye. I. Vinogradova, Yu. B. Shvetsov, M. M. Shemyakin, Lab of Org Chem, Inst of Biol and Med Chem, Acad Med Sci USSR, and Chair of Anal Chem, Moscow Textile Inst, 11 pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 1

Study the interrelationship of various types of pnaphthoquinone derivative bisulfites containing replaceable hydrazines, and observe the properties of the hydrazines formed. Show fallacies contained in formulas suggested by Palladin for bisulfite produced 2-methyl-1,4-naphthoquinone and by Ufimtsev for bisulfite produced 2-methyl-1,4-naphthoquinone-2-sulfonate.

Submitted 14 Jan 1947

PA 64T39

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Mechanism of the thermal decomposition of salts of carboxylic acids. IV. Thermal decomposition of copper salts of carboxylic acids. B. M. Bamdas and M. M. Shemyakin. *Zhur. Obshchei Khim.* (J. Gen. Chem.) **18**, 324-36(1948); cf. Kanevskaya and Sh., *C.A.* 31, 98[9].—

The results of investigation of the products of dry distn. of Cu salts of AcOH, BzOH, and opianic acid are consistent with the assumption that, in all cases, cleavage is to CuO and the corresponding anhydride is the primary step. In particular, decompn. of $Cu(OAc)_2$ gave about 2% of Ac_2O, and 50% AcOH, the latter being obviously a secondary product of hydration of Ac_2O by the H_2O formed in profound decompn. of part of the $Cu(OAc)_2$. $Cu(OBz)_2$ is decompd. in the main at 180-200°, yielding Bz_2O 10%, BzOH 28%, PhOH 14%, BzOPh 8%, and Cu salicylate 14%; of these, Bz_2O was detected for the 1st time. On the other hand, C_6H_6 and Ph_2, detected by other authors at higher temps., are not formed at 180-200°. The processes are summarized in the scheme $(BzO)_2Cu \rightarrow CuO + Bz_2O$; $Bz_2O + H_2O \rightarrow BzOH$; $Bz_2O + CuO \rightarrow PhOH + CO_2$; $PhOH + Bz_2O \rightarrow BzOPh + BzOH$; $(BzO)_2Cu + CuO \rightarrow (HOC_6H_4CO_2)_2Cu$. This mechanism was confirmed by heating Bz_2O with CuO which yielded the same products as the dry distn. of $(BzO)_2Cu$. The Cu salt of opianic acid is decompd. at 220-40°, yielding opianic acid 21, veratraldehyde 18, hemipic anhydride 2%, and a slight amt. of isovanillin; at the given temp. the intermediate opianic anhydride has undergone further reactions and cannot be detected. However, if beginning decompn. is carried out at 180-200°, the products include some anhydride (1.5% of the theory) along with the other products, with the exception only of isovanillin. Heating of a mixt. of opianic anhydride with CuO gave the same products, in somewhat different proportions, plus some veratric acid. The following reaction scheme summarizes the decompn. process: $[(MeO)_2C_6H_2(CHO)CO_2]_2Cu \rightarrow CuO + [(MeO)_2C_6H_2(CHO)CO]_2O \xrightarrow{+CuO} (MeO)_2C_6H_2(CO)_2O$ or $\xrightarrow{+H_2O} (MeO)_2C_6H_2CH(OH)OCO$ or $\xrightarrow{CO_2} (MeO)_2C_6H_2CHO + CuO \rightarrow (MeO)_2C_6H_2CO_2H$ and $(MeO)_2C_6H_2CHO \rightarrow MeO(HO)C_6H_2CHO$. The reactions of the Cu salts are entirely analogous to those of the Ag salts. The primarily formed anhydride partly undergoes hydration to the acid; some of it is oxidized by the metal oxide set free, while another fraction may suffer decarboxylation. These main secondary products may further undergo side reactions such as the reaction between PhOH and Bz_2O.

N. Thon

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

USSR/Chemistry - Acids, Carboxylic, Calcium Salts of Apr 48
Chemistry - Decomposition, Thermal

"Mechanism of the Process of Thermal Decompostion of Caroxylic Acid Salts: V, Thermal Decomposition of Calcium Salts of Carboxylic Acids," E. M. Bambas, M. M. Shemyakin, Lab Org Chem, Inst Biochem and Med Chem, Acad Med Sci USSR, 8 pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 4, 627

Experimental study of thermal decomposition of the Ca salts of various carboxylic acids. Many factors indicate that the Ca slats, like those of Ag and Cu, are first decomposed into metallic oxide and acid anhydride, which then undergo a secondary transformation—usually, as with Ca salts, formation of ketones and hydrocarbons. Submitted 13 Jan 1947.

PA 8/49T35

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

PA 67/49T24

SHEMYAKIN, M. M.

USSR/Chemistry - Quinones
Oxidation

Nov 48

"Oxidizing and Oxidizing-Hydrolytic Conversions of Organic Molecules: I, Hydrolytic and Oxidizing-Hydrolytic Conversions of Quinones," M. M. Shemyakin, L. A. Shchukin, Lab of Org Chem, Inst of Biol and Med Chem, Acad Med Sci USSR, 19 $\frac{1}{4}$ pp

"Zhur Obshch Khim" Vol XVIII, No 11

Discusses reactions of the hydrolytic and oxidative-hydrolytic cleavage of quinones. Submitted 2 Nov 47.

67/49T24

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

Shchukin, L. A., Kondrat'yeva, A. P., Shemyakin, M. M., "Oxidation and Oxidation-Hydrolyic Conversions of Organic Molecules. III. Hydrolytic Conversions of 2-Methyl-3-oxy-1,4-naphthoquinone." (p. 2121)
(Lab of Org Chem, Inst of Biol and Med chem, USSR Acad Med Sci.)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1948, Volume 18, (LXXX), No. 12

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washed with 10% H_2SO_4 and water, washing the org. layer with 10% NaOH readily exts. I after 5 extns.; evapn. of the Et_2O yielded 91% 2-hydroxy-1,4-naphthoquinone anilide(?), m. 186.8°, while acidification of the alk. soln. and extn. with Et_2O gave 100% I, m. 172° (from MeOH). Hydrolysis of 4 g. 2-methyl-1,4-naphthoquinone in 2 l. water with 0.24 g. $CaCO_3$ with air blowing over 24 hrs. gave, after the above treatment, 0.4 g. I. Repetition using H instead of air, with careful exclusion of all sources of O_2 gave 3.9% phthalic acid (0.118 g.) and 0.1 g. I. Boiling 1,4-naphthoquinone or the 2-Et deriv. in water with air bubbling gave in 72 hrs. 9.68% phthalic acid from 1,4-naphthoquinone at pH 7.3, 6.1% from 2-methyl-1,4-naphthoquinone, and 5.38% from 2-ethyl-1,4-naphthoquinone; if the phosphate buffer is replaced by 0.24 g. $CaCO_3$ (in the same 2 l. water), the values are 2.34, 10.75, and 4.05%, resp. III. **Hydrolytic transformations of 2-methyl 3 hydroxy 1,4 naphthoquinone** *Ibid.* 2121-8.

The quinone ring of 2-methyl-3-hydroxy-1,4-naphthoquinone (I) is capable of hydrolytic cleavage on boiling with water at pH above 7, as a result, there is formed *o-propionylphenylglyoxylic acid* (II), which is partially converted to *2-methyl-1-indenone-3-carboxylic acid* (III). I boiled in H_2O is stable at pH below 7, however, even at pH 7.3 in the absence of atm. O purely hydrolytic reaction takes place. Boiling 3.3 g. I in phosphate buffer at pH 7.3-7.35 72 hrs. with an air-bubbler (50 l. air passed in) gave 1.1 g. III, m. 211-13° (from AcOH), and evapn. of the soln. gave an addnl. 0.6 g. (total yield 51.5%), the aq. soln. on neutralization with soda to pH 5.5 and extn. with Et_2O gave 12% II, m. 173° (from H_2O), similar results are obtained when $CaCO_3$ is used in the hydrolysis instead of phosphate buffer. If the expt. is conducted in phosphate buffer with H bubbling for 24 hrs., approx. the same yields of II and III are obtained. III heated with MeOH in the presence of H_2SO_4 gives the *Me ester*, m. 63°, orange needles (from heptane); *semicarbazone* of II decomp. 268° (from EtOH). II heated 5 min. with H_2SO_4 to 100° gives III; II with $H_2NCONHNH_2.HCl$ gives III semicarbazone; heating II with *o*-$C_6H_4(NH_2)_2$ in H_2O results in no reaction. Oxidation of II with Cr oxide-AcOH (50%) gives phthalic acid and *o-propionylbenzoic acid*, m. 93-4° (from 50% EtOH). G. M. Kosolapoff

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

USSR/Chemistry - p-Toluenesulfonamide. Jun 48
α-Amino
Chemistry - Synthesis

"Synthesis of Homosulfanilamide and Some of Its Derivatives," Z. F. Komokina, S. B. Levitskaya, S. L. Lur'ye, T. A. Chentsova, M. M. Shemyakin, Lab of Org Chem, All-Union Sci Res Inst of Biol Prophylactics for Infections, 4 pp

"Zhur Priklad Khimii" Vol XXI, No 6

Describes improved method of synthesizing homosulfanilamide. Synthesizes two derivatives of homosulfanilamide: N^4-(sulfanil-)-homosulfanilamide and N^4-(homosulfanil-)-sulfanilamide. Submitted 9 Mar 47.

PA 10/49T30

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMIAKIN, M. M.

L. A. Shchukina, A. P. Kondratieva and M. M. Shemiakin, Oxydizing and oxydizing-hydrolytic transformations of organic molecules. III. Hydrolytic transformations of 2-methyl-3-oxy-1,4-naphthoquinone. p. 2121.

It is shown that the quinone ring of 2-methyl-3-oxy-1,4-naphthoquinone is capable of undergoing hydrolytic splitting. This process proceeds at boiling of the quinone with water if the pH is above 7.

Lab. of Organic Chemistry of the
Institute of Biologic and Medical Chem.
Academy of Medical Sciences, USSR.
November 2, 1947

SO: J. Gen. Chem. (USSR) 28, (80) No. 12, 1948

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

CA SHEMYAKIN Mikhail Mikhaylovich 1D

The formation of oxazolones from acyl derivatives of glycine. M. M. Shemyakin, S. I. Lur'e, and R. I. Roshonovskaya. *J. Gen. Chem.* (U.S.S.R.) 19, 749-51 (1949) (English translation). -See C.A. 44, 1096d.
E. J. C

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

USSR/Chemistry - Hooker Reaction Mar 49

"Oxidation and Oxidation-Hydrolysis Conversions of Organic Molecules: VI, Study of S. Hooker's Reaction," L. A. Shukina, A. P. Kondratyeva, M. M. Shemyakin, Lab of Org Chem, Inst of Biol and Med Chem, Acad Med Sci USSR, 11 3/4 pp

"Zhur Obshch Khim" Vol XIX, No 3

In oxidation by an alkaline solution of $KMnO_4$, phthiocol is subjected to a series of oxidative hydrolytic transformations, which can be interrupted at the stage of formation of o-pyruvyl-phenylglyoxylic acid. Describes conditions for converting the latter compound to 2-hydroxy-1, 4-naphtho-quinone. Discusses machanism of Hooker's reaction on the basis of the experiments. Submitted 2 Nov 47.

62/49T9

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

Jan 49

USSR/Chemistry - 1,4-Naphthoquinone
Chemistry - Hydrolysis

"Oxidation and Oxidation-Hydrolysis Conversions of Organic Molecules: IV, Oxidation-Hydrolysis Conversion of 2-Methyl-1, 4-Naphthoquinone Oxide," L. A. Shchukina, A. P. Kondrat'yeva, M. M. Shemyakin, Lab of Org Chem, Inst of Biol and Mem Chem, Acad Med Sci USSR, 8 pp

"Zhur Obshch Khim" Vol XIX, No 1

Boiling of this compound with water ultimately results in formation of phthiocol, 2-methyl-1,4-naphthoquinone, and o-lactyl-phenylglyoxylic acid. Studies the third compound and its cyclization into 2-oxy-1, 4-naphthoquinone. Submitted 2 Nov 47.

58/49T35

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN

"Oxidative and Oxidative-hydrolytic transformations of Organic Molecules - 7: Study of the Mechanisms of the Oxidative-Hydrolytic transformations of the Oxide of 2-Methyl-1, 4-Naphthoquinone".
Shchukina, and Shemyakin. (p. 175)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1949, Vol. 19, No. 1

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

FA 5/49T33

USSR/Chemistry - Oxazolones
Glycine

Apr 49

"Formation of Oxazolones From Acylated Glycocolls," M. M. Shemyakin, S. I. Lur'ye, E. I. Rodionovskaya, Lab of Org Chem, Inst of Biol and Med Chem, Acad Med Sci, All-Union Sci Res Inst of Biol Prophylaxis, 4 pp

"Zhur Obshch Khim" Vol XIX, No 4 p 769

These glycocolls, specifically hippuric and phenaceturic acids, are converted into their corresponding oxazolones. In the case of the oxazolone of the latter acid, it is more expedient to extract

65/49T33

[redacted]

USSR/Chemistry - Oxazolones (Contd)

Apr 49

it in the form of an N-acetyl derivative. Submitted 15 Jan 48.

65/49T33

[redacted]

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[illegible]

"[illegible] Hydrolitic Conversions of Organic Molecules: [illegible]. Hydrolitic Conversions of [illegible] Series." Zhur. [illegible]. Khim. [illegible], No. [illegible], [illegible]. Lab. of Org. Chem. Inst. of Biol. and Med. Chem., Acad. Med. Sci. -c1949-.

[illegible]

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"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

CHEMISKIN, M. M.

"Oxidising and dehydro-hydrolitic conversion of organic molecules: VIII. Hydrolitic conversions of oxi-and acetoxytriketones of a tetra-hydronaphthalene series." Chvetsov, Yu. B. and Chukina, L. A. and Chemiskin, M. M. (p. 499)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1949, Vol. 19, No. 3

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

SHEMYAKIN, M. M.

USSR/Chemistry - Cyclic Compounds Mar 49

"Oxidation and Oxidation-Hydrolysis Conversions of Organic Molecules: IX, Study of Conversion of o-(Alpha-Chloropropionyl) Acids Into Carbocyclic Compounds," Ye. I. Vinogradova, Yu. B. Shvetsov, M. M. Shemyakin, Lab of Org Chem, Inst of Biol and Med Chem, Acad Med Sci USSR, 10 pp

"Zhur Obshch Khim" Vol XIX, No 3

Made a study of conditions and mechanism of the preparation of 5-and 6-member carbocyclic compounds from O-(alpha-chloropropionyl) -phenyl-glyoxylic acid. Submitted 2 Nov 47.

62/49T8

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

BOCHVAR, D.A.; CHERNYSHEV, A.S.; SHEMYAKIN, M.M.

Observations on Ufimtsev's paper on the bisulphite compound of 1 : 4-naphthaquinone. J. Gen. Chem. USSR, '50, 20, 2118-2120 [U.S. transl., 2195-2197]. (MLRA 3:11)
(BA - A II Ja '53:55)

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

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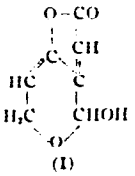
10

Structure and chemical peculiarities of patulin. M. M. Shemyakin and A. S. Khokhlov. *Doklady Akad. Nauk S.S.S.R.* 75, 17-50(1950). A review of the literature on the chem. structure of patulin is presented (9 references). Although patulin acetate has been synthesized (Wasserman and Singh, C.A. 44, 5877h) its structure is not rigidly established, since in the last step of the synthesis the conditions used did not eliminate possible ring opening and reclosure. Chem. considerations indicate that the correct structure of patulin is (I). The 2 objections to this formulation are met



(I)

as follows. The asym. C in the formula is not excluded by the lack of optical activity of natural patulin, since the formula is that of the acetal type (bottom of ring) and in aq. solns. rapid racemization, via ring opening, is to be expected. The cleavage of patulin by hot dil. H_2SO_4 into HCO_2H and tetrahydrocomanic acid, having CO_2H group at the 2-position in pyran ring, is readily explained by opening of both the acetal and the lactone rings, giving $HOCH_2CH_2COC(:CHCO_2H)CHO$, which would normally go over into 2-carboxy-3-formyl-4-pyrone (cf. Nazarov, C.A. 45, 6572c), which, as expected, splits off the elements of HCO_2H in dil. H_2SO_4.

G. M. Kosolapoff

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USSR/Chemistry - Organic Reactions Nov/Dec 51

"Review of 'Reactions and Methods for Investigating Organic Compounds. Vol I, 'Edited by S. S Nametkin (Deceased), V. M. Rodionov, N. N. Mel'nikov," M. M. Shemyakin

"Uspekh Khim" Vol XX, No 6, pp 791, 792

Vol I contains an article on Kizhner's reaction (conversion of carbonyl compds into hydrocarbons) by V. M. Rodionov and N. G. Yartsova, an article on oxidation with SeO_2 by N. N. Mel'nik, and a review of work in chromotography by N. A. Fuks. The following articles will be

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USSR/Chemistry - Organic Reactions (Contd 1) Nov/Dec 51

published in subsequent volumes of the series: B. A. Arbuzov, "Addition of Halogenated Paraffins to Olefins" (Reaction of Butlerov-El'tekov); B. A. Arbuzov, "Arbuzov's Rearrangement"; L. D. Bergel'son, "Yotsich's Reaction"; B. M. Bogoslovskiy, "Beykart's [?] Reaction"; I. L. Knunyants, B. P. Fabrichnyy, "Beckmann Rearrangement"; N. G. Laptev, "Oxidative Nitration of Organic Nitrocompounds"; B. M. Bogoslovskiy, "Structure Catalysts (Raney Nickel) and Their Application"; E. E. Ivanovskiy, "Sulfochlorination of Paraffin Hydrocarbons"; A. P.

193T23

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SHEMYAKIN, M. M.

USSR/Chemistry - Organic Reactions Nov/Dec 51
(Contd 2)

Terent'yev, L. A. Kazitsina, "Sulfonation With SO_3 Bound in a Complex"; A. P. Terent'yev, A. N. Kost, "Reaction of Cyanoethylation"; A. P. Terent'yev, L. A. Yanovskaya, "Substitution by Halogen Through the Action of Halogen-Containing Compounds." Vol I published by Goskhimizdat, 1951.

193T23

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

[illegible], M. [illegible].

"Oxidation [illegible] derivative-hydrolytic transformations of organic molecules. X. Approximate [illegible]-chloro-[illegible]-[illegible]-1, 3, 4,-[illegible]." by Yu. I. Shvetsov, I. A. Rod'kin and M. M. Shemyakin. (p.[illegible])

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Volume 21, No.2

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

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[illegible], [illegible]

"Oxidative and [illegible]-hydrolytic [illegible] of organic molecules. XI. The mechanism of the Hooker reaction." by L. A. Shchukina, Yu. B. Shvetsov, and M. M. Shemyakin. ([illegible])

S.: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Volume 21, No.2

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

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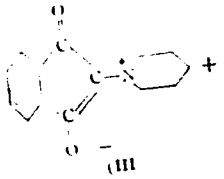
Oxidative and oxidative hydrolytic reactions of organic molecules XII Hydrolytic cleavage of 1-3-1 hydroxy-1 4 3,4 naphthoquinon 2 yl pyridinium betaine D. P. Vitkovskii and M. M. Shemyakin. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 240-7(1951); cf. C. 1 43, 7199g; 45, 2296. Hydrolytic cleavage of the *1-(3'1'-hydroxy-1,4(3,4)-naphthoquinon 2 yl pyridinium betaine* (I) on long boiling in aq. alk. soln. yields phthalic acid, pyridine, and *1-hydroxy-4-carboxy-2-naphthoquinone* (II; cryst. to 18°, m. 16°; NaOH), decomp. 295-6°. The latter forms as a result of cleavage not only of the quinone but also of the pyridine rings, first forming $o\text{-}C_6H_4(CO_2H)COCOCH_2NH_2$, which then undergoes a benzilic rearrangement, yielding $o\text{-}C_6H_4(CO_2H)C(OH)(CO_2H)CH_2NH_2$, which then loses 2 H_2O to give the final product. II yields an *insol. Ag salt* and on distn. with Zn dust gives *isoquinoline* (*picrate*, m. 230-1°). Pyrolysis of II Ag *salt* in a N atm. gave *isocarbostyryl*, m. 207-8°. Esterification of II with EtOH-H_2SO_4 gave the *Et ester*, m. 226-7°.

XIII. **Hydrolytic cleavage of 1-(2-chloro-1,2,3,4-tetrahydro-1,3,4-trioxo-2-naphthyl)pyridinium chloride.** *Ibid.* 547-58.

Chlorination of dry *1-(3'1'-hydroxy-1,4(3,4)naphthoquinon-2-yl)pyridinium betaine* (I) in $CHCl_3$ with cooling gave 90% *1-(2-chloro-1,2,3,4-tetrahydro-1,3,4-trioxonaphthalyl)pyridinium chloride* (II), darkening at 105°, does not m. 250°. On standing in H_2O it readily yields the *betaine* (III), m. 256-7° (from H_2O) (47% after 3 days). If the aq. mixt. is heated 20 min. to 95° 55% III is formed while 19% pyridine and 12% phthalic acid may be recovered. In very dil. NaOH, formation of III is instantaneous, as it is in soln. NH_4OH, or NaOAc solns. Oxidation of III with $KMnO_4$ gives phthalic acid and pyridine. A boiling aq. soln. of II,



(III)

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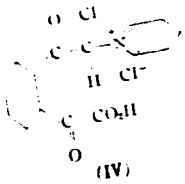
followed quantitatively, reveals a loss of 80% CO_2 and 87% HCl, with formation of 37% III. Letting II stand with Me_2CO-KI 1 hr. gives 23% III, while longer standing yields 13% I, m. 280-90° (from H_2O), and further amts. of III may be obtained by addn. of 10% Na_2CO_3 to the filtrate. The above mixt., treated after 2 hrs. with 2% Na hyposulfite forms a mixt. of III and I, and the mother liquor boiled 20 min. gives up to 57% bright red *S-contg. analog* of III, $C_{13}H_9ONS$, m. 198-9°, which with $Pb(OAc)_2$ readily gives III of II with 10% HCl rapidly yields a ppt. (IV) (57%), darkening at 100°, does not m. 250°. When II is hydrolyzed without access of air, the course of the reaction is not altered and III, phthalic acid, and pyridine are formed. IV with Me_2CO-KI yields 79% III in 1 hr. at room temp. Reaction of IV with Me_2CO-KI, followed by 2% Na hyposulfite, yields 27% III and 57% of its *S analog* (see above). II with 10% HNO_3 yields IV *nitrate*, similar in properties to the *chloride*. Soln. of I in 10% H_2SO_4 yields the *bisulfate*, $C_{13}H_{11}O_6NCl.HSO_4$, apparently having the structure of IV.

IV in the form of chloride, nitrate, or bisulfate, or II, stirred in aq. soln., forms a ppt. of $C_{13}H_{11}O_6NCl(OH)$ (V), darkening at 80-5°, does not m. 250°, which has no ionic Cl, but the halogen in the mol. is capable of oxidizing KI. On standing in aq. soln. however, III forms readily (61% in 7 hrs. at 19°), but in the presence of HCl the yield is significantly smaller; phthalic acid and pyridine also form. Soln. of V in 10% HCl, brief warming, and cooling yield V *chloride*, darkening at 115-20°, does not m. 250°, which forms V on warming in H_2O, and III on long standing in H_2O, while Na hyposulfite yields the S analog of III; with 10% H_2SO_4, V forms the *bisulfate*, whose properties are similar to the above chloride.



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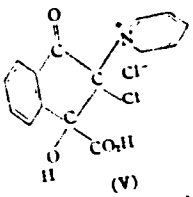

(V)

G. M. Kosolapoff

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[illegible], M. [illegible].

"[illegible] XV. [illegible] of 1,4-[illegible]," [illegible] Shchukina, L. A., [illegible], A. S., [illegible] Shchukin, M. M.
([illegible])

SO: Journal of [illegible] Chemistry (Zhurnal Obshchei Khimii) 1951, Volume [illegible], No. 5

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SHEMYAKIN, M. M.

Jun 51

USSR/Chemistry - Quinones

"Oxidative and Oxidative-Hydrolytic Transformations of Organic Molecules, XVI," A. S. Khokhlov, L. A. Shchukina, M. M. Shemyakin, Lab Org Chem, Inst Biol and Med Chem, Acad Med Sci USSR

"Zhur Obshch Khim" Vol XXI, No 6, pp 1016-1033

Studied conditions character, and mech of above reaction on 2,3-dioxy-1,4-naphthoquinone (i-naphthazarin) and 1,2,3,4-tetraoxotetraline. In presence of oxidizers and hydrolyzing media these compds can undergo number of alternating oxidative and hydrolytic reactions which are additionally complicated by transformation of intermediate products. Detd basic stages of this type of processes and their dependence on pH of the medium, on temp and on presence of oxidants.

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USSR/Chemistry - Quinones Jun 51

"Oxidative and Oxidative-Hydrolytic Transformations of Organic Molecules," D. P. Vitkovskiy, M. M. Shemyakin, Lab Org Chem, Inst Biol and Med Chem, Acad Med Sci USSR

"Zhur Obshch Khim" Vol XXI, No 6, pp 1033-1045

Substituted 3-hydr oxy-1,4-naphthoquinones with OH group, Cl, or amino group in the 2-position can undergo single-type transformation in presence of oxidants and hydrolyzing media, in which the quinone ring is broken, while the substitute in the 2-position is split off. Final products are always

186T22

phthalic, phthalonic and phthalidic carboxyl acids. Reaction proceeds by way of formation of 1,2,3,4-tetraoxotetraline, which is then transformed into final acids.

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SHEMYAKIN, M. M.

"The structure of bisulphite derivatives of aromatic compounds." E. M. Bamdas, D. A. Bochvar, and M. M. Shemyakin. (p. 1287)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Vol 21, No 7.

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

USSR/Chemistry - Biological

Sep 51

"Oxidation and Oxidative-Hydrolytic Conversion of Organic Molecules. XVIII. Synthesis and Properties of Certain Quinone Oxides," L. A. Shchukina, Ye. I. Vinogradova, M. M. Shemyakin, Lab Org Chem, Inst Biol and Med Chem, Acad Med Sci USSR

"Zhur Obshch Khim" Vol XXI, No 9, pp 1661-1667

Synthesized several oxides of 1,4-benzoquinones and 1,4-naphthoquinones; studied certain of their properties: namely, their oxidizing ability and their capacity for being converted into esters of the corresponding glycols.

191T47

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191T48

USSR/Chemistry - Biological Sep 51

"Oxidation and Oxidative-Hydrolytic Conversions of Organic Molecules. XIX. Relation Between the Degree of Oxidation of Carbocyclic Compounds and the Capacity of Their Ring Groupings to Undergo Hydrolytic Splitting," M. M. Shemyakin, L. A. Shchukina, Yu. B. Shvetsov, D. P. Vitkovskiy, A. S. Khokhlov, Lab Org Chem, Inst Biol and Med Chem, Acad Med Sci USSR

"Zhur Obshch Khim" Vol XXI, No 9, pp 1667-1677

Clarified principles and nature of relation between deg of oxidation and capacity for hydrolytic splitting. Showed expediency of use of concept of

191T48

USSR/Chemistry - Biological (Contd) Sep 51

oxidative-hydrolytic conversions in study of oxidation of carbocyclic and acyclic compds.

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SHEMYAKIN, M. M.

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1. [illegible]

2. [illegible]

4. [illegible]

5. [illegible] Reviewed by [illegible] Shemiakin. [illegible] 21, No. 12, [illegible]

6. [illegible] List of Russian Accessions. Library of Congress. March, [illegible]. [illegible]

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SHEMYAKIN, M M

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

(4)

Oxidative and oxidative-hydrolytic transformations of organic substrates. XX. The structure of oxides of unsaturated compounds. M. M. Shemyakin, D. A. Bochvar, and L. A. Shchukina (Moscow Textile Inst.). *J. Gen. Chem. U.S.S.R.* 22, 505–7(1952)(Engl. translation).—See *C.A.* 47, 2741*e*. XXI. Hydrolytic cleavage of 6-methyl-3-hydroxy-*p*-benzoquinone. L. A. Shchukina. *Ibid.* 733–8. See *C.A.* 47, 5378*i*. XXII. Hydrolytic and oxidative changes of 1-phenylazo-3,4-dihydroxynaphthalene. O. M. Shemyakina, B. M. Boroslovskii, and M. M. Shemyakin. *Ibid.* 739–42. XXIII. Mechanism in the oxidative-hydrolytic and hydrolytic transformations of 2-chloro-3-hydroxy-1,4-naphthoquinone. D. P. Vitkovskii and M. M. Shemyakin. *Ibid.* 743–9. See *C.A.* 47, 5379*e*.

H. L. H.

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SHEMYAKIN, M.M.

USSR/Chemistry - Quinones Apr 52

"Oxidative and Oxidative-Hydrolytic Transformations of Organic Molecules. XXII. Hydrolytic and Oxidative Conversion of 1-Benzeneazo-3,4-Dihydroxynaphthalene," O.M. Shemyakina, B.M. BOGOSLOVSKIY, M.M. SHEMYSKIN, MOSCOW TEXTILE INST

"Zhur Obshch Khim" Vol XX II, No 4, 675-679

1-Benzeneazo-3,4-dihydroxynaphtahalene can be very easily changed by oxidizing and hydrolyzing agents. It is easily oxidized by atm O_2 in an alk water-alc soln at 5 to 10° into 1-benzeneazo-3,4-naphthoquinone. It is hydrolyzed in presence of atm O_2 in an aq soln with a pH of 9. In this case, it is 1st transformed into a tautomeric quinoid (3-hydroxy-1,4-naphthoquinone phenyl hydrazone) which splints off the phenyl-hydrazone radical and forms 3-hydroxy-1,4-naphthoquinone which can then be partially split to form o-acetylphenylglyoxylic acid.

224T46

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[illegible] V47
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[illegible] & Physical
[illegible]

Sof'ya Iosifovna [illegible]
M. M. Shefiyakin [illegible]
Obituary [illegible]

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SHEMYAKIN, M.M.

USSR/Chemistry - Quinones Apr 52

Oxidative and Oxidative-Hydrolytic Transformations of Organic Molecules XXIII. Mechanism of Oxidation-Reduction and Hydrolytic Conversion of 2-Chloro-3-Hydroxy-1, 4-Naphthoquinone," D. P. Vishkovskiy, M. M. Shemyakin, Lab of Org Chem, Inst of Biol and Med Chem, Acad Med Sci USSR

"Zhur Obshch Khim" Vol XXII, No 4, pp 679-687

The above reaction was investigated by boiling the substance in a water-alkali soln in presence of atm O_2. Phthalide carboxylic acid, phthalonic acid, phthalic acid, indanone-1-carboxylic acid-(3), isonaphthazarine, and a substance with the general formula $C_{27}H_{12}O_3$ which are formed, are the result of 2 parallel but connected processes, one of which is oxidative-hydrolytic, the other reductive-hydrolytic. 224T47

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BRAUNSHTEYN, A.Ye.; SHEMYAKIN, M.M.

Theory of metabolism of amino acids catalyzed with pyridoxal enzymes. Doklady Akad nauk SSSR 85 no. 5:1115-1118 11 Aug 1952. (CIML 23:3)

1. Active Member of the Academy of Medical Sciences USSR for Braunshteyn. 2. Institute of Biological and Medical Chemistry, Academy of Medical Sciences USSR.

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[illegible]: [illegible]:

Carbohydrates

Mechanism of certain transformations and means of biosynthesis of carbohydrates with a branched carbon chain. Dokl. [illegible] SSSR [illegible], no. [illegible], 1952.

Monthly List of Russian Accessions, Library of Congress, December 1952. Unclassified.

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1"

"APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020018-1

SHEMYAKIN, M. M.

Organic Chem

Paths of synthesis of optically active analogs of *p-threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediol*. M. M. Shemyakin, E. M. Gavrilova, K. I. Vinogradova, M. G. Ivanovskaya, M. N. Kolosov, A. S. Khokhlov, Yu. B. Shvetsov, and G. A. Sokolskaya. *Doklady Akad. Nauk S.S.S.R.* 86, 505-8(1952).—Two synthetic paths for prepn. of analogs which contain substituents other than NO_2 are outlined. D- *or* L-*threo-1-(p-Nitrophenyl)-2-amino-1,3-propanediol* (I) treated with BzCl and 0.5*N* NaOH gave 70% of the corresponding *N-Bz derivs.* (II): D-form, m. 171° (from EtOH), $[\alpha]^{22}D$ −120° (MeOH); L-form, m. 171°, $[\alpha]^{22}D$ 121°; DL-form, m. 163° (from EtOH). These, reduced with H over active Ni at 20° and 50 atm., gave the corresponding *p-H_2N analogs* (III) in 95% yield; D-form, m. 171°, $[\alpha]^{22}D$ −100° (MeOH); L-form, m. 171°, $[\alpha]^{22}D$ 99°; DL-form, m. 152°. Diazotization of III at 0–5° in HCl or H_2SO_4 (3 hrs.) and treatment with the customary reagents gave the substituted derivs. as follows: CuCl gave 75% L-*p-Cl deriv.*, m. 172°, $[\alpha]^{22}D$ 102°; the D-*isomer*, m. 172°, $[\alpha]^{22}D$ −103°. KI in dil. soln. after 12 hrs. at 0°, followed by treatment at 20°, gave 50% *p-iodoanalog*; D-*form*, m. 179°, $[\alpha]^{22}D$ −87°; L-*isomer*, m. 179°, $[\alpha]^{22}D$ 86°; DL-*form*, m. 174°. Heating to 70–90° 0.5 hr. at pH 5–6 gave the *p-HO analog*; L-form, decomp. 196–8°, $[\alpha]^{22}D$ 103°. CuCN at pH 7 and −5° gave 80% *P-NC* deriv.: L-form, m. 140°, $[\alpha]^{22}D$ 130°; D-form, m. 140°, $[\alpha]^{22}D$ −130°. Na_3AsO_3 with $CuSO_4$ at 15° gave 22% *p-H_2O_3As* deriv.: L-form, decomp. 142–3°, $[\alpha]^{22}D$ 89°. Treatment with EtOH-Cu gave the *unsubstituted compd.*, L-form, m. 180°, $[\alpha]^{22}D$ 99°. These compds. (V) on refluxing several hrs. with 20% HCl lost the *N*-Bz group and yielded *p-$ZC_6H_4CH(OH)CH(NH_2)CH_2OH$* of the threo type as follows (*Z shown*): *Cl*, 56%: L-form, m. 147°, $[\alpha]^{22}D$ 35°; D-form, m. 147°, $[\alpha]^{22}D$ −34°; *Iodo* 55%: L-form, m. 104°, $[\alpha]^{22}D$ 21°; D-form, m. 104°; *CO_2H*, 65%: L-form, decomp. 318–9°, $[\alpha]^{22}D$ 33°; D-form, decomp. 318–9°, $[\alpha]^{22}D$ −32°. The former 2 substances heated briefly with Cl_2CHCO_2Me at 95°, or the last substance treated at −5° with $Cl_2CHCOCl$, gave the *N-dichloroacetyl derivs.* (*p*-substituent shown): *Cl*, 47%: L-form, m. 93°, $[\alpha]^{22}D$ −9°; D-form, m. 93°, $[\alpha]^{22}D$ 8°; DL-form, m. 120°; *Iodo*, 72%: L-form, m. 104°, $[\alpha]^{22}D$ −11°; D-form, m. 104°, $[\alpha]^{22}D$ 10°; DL-form, m. 123°; *CO_2H*, 70%: L-form, m. 191°, $[\alpha]^{22}D$ −14°; D-form, m. 191°, $[\alpha]^{22}D$ 12°. Racemates obtained by mixing the L- and D-forms of the *p*-Cl or *p*-iodo derivs. were identical with the Cl or iodo analogs of chloramphenicol, thus showing the preservation of threo-structure. The 2nd route was as follows. Hydrogenation of D- or L-I gave 90% of the corresponding *p-H_2N derivs.*: L-form, m. 136°, $[\alpha]^{22}D$ 28°; D-form, m. 136°, $[\alpha]^{22}D$ −29°. These with Cl_2CHCO_2Me in MeOH after 24 hrs. at 18–23° gave the *2-dichloroacetamido derivs.*, isolated as *HCl salts* in 25% yield: L-form, $[\alpha]^{22}D$ −9°; D-form, $[\alpha]^{22}D$ 8°. These diazotized rapidly and were converted conventionally to the following derivs.: *p-Cl*, identical with that described above; *p-CN*; 52%. L-form, m. 136°, $[\alpha]^{22}D$ [illegible]. D-form, m. 136°, $[\alpha]^{22}D$ 15° (hydrolyzed to [illegible] analog, identical with that described above. [illegible] *deriv.*, 46%: L-form, m. 156°, $[\alpha]^{22}D$ 8°; D-form, m. 156°, $[\alpha]^{22}D$ −8°. G. M. Kosolapoff

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SHEVANTSV, V.V.: BANDL, YE.M.: [illegible], YE. I.: [illegible], V.G.: [illegible], V.V.: [illegible], A.V.: [illegible], YU. [illegible].: [illegible]FIA, L.A.

PROPANEDIOL

Methods for synthesizing optically active analogues of D-threo-1 -(p-nitrophenyl)-2-dichloroacety-lamino-1, 3-propanediol. Dokl. An SSSR, 86, No. 3, 1952.

Monthly List of Russian Accessions, Library of Congress, December 1952, UNCLASSIFIED

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Braunshteyn, A. Ye. [illegible], [illegible] Goryachenkova, Ye.V. [illegible], [illegible] [illegible], [illegible]	"Investigations of the Processes of Amino Acid Metabolism and the Role of [illegible] in Vitamins of the B Complex in These Processes	Institute of Biological and Medical Chemistry, Academy of Medical Sciences USSR

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Shemyakin, M. M., and Khokhlov, A. S.: Khimiya anti-biotichesikh veshchestv (Chemistry of Antibiotics). 2nd ed. Moscow: Goskhimizdat. 1953. 653 pp. 31R. 20K. Reviewed in *Biokhimiya* 19, 509-10(1954).

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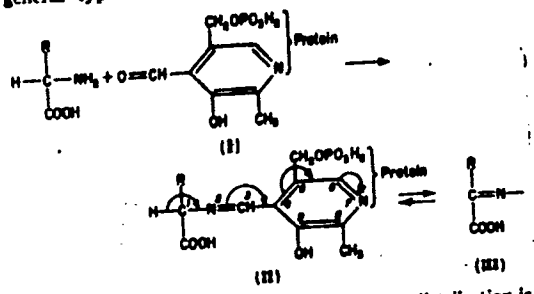
Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Biological Chemistry

A theory of amino acid metabolic processes catalyzed by pyridoxal-dependent enzymes. A. E. Braunshtein and M. M. Shemyakin (Inst. Biol. and Med. Chem., Acad. Med. Sci. U.S.S.R., Moscow). *Biokhimiya* 18, 393-411 (1953); cf. *C.A.* 47, 620c.—All presently known amino acid changes taking place as a result of the action of pyridoxal phosphate-dependent enzymes can be explained by a monistic theory based on the ability of the aldehyde group of such proteins (I in the diagram) to interact with the amino group of amino acids. As a result, azomethines are formed of the general type II. Because of its structural peculiarities,



under the influence of external conditions, a redistribution is possible in the electronic d., changing the character of C atom 1. In this atom the electronic d. must be considerably lower than in the α-C atom of the parent amino acid and is the cause of the difference in these two C atoms. As a result, the formed azomethines can undergo a series of changes not observed in amino acids proper. Some of the changes are related to the dissocn. of H atom closest to C atom 1. Concomitantly, in the formed anion an increased electronic d. must arise in atoms 1, 3, 5, 7, and 9. Along with type II azomethines and as result of valency changes, tautomeric azomethines of type III can be formed, which are *N*-substituted α-amino acids. It follows that in their chem. characteristics azomethines types II and III should be nearer not to the original α-amino acids, but to their corresponding

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SHEMYAKIN, M. M.

Chemical Abst.
Vol. 48
Apr. 10, 1954
General and Physical Chemistry

(2)

Academician Vladimir Mikhailovich Rodionov. M. M. Shemyakin. *Zhur. Obshchei Khim.* 23, 1785-94(1953). Brief biographical sketch with summary of scientific work and bibliography covering 1918-53, on occasion of 75th birthday.
G. M. Kosolapoff

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Chemistry of chloromycetin (levomycetin). II. Study of the paths of synthesis and synthesis of optically active analogs of chloromycetin. M. M. Shemyakin, E. M. Bamdas, E. I. Vinogradova, M. O. Karapetyan, M. N. Kolosov, A. S. Khokhlov, Yu. B. Shvetsov, and L. A. Shchukina (Inst. Biol. and Med. Chem., Acad. Med. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 23, 1854-57 (1953); cf. *Doklady Akad. Nauk S.S.S.R.* 70, 601(1951); C.A. 43, 6[illegible].—Two general paths of synthesis of optically active analogs of chloromycetin of type *p*-$XC_6H_4CH(OH)$-$CH(NHCOCHCl_2)CH_2OH$ with various groups X are described; both methods start with substances of known spatial structure which is unchanged during the synthesis. It was shown that the method of Long and Troutman (*C.A.* 44, 568*i*) in a number of instances can yield analogs of chloromycetin that belong to the *threo* series. Benzoylation of D- (I), L- (II), and DL-forms (III) of *threo-1-(p-nitrophenyl)-2-amino-1,3-propanediol* with BzCl in 0.5*N* KOH and Et_2O gave 70-5% yields of the *N-Bz derivs.* of: I, m. 171-2°, $[\alpha]^{18}_{D}$ −120.5° (MeOH); II, m. 171-2°, $[\alpha]^{17}_{D}$ 121.5°; III, m. 162-3°. Hydrogenation of these in EtOH over Raney Ni at 75-80° and 40-50 atm. H initially gave 91-6% corresponding *p*-amino analogs of the *N*-Bz derivs. of: I, m. 170-1°, $[\alpha]^{18}_{D}$ −100.5°; II (IV), m. 170-1°, $[\alpha]^{17}_{D}$ 99.5°; III, m. 151-2°. IV (6 g.) in 60 ml. 5% H_2SO_4 was diazotized with 20% $NaNO_2$ at 0-5° (excess HNO_2 being destroyed by urea), the soln. treated with 60 ml. EtOH and 6 ml. concd. H_2SO_4 and followed at 0-5° by 0.75 g. Cu bronze; after the reaction subsided, the mixt. was heated to 50-60° until the reaction was complete (0.5 hr.) and the filtrate was adjusted to pH 5.5-6.0 with 20% NaOH; EtOH was removed *in vacuo*, the residue extd. with EtOAc, the ext. washed with dil. NaOH and H_2O, dried, clarified with C concd., and cooled yielding 55% L-*threo*-1-[illegible] *amino-1,3-propanediol*, m. 184-6°, $[\alpha]^{18}_{D}$ 98.[illegible] the diazo deriv. with H_3PO_2 gave a product [illegible] above but which required more extensive [illegible] diol warmed with Ac_2O-pyridine gave the [illegible] m. 146-8° (from 50% EtOH). When I7 was diazotized in 17% HCl at 0-5° and treated at 0° with CuCl, there was obtained 75% L-*threo-1-(p-chlorophenyl)-2-benzoylamino-1,3-propanediol*, m. 171-2°, $[\alpha]^{18}_{D}$ 102.4°; similarly the D-*threo* compd. (m. 171-2°, $[\alpha]^{18}_{D}$ −102.8°) was obtained from D-*threo analog* of IV. In a few instances the D- and L-derivs. were obtained which m. 156°, but showed the same optical activity as the specimens described above and gave the same aminodiols on hydrolysis of the Bz groups. Diazotization in dil. H_2SO_4 and treatment with KI gave the *p-iodo analogs*: D-*threo*, m. 178-9°, $[\alpha]^{18}_{D}$ −87.3°; L-*threo*, m. 178-9°, $[\alpha]^{18}_{D}$ 86.2°; DL-*threo*, m. 173.5-4.5°. If the diazotized L-*threo* compd. in dil. H_2SO_4 was neutralized with $NaHCO_3$ to pH 6 and heated to 70-90°, there was obtained 40% L-*threo p-HO analog*, m. 196-8° (decompn.), $[\alpha]^{18}_{D}$ 103°. Treatment of the diazotized soln., after adjustment to pH 5.5-6, with $Cu_2(CN)_2$ soln. under MePh gave the corresponding *p-cyano analog*: D-*threo*, m. 139-40°, $[\alpha]^{18}_{D}$ −130.4°; L-*threo*, m. 139-40°, $[\alpha]^{18}_{D}$ 129.8°. IV (2.8 g.) in 14 ml. 10% H_2SO_4 was diazotized at 0-5° with 20% $NaNO_2$, neutralized with $CuCO_3$ to Congo red, filtered, and the filtrate treated with 1.5 g. $Na_3Co(NO_2)_6$ and cooled to 3-5°; after 15 min. the soln. was decanted from the ppt. and this was treated with cooling with 0.4 g. Cu_2O suspended in 1 $NaNO_2$ and 1 g. $CuSO_4.5H_2O$ in 6 ml. H_2O; after 10-12 hrs. the mixt. was extd. with EtOAc and the washed and dried ext. gave after evapn. and extn. with H_2O, the *p-O₂N analog* of IV: this was identical with II. Treatment of th

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[illegible] neutralized (pH 6.6) soln. of IV with As_2O_3 [illegible] $CuSO_4$ similarly gave *p-arsono analog* of IV: L-*threo*, m. [illegible] 3° (decompn.), $[\alpha]^{20}_{D}$ 88.5°. Treatment of diazotized IV with 2-C_6H_5OH in cold $NaOH$-Na_2CO_3 gave the red [illegible] *deriv.*: L-*threo*, decomp. 224–6° (from MeOH), $[\alpha]^{20}_{D}$ 180°. Hydrolysis of the corresponding benzoyl derivs. by heating 4 hrs. with 20% HCl gave 56% D-*threo-1-(p-chlorophenyl)-2-amino-1,3 propanediol* (V), m. 145–7°, $[\alpha]^{20}_{D}$ −33.6°; L-*threo analog*, m. 145–7°, $[\alpha]^{20}_{D}$ 35.0°; DL-*threo analog*, m. 122–3°, was obtained by mixing the 2 forms. The *p*-iodo derivs. were hydrolyzed by refluxing with 10% HCl 10 hrs.: D-*threo-1-(p-iodophenyl)-2-amino-1,3-propanediol* (VI), m. 103–4°; similarly was obtained the L-*threo analog*, m. 103–4°, $[\alpha]^{20}_{D}$ 23.0°; DL-*threo analog*, m. 180–1°. The cyano derivs. were hydrolyzed 20 hrs. with 20% HCl yielding *p-carboxy analogs*: D-*threo-1-(p-carboxyphenyl)-2-amino-1,3-propanediol* (VII), decomp. 348–9°, $[\alpha]^{20}_{D}$ −32.4°; L-*threo analog*, decomp. 348–9°, $[\alpha]^{20}_{D}$ 32.0°. These are inner salts and are insol. in org. solvents, but are sol. in alk. solns. or in acids; they are not dichloroacetylated with Cl_2CHCO_2Me, but are acylated by the acyl chloride in presence of K_2CO_3. Heating 2.9 g. Cl_2CHCO_2Me with 2.7 g. *p-threo*-V to 90° 5 min., rubbing the mixt. 3 times with 5-ml. portions of heptane, dissolving the residue in 2–3 ml. $(CH_2Cl)_2$, adding 3 ml. heptane and allowing the mixt. to stand overnight gave 47% D-*threo-2-(dichloroacetamido) analog* of V, m. 92–3°, $[\alpha]^{20}_{D}$ 8.2°; similarly was obtained the L-*threo analog*, m. 92–3°, $[\alpha]^{20}_{D}$ −9°; mixing these gave the DL-*threo analog*, m. 119–20°. Similarly was obtained *2-(dichloroacetamido) analog* of VI: D-*threo form*, m. 103–4°, $[\alpha]^{20}_{D}$ 9.7°; L-*threo form* (VIII), m. 103–4°, $[\alpha]^{20}_{D}$ −10.8°; DL-*threo form* was obtained by mixing the D- and L-forms m. 122–3°. VII treated with $Cl_2CHCOCl$ in the presence of aq. K_2CO_3 and Et_2O gave 71% [illegible] *mido) analog*, m. 190–1°, $[\alpha]^{20}_{D}$ 12.0°; L-*threo form*, m. [illegible] 1°, $[\alpha]^{20}_{D}$ −13.9°; mixing these gave the DL-*form*, m. [illegible] Hydrogenation of D- or L-*threo* forms of II in EtOH [illegible] Raney Ni at 75–80° and 40–50 atm. H gave 90–2% [illegible] *amino analogs*: D-*threo form*, m. 135–6°, $[\alpha]^{20}_{D}$ −28.[illegible] L-*threo form*, m. 135–6°, $[\alpha]^{20}_{D}$ 27.5°. Treatment of these with Cl_2CHCO_2Me in abs. MeOH 24 hrs. at 18–22° gave *1-(p-aminophenyl)-2-(dichloroacetylamido)-1,3-propanediol*, isolated as *HCl salts* (from MeOH-Et_2O): D-*threo form*, $[\alpha]^{20}_{D}$ 3.1°; L-*threo form*, $[\alpha]^{20}_{D}$ −8.5°; these do not melt, but showly decomp. on heating. Hydrogenation over Raney Ni at atm. pressure of D- and L-*threo-1-(p-nitrophenyl)-2-(dichloroacetamido)-1,3-propanediols* and treatment of the products with alc. HCl gave 36–9% *HCl salts* of the *p-amino analogs*, with 23–7% original nitro derivs. being recovered. Diazotization of D- or L-*threo-1-(p-aminophenyl)-2-(dichloroacetamido)-1,3-propanediols* (IX) in 5% HCl with aq. $NaNO_2$ gave ppts. of the corresponding *diazonium chlorides*: D-*threo*, 44%, $[\alpha]^{20}_{D}$ 9.5°; L-*threo*, $[\alpha]^{20}_{D}$ −9.8°; these decomp. on heating, but do not melt. Treatment of the diazotized soln. with Cu_2Cl_2 gave 45% VIII (from $(ClCH_2)_2$ and heptane), identical with the previous prepn. If the diazotized soln. in dil. H_2SO_4 is heated to 70–90° after adjustment to pH 5.5, there is formed *p-HO analog*: D-*threo form*, decomp. 160–1.0°, $[\alpha]^{20}_{D}$ −8.1°; L-*threo form*, decomp. 160–1.0, $[\alpha]^{20}_{D}$ 7.80°; mixing these gave the DL-*form*, m. 138–40°. Treatment of the diazotized soln. with $(CuCN)_2$ as described above gave the *p-cyano-* [illegible] *form*, m. 135.5–6.5°, $[\alpha]^{20}_{D}$ −17.0°; mixing these gave the

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DL-*form*, m. 152.5–3.5°. Hydrolysis with HCl gave the *p-aminobenzy deriv.* Treatment of the diazotized and neutralized soln. with As_2O_3 and $CuSO_4$ similarly gave the *p-arsonophenyl deriv.* in 16% yield: L-*threo form*, $[\alpha]^{23}_{D}$ 8.6°; L-*threo form*, $[\alpha]^{23}_{D}$ −7.8°; neither shows a definite decompn. temp. IX.HCl (D- or L-*threo* forms) diazotized as usual in dil. HCl and treated with *o-*$O_2NC_6H_4OH$ in the presence of NaOH and Na_2CO_3 at 15–20° 2 hrs. gave on acidification the *3-nitro-4-hydroxyphenylazo deriv.*, purified by pptn. from $(CH_2Cl)_2$ with heptane, followed by crystn. from 30% AcOH: D-*threo form*, m. 157–9°, $[\alpha]^{23}_{D}$ 21.2°; L-*threo form*, m. 157–9°, $[\alpha]^{23}_{D}$ −22° mixing these gave the DL-*form*, m. 153–5°. IX.HCl (D- or L-*threo* forms) (2.31 g.) in 15 ml. MeOH was treated with 0.8 g. AcONa in 10 ml. MeOH and filtered; at 5° the soln. was treated with 0.95 g. *p-*$ONC_6H_4NO_2$ in 15 ml. AcOH; after 10–12 hrs. there was obtained 56% *p-nitrophenylazo der v.*, D-*form*, m. 173–4°, $[\alpha]^{23}_{D}$ −62.2°; L-*threo form*, m. 173–4°, $[\alpha]^{23}_{D}$ 64.9°; mixing these gave the DL-*threo form*, m. 171–2°. A small amt. of *p,p'-dinitroazoxybenzene*, m. 191–2° was isolated from the reaction mixt. Condensation of IX with *p-*$O_2NC_6H_4CHO$ in the presence of KOAc in MeOH gave the *p-nitrobenzylidene deriv.*: D-*threo form*, m. 164–6° (decompn.; from EtOH), $[\alpha]^{23}_{D}$ −18.8°; L-*threo form*, decomp. 165–7°, $[\alpha]^{23}_{D}$ 19.7°; mixing these gave the DL-*form*, m. 155–7° (decompn.).

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BOGOSLOVSKIY, B.M.; KAZAKOVA, Z.S.; SHEMYAKIN, M.M.

Fading of azo dyes. Zhur. Priklad. Khim. 26, 435-8 '53. (MLRA 6:4)
(CA 47 no.18:9617 '53)

1. Moscow Textile Inst.

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SHEMYAKIN, M. M.

USSR/Chemistry - Antibiotics 21 Mar 53

"The Structure of Aureomycin and Terramycin," M. M. Shemyakin and L. A. Shchukina, Inst of Biol and Chemistry, Acad Med Sci USSR

DAN SSSR, Vol 89, No 3, pp 499-500

Carried out the final step in detn of the structure of aureomycin. The $N(CH_3)_2$ group was found to be located in the 10 position and not the 6 position of the tetracyclic nucleus. This was concluded from behavior of the compd towards HI. Using an analogous method, terramycin was found to have the $N(CH_3)_2$ group in the 10 position.

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SHEMYAKIN, M. M.

Chemistry of chloromycetin (levomycetin). V. Racemization of L-*threo*-1-(*p*-nitrophenyl)-2-dichloroacetamidomate into chloromycetin (levomycetin). M. M. Shemyakin, E. M. Bamdas, E. I. Vinogradova, D. P. [redacted] Gubernier, V. N. Orekhovich, A. S. Khokhlov, Yu. B. [redacted] Shvetsov, and L. A. Shchukina. *J. Gen. Chem. U.S.S.R.* 24, 2045-53(1954)(Engl. translation).—See *C.A.* 49, 14074*a*.

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SHEMYAKIN, M.M.

Theoretical basis of oxidation-hydrolytic transformations CH of organic compounds. M. M. Shemyakin and L. A. Shchukina. *Voprosy Khim. Kinetiki, Kataliza i Reakt. Sposobnosti, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 757-64.—A brief discussion of the possible mechanisms of oxidative hydrolysis reactions in the field of a naphtho- and anthraquinones. 33 references.

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Shemyakin, M. M.

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Chemistry of chloromycetin (levomycetin). VI. Synthesis of new optically active analogs of chloromycetin (levomycetin). M. M. Shemyakin, M. N. Kolosov, M. G. Karapetyan, E. M. Bamdas, Yu. B. Shvetsov, E. I. Vinogradova, and L. A. Shchukina. *Zhur. Obshchei Khim.* 25, 1199-1206(1955); cf. *C.A.* 49, 946*b*, 14674*e*.—Diazotization of 10 g. D- or L-*threo*-*p*-$H_2NC_6H_4CH(OH)CH(CH_2OH)$-$NHCOCHCl_2$ (I) in 10% H_2SO_4 at 0–3° with $NaNO_2$, treatment with 40–50 g. SO_2 in 200 g. 25% H_2SO_4, satn. at −10° with SO_2 with slow addn. of 10 g. powd. Cu at −5 to −10° followed by filtration, extn. of the filtrate with EtOAc, and evapn. of the dried ext. gave 53–8% *p*-$HO_2SC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$ (further purification by treatment with AcOH); D-*threo isomer*, softens at 125–7°, $[\alpha]^{17}_D$ −40.6° (Me_2CO); L-*threo isomer*, softens at 125–6°, $[\alpha]^{23}_D$ 45.2° (Me_2CO). The sulfinic acid (1 g.) in 2 ml. H_2O treated with 0.25 g. $NaHCO_3$ in 0.5 ml. H_2O and 0.5 g. $AgNO_3$ gave the ppt. of Ag sulfinate, which dried rapidly *in vacuo* and darkness at 30°, then shaken in the dark with MeI gave 65% *p*-$MeO_2SC_6H_4CH(OH)CH(CH_2OH)NH$-$COCHCl_2$: D-*threo isomer*, m. 165–6°, $[\alpha]^{17}_D$ 13.2° (EtOH); L-*threo isomer*, m. 165–6°, $[\alpha]^{19}_D$ −13.2° (EtOH). Treatment of the sulfinic acid with aq. $NaHCO_3$, filtration, and filtered and recrystd. from C_6H_6 gives 1.4 g. $BzC(:NOH)$-CH_2OH (I), leaves, m. 106.5–8.0°. I (500 mg.) in 10 ml. MeOH reduced with Pd-C and H 30 min. at 25°, and the product concd. and recrystd. from MeOH-AcOEt gives 250 mg. *dl*-$PhCH(OH)CH(NH_2)Me.HCl$ (II), leaves, m. 190–2°. II (40 mg.) in 0.4 ml. water and 0.4 ml. C_6H_6 benzoylated with 30 mg. BzCl and 10% NaOH and the product recrystd. from water give *dl*-$PhCH(OH)CH(NH$-$Bz)Me$ (III), needles, m. 142–4°. Catalytic reduction of 300 mg. I in 18 ml. *N* HCl with 150 mg. 10% Pd-C at 10° (117.6 ml. H absorbed in 1 hr.), the product concd. *in vacuo*, washed with AcOEt, the aq. layer concd., the residue in MeOH treated with Et_2O, the NH_4Cl filtered off, the filtrate concd., the residue in 0.5 ml. C_6H_6 benzoylated with 0.25 g. BzCl and 10% NaOH yields 110 mg. of a mixt. (IV) of *dl*-*N*-benzoylnorephedrine and its ψ-isomer, leaves, m. 130–3°; IV heated 5 min. with 1 ml. 10% HCl and the product recrystd. from MeOH-Me_2CO give 80 mg. *dl*-1-

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and p-$O_2NC_6H_4COCl$ gave 95% p-$O_2NC_6H_4CONHC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$: D-*threo isomer*, m. 203–4° (decompn.), $[\alpha]^{18}_D$ −29.3°. Treatment of p-$HOC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$ with Me_2SO_4 in the presence of aq. NaOH at 25–30° gave 23% p-$MeOC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$: D-*threo isomer*, m. 101–2°, $[\alpha]^{18}_D$ −34.2° (Me_2CO); L-*threo isomer*, m. 101–2°, $[\alpha]^{18}_D$ 33.2° (Me_2CO); DL-*threo form*, m. 107–7.5°. p-$HO_2CC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$ treated with aq. $NaHCO_3$, followed by $AgNO_3$, and the dried Ag salt treated with MeI 8 hrs. gave 80% p-$MeO_2CC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$: L-*threo isomer*, m. 128–9°, $[\alpha]^{18}_D$ −29.0° (Me_2CO). I.HCl treated with KOAc in MeOH, followed by BzH, kept 1 hr. at 20° and heated to reflux, gave after dil. with H_2O 71% p-$PhCH:NC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$: D-*threo isomer*, m. 153–4°, $[\alpha]^{18}_D$ −47.5° (Me_2CO); L-*threo isomer*, m. 153–4°, $[\alpha]^{18}_D$ 45.6° (Me_2CO); DL-*threo form*, m. 146–7°. I.HCl in MeOH with KOAc, followed by PhNO in AcOH gave after 12 hrs. at 15–20° and diln. with H_2O 40% p-$PhN:NC_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$: D-*threo isomer*, m. 144–5°, $[\alpha]^{18}_D$ −59.1° (Me_2CO); L-*threo isomer*, m. 144–5°, $[\alpha]^{18}_D$ 57.1° (Me_2CO); DL-*threo form*, m. 150–1°. I.HCl with NaOAc in MeOH, followed by m-$ONC_6H_4NO_2$ in AcOH 20 hrs. at 4–5° gave 78% p-$(m\text{-}O_2NC_6H_4N:N)C_6H_4CH(OH)CH(CH_2OH)NHCOCHCl_2$: D-*threo isomer*, m. about 100°, $[\alpha]^{22}_D$ −41.2° (Me_2CO); the product crystallizes with 1.5 moles solvent (CCl_4 or C_6H_6). I.HCl diazotized in aq. HCl and treated with PhOH in aq. NaOH-Na_2CO_3 gave 52% p-$(p\text{-}HOC_6H_4N:N)C_6H_4CH(OH)CH(CH_2OH)HNCOCHCl_2$: D-*threo isomer*, m. 179–81°, $[\alpha]^{18}_D$ −59° (Me_2CO); L-*threo isomer*, m. 179–81°, $[\alpha]^{18}_D$ 57.4° (Me_2CO); DL-*threo form*, m. 171–2°. Also in *J. Gen. Chem. U.S.S.R.* 25, 1147–51(1955)(Engl. translation). G. M. Kosolapoff

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α-Substituted α-amino acids series. I. Synthesis and properties of the simplest α-hydroxy-α-acylamino carboxylic acids. E. S. Chaman and M. M. Shemyakin. *Zhur. Obshchei Khim.* 25, 1360–5(1955) [illegible] 1096*d*.—A characteristic of *N*-acylated α-hydroxy-α-amino acids is their ability to be readily hydrolyzed to the corresponding oxo acid and amide. Heating hippuric acid with Ac_2O gave 2-phenyl-2-oxazolin-5-one (I). Heating *N*-benzoyl-α-alanine with 5 parts Ac_2O 0.5 hr. at 70–80° gave 80% *4-methyl-2-phenyl-5-oxazolinone* (II) b_{2-3} 108–12°. *4-Et analog* (III), m. 48–50°, b_{2-3} 114–17° prepd. in 90% as above, with aq. NH_4OH gave $PrCH(NHBz)CONH_2$, m. 198–200°. To 12.8 g. I in dry $(CH_2Cl)_2$ at 4–7° was slowly added 6.9 g. Br_2 in $(CH_2Cl)_2$ yielding a ppt. of 2-phenyl-5-oxazolinone HBr salt, which after sepn. and soln. in 5% NaOH gave on acidification 40% hippuric acid. The $(CH_2Cl)_2$ soln. stirred 2–3 hrs. with H_2O gave 35% *N-benzoyl-hydroxyglycine*, m. 200–2° (from dioxane-$CHCl_3$). If the $(CH_2Cl)_2$ soln. obtained above is treated with EtONa-EtOH, there is formed *N-benzoylethoxyglycine Et ester*, b_{2-4} 130–5°, m. 69–71°. Similarly bromination of II gave 33% *N*-benzoyl-α-alanine, while the org. layer stirred with H_2O gave 27% *N-benzoyl-α-hydroxy-α-alanine*, m. 103–5°. III similarly gave 26% *N-benzoyl-α-hydroxyl-α-aminobutyric acid*, m. 98–9° and 24% $PrCH(NHBz)CO_2H$. Stirring *N*-benzoylhydroxyglycine 2–3 min. with 8% $NaHCO_3$ gave $BzNH_2$ and glyoxylic acid (identified by 2,4-dinitrophenylhydrazone, m. 188–90°, and by aminoguanidine deriv., m. 141–2°); heating with aq. alc. HCl gave the same result. *N*-Benzoyl-α-hydroxy-α-alanine and *N*-benzoyl-α-hydroxy-α-aminobutyric acid are similarly rapidly hydrolyzed by $NaHCO_3$ and by HCl. Also in *J. Gen. Chem. U.S.S.R.* 25, 1309–12(1955)(Engl. translation).

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α-Substituted α-amino acids. II. Structure and properties of the product of reaction of phenaceturic acid with acetic anhydride. S. I. Lur'e, E. S. Chaman, and M. M. Shemyakin. *Zhur. Obshchei Khim.* 25, 1799–1802 ([illegible]), [illegible]014a.—Ac_2O and $PhCH_2CONHCH_2CO_2H$ is *2-benzylidene-3-acetyl-5-oxazolidinone* (I). I in $(CH_2Cl)_2$ at 7–9° with Br gave a ppt. of 2-methyl-3-oxazolin-5-one-HBr, which ground with H_2O gave 24% $AcNHCH_2CO_2H$ (II), m. 200–3°; treatment with $PhNH_2$ gave $AcNHCH_2CONHPh$, m. 101–3°. The residual soln. treated with concd. NH_4OH gave 59% $PhCHBrCONH_2$, m. 143–5°. Heating 4 g. I with 2.5 g. BzH, 2.5 g. K_2CO_3, and 12 ml. Ac_2O 2 hrs. at 100–10° and quenching the mixt. in ice gave *2-methyl-4-benzylidene-3-oxazolin-5-one*, m. 149–52°, identical with that prepd. from BzH and II (cf. Lur'e, *et al.*, *C.A.* 47, 12245h); the mother liquor gave α-phenylcinnamic acid, m. 170–2°. Possible paths of bromination of I are discussed.

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SHEMYAKIN, M.M.

USSR/Chemistry - Antibiotics

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Authors : Shemyakin, M. M., Memb.Cor.Acad. of Sc., USSR; Koloscv, M. N.; Levitov, M. M.; Germanova, K. I.; Karapetyan, M. G.; Shvetsov, Yu. B.; and Bamdas, E.M

Title : Relation between structure and antimicrobic activity of chloromycetin (levomycetin) and the mechanism of its reaction

Periodical : Dok. AN SSSR 102/5, 953-956, Jun 11, 1955

Abstract : It is shown that the high selectivity of the biological effect of chloromycetin on microbes is determined simultaneously by the following factors: 1) strong polarizing effect of the p-nitrophenyl radical, the geometrical dimensions of which are of no importance; 2) strong polarizing effect of the dichloroacetyl radical, which should satisfy even the most specific geometrical requirements; and 3) defined geometrical dimensions and corresponding conformation of the aminopropanediol group. The relation between the structure and biological activity of chloromycetin is explained.

Institution : Acad. of Med. Sc., USSR, Inst. of Biol. and Med. Chem.

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Periodical : Dok. AN SSSR 102/5, 953-956, Jun 11, 1955

Abstract : Five references: 2 USSR and 3 USA (1858-1955). Diagrams.

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