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TORGONSKIY, Mikhail Nikolayevich, kandidat tekhnicheskikh nauk; TITOV, P.V., inzhener, ofitsial'nyy retsenzent; LESKOV, T.N., inzhener, ofitsial'nyy retsenzent; SAMUYLLO, V.I., redaktor; PITERMAN, Ye.L., redaktor izdatel'stva; KARASIK, N.P., tekhnicheskiy redaktor

[Structures for forest roads] Iskusstvennye sooruzheniia lesovoznykh dorog. Moskva, Goslesbumizdat, 1956. 151 p. (MLRA 9:9)
(Forest roads)

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TORGONSKIY, M. N.

"Effect of Types of Track Superstructure on the Wear and Life of Narrow-Gauge Rails." Sub 27 Jun 51, Moscow Forestry Inst

Dissertations presented for science and engineering degrees in Moscow during 1951.

SO: Sum. No. 480, 9 May 55

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PHASE I BOOK EXPLOITATION SOV/4233

Moscow. Vyssheye tekhnicheskoye uchilishche

Raschety detaley i mekhanizmov tochnykh priborov; sbornik statey (Design of Parts and Mechanisms of Precision Instruments; Collection of Articles) Moscow, Mashgiz, 1960. 260 p. 5,000 copies printed.

Ed. (Title page): T. A. Gevondyan, Doctor of Technical Sciences, Professor; Ed. (Inside book): Ya. G. Alaverdov, Engineer; Tech. Ed.: A. F. Uvarova; Managing Ed. for Literature on Machine Building and Instrument Making (Mashgiz): N. V. Pokrovskiy, Engineer.

PURPOSE: This collection of articles is intended for scientific workers and engineers engaged in instrument making.

COVERAGE: The results of investigations on making instruments with complex and design-perfect parts, pairs, and mechanisms, it is claimed, are published here for the first time. The articles cover theory and methods of spherical cogwheel engagement, a new method of manufacturing toothed wheels with alternating ratio within one revolution, a universal method for designing an oscillating system for stability by means of complex variables, and precision methods for designing brake centrifugal governors used in instrument design. Some of the articles are accompanied by Soviet and non-Soviet references. No personalities are mentioned.

Kunayev, I. P., Candidate of Technical Sciences, Docent. Design of a Free Oscillating System "Balance Arm -Strip Spring" Allowing for the Constant Angular Velocity of the Motion of the Spring 50
The exact as well as an approximate analytical method for the above design are presented.

Torgov, A. M., Candidate of Technical Sciences, Docent. Theory and Practical Methods of Balancing the "Balance Wheel -Spiral Spring" Oscillating System in Timepieces 82
A development of the problems concerning the effect of the unbalance of the oscillating system on the running of a clockwork is presented.

Tsvetkov, N. N., Engineer. Design of Centrifugal Governors 106
The problem of methodology used for the perfected design calculation of the brake centrifugal governors in instrument making is discussed. The motion of the governed mechanism is investigated (including the governor and mover) by taking into account inertial and frictional losses in the whole mechanism. Sample calculations using simplified design formulas are presented.

Valedinskiy, A. S., Candidate of Technical Sciences, Docent. "Spring Hinges" and Mechanisms in Measuring Instruments 171
"Spring hinges" are crossed cantilever strip-springs replacing hinges in small angular movements. Various designs of spring suspensions are given and the problems of compensating the drop in the force during measuring in instruments with spring mechanisms are discussed.

Chetverikov, V. N., Candidate of Technical Sciences. The Reversing Ferromagnetic Powder Clutch 198
The theory and design of the above clutch are presented.

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TORGOV, A.M., kandidat tekhnicheskikh nauk.

Graphicanalytic method for evaluating the precision of watch rate. Chas.mekh. no.1:55-102 '55. (MLRA 9:12)
(Clockmaking and watchmaking--Testing)

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1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

Derivatives of acetylene. XXXII. Condensation of vinylacetylene with hydroxy ketones and tetrahydro-γ-pyrones. I. N. Nazarov and I. V. Torgov. *Bull. acad. sci. U. R. S. S., Classe sci. chim.* 1943, 129-38(English summary).—$MeC(OH)Ac$ (I) (97 g.) and 57 g. $CH_2:CHC:CH$ in 300 cc. Et_2O (dry) were added over 3 hrs. to a cooled stirred mixt. of 100 g. powd. KOH and 200 cc. dry Et_2O; after stirring for 10 hrs., washing with water and 10% HCl, there was obtained 90 g. *$MeC(OH)C(OH)MeC:CCH:CH_2$*, b_3 90-2°, n_D^{20} 1.4967, d_4^{20} 0.9922, which polymerizes to a solid on standing; hydrogenation of this glycol in presence of Pt gave *trimethylbutylethylene glycol*, b_4 81-2°, m. 20-7°, which with concd. H_2SO_4 at 10° gave *3,3-dimethyl-2-heptanone*, b. 168-72°, n_D^{20} 1.4202; *semicarbazone*, m. 130-0.5°. The glycol yields the diacetate, $b_{3.4}$ 94-5°, n_D^{20} 1.4709, d_4^{20} 1.0317, when treated with Ac_2O in the presence of H_3PO_4, at 40°. Treatment of the glycol with $AcCl$-Ac_2O yielded impure *chlorohydrin*, $b_{3.4}$ 77-81°. $CH_2:CHC:CH$ (130 g.) and 200 g. $AcCH_2CH_2CH_2OH$ in 400 cc. Et_2O were added with cooling and stirring to 210 g. KOH in Et_2O to yield, after the usual treatment, 169 g. *$CH_2:CHC:CC(OH)MeCH_2CH_2CH_2OH$*, b_3 122-4°, n_D^{20} 1.5049, d_4^{20} 1.004, which, hydrogenated in presence of Pt, gave *4-methyl-1,4-octanediol*, $b_{3.4}$ 110°, n_D^{20} 1.4587, d_4^{20} 0.9189. Acetylation with Ac_2O-H_3PO_4 gave *$CH_2:CHC:CC(OAc)MeCH_2CH_2CH_2OAc$*, b_3 115-16°, n_D^{20} 1.4755, d_4^{20} 1.022, while formylation with HCO_2H (standing at room temp. 1 day, then heated to 80-90° for 20 min.) gave *$CH_2:CHC:CC(OH)MeCH_2CH_2CH_2OCOH$*, b_3 111-12°, n_D^{20} 1.4870, d_4^{20} 1.0316. The Grignard reagent from 60 g. vinylacetylene and 100 g. EtBr and 25 g. Mg was treated with 51 g. $Me_2C(OH)CH_2Ac$, to yield 37 g. *$Me_2C(OH)CH_2C(OH)MeC:CCH:CH_2$*, b_3 101°, n_D^{20} 1.4835, d_4^{20} 0.9837, which, hydrogenated in presence of Pt, gave *3,4-dimethyl-3,4-octanediol*, b_3 90-103°, n_D^{20} 1.4440, d_4^{20} 0.9020. Condensation of vinylacetylene with 2,2-dimethyltetrahydro-1,4-pyrone in the presence of KOH in Et_2O yielded *2,2-dimethyl-4-(vinylethynyl)tetrahydro-1,4-pyranol*, $b_{3.4}$ 104-6°, d_4^{20} 1.015, n_D^{20} 1.5051, which, hydrogenated with Raney Ni, gave *2,2-dimethyl-4-butyltetrahydro-1,4-pyranol*, $b_{3.4}$ 102-3°, n_D^{20} 1.4625, d_4^{20} 0.9512. The pyranol (58 g.) in 20 cc. MeOH was added to 2 g. HgO, 2 cc. $BF_3.Et_2O$ and 35 cc. MeOH, heated to 40° for 5 hrs. and dild. with Et_2O to yield 15 g. of a product b_4 100-10°, n_D^{20} 1.4822, d_4^{20} 1.028, apparently $CH_2CH_2C(O.CMe_2.CH_2)CHCOCH_2CH_2OMe$. $CH_2:CHC:CH$ condensed with 2-methyltetrahydro-1,4-pyrone in the presence of KOH in Et_2O gave *2-methyl-4-(vinylethynyl)tetrahydro-1,4-pyranol*, b_4 100-1°, n_D^{20} 1.5070, d_4^{20} 1.020, which, hydrogenated in presence of Pt, gave *2-methyl-4-butyltetrahydro-1,4-pyranol*, b_4 80-90°, n_D^{20} 1.4622, d_4^{20} 0.9920.

G. M. Kosolapoff

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

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B

Derivatives of Acetylene. LIV. Vinylethenylcarbinol and Its Transformations. (In Russian.) I. N. Nazarov and I. V. Torgov. *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* (Bulletin of the Academy of Sciences of the USSR, Section of Chemical Sciences), Sept.-Oct. 1947, p. 495-499.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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TORGOV, I.V., redaktor; ZALEPUGIN, D.Ye., tekhnicheskiy redaktor

[redacted]

[Transactions of scientific research institutes; collection of summarized research papers] Trudy nauchno-issledovatel'skikh institutov; sbornik referatov rabot. Moskva, Gos. nauchno-tekhn. izd-vo khim. lit-ry, 1948. 218 p. (MLRA 8:6)

1. Russia (1923- U.S.S.R.) Ministerstvo khimicheskoy promyshlennosti.
(Chemistry--Abstracts)

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TORGOV, I. V.

I. N. Nazarov and I. V. Torgov, Derivatives of acetylene. 76. Transformations of 2, 2-dimethyl-4-vinylethinyltetrahydropyrano-4.

Isomerization is obtained under the influence of mercury sulfate in a methanol solution of 2,2-dimethyl-4-vinyl-ethinyltetrahydropyranol-4 (I) into dienone (II). By splitting methanol from methoxy ketone (IV) free dienone (II) is obtained.

Institute of Organic Chemistry of the
Academy of Sci. (USSR)
April 7, 1947

SO: Journal of General Chemistry (USSR) 18, (80) No. 7 (1948).

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"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001756320009-8

TORGOV, I. V.

I. N. Nazarov and I. V. Torgov, Derivatives of acetylene. P. 1332. 75. The mechanism of hydration of dimethyl-vinyl ethinyl carbinol.

It is established that the hydration goes in two directions: a) with a preliminary isomerization of carbinol into $\beta\beta$-dimethyldivinyl ketone which adds a molecule of water on the nonsaturated vinyl group and then cyclates into 2, 2-dimethyltetrahydro-4 pyrone; b) with preliminary hydration of the triple bond and following cyclation into 2,2,5-trimethyltetrahydro-3-furan.

Institute of Organic Chemistry of the
Academy of Sci. (USSR)
April 7, 1947

SO: Journal of General Chemistry (USSR) 18, (80) No. 7 (1948).

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TORGOV, I. V.

USSR/Chemistry - Acetylene, Derivatives Aug 48
Chemistry - Glycols, Dehydration of

"Acetylene Derivatives: No 77, Dehydration and Isomerization of Vinylacetylene Glycols," I. N. Nazarov, I. V. Torgov, Inst Org Chem, Acad Sci USSR, 12½ pp

"Zhur Obshch Khimii" Vol XVIII (LXXX), No 8

Dehydrated vinylacetylene α,β-and γ-glycols using potassium bisulfate. In case of two glycols only one hydroxyl is detached adjacent to carbon atom linked to vinylacetylene chain. 4-Methyl-octene-7-yne-5-diol-1,4 on dehydration behaves similarly to saturated 1,4-diols and yields 2-methyl-2-vinylethyl-tetrahydrofuran. α-and β-glycols yield stable complexes with mercury salts. These complexes, when subjected to action of acids, either do not decompose or are resinified; for this reason, attempted isomerization of these glycols was unsuccessful. γ-Glycol does not yield such complexes and isomerizes under influence of mercury sulfate in methanol, forming a complex mixture of substances, from which 2-methyl-2-(1'-deto-3'-metoxy-butyl)-tetrahydrofuran (I) and 4-methyl-8 metoxy-octene-4-ol-1-on-1-on-6 are obtained. I can also be obtained by hydration of furan with simultaneous combination of a methanol molecule. Submitted 7 Apr 47.

PA 19/49T13

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TORGOV, I. V.

May/June 49

USSR/Chemistry - Acetylene

"Acetylene Derivatives: No 89, Transformations of 2-Butyne, 4-Diol," I. N. Nazarov, L. N. Terekhova, I. V. Torgov, Inst of Org Chem, Acad Sci USSR, 6pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 3

Describes transformation of 2-butyne-1, 4-diol in a solution of methanol by mercury into 1-methoxy-butane-4-ol-3-on, and latter's behavior in the splitting off of methanol, and in hydrolysis. Isolates 1-butene-4-ol-3-on and studies its properties. Submitted 20 Mar 48.

PA 56/49T9

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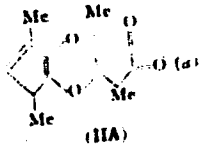
CA

Acetylene derivatives. C. 3,5-Dimethyl-3-cyclopentene-1,2-dione and its transformations. I. N. Nazarov and I. V. Torgov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1951, 417-37; cf. C.A. 46, 914h, 2088f, 3507c, 1528e, 6084f. 2,4-Dimethyl-2-cyclopenten-1-one (*C.A.* numbering) (37 g.) with 43 g. SeO_2 in 70 g. AcOH at 100-10° gave 34.6% *3,5-dimethyl-3-cyclopentene-1,2-dione* (I), m. 64.0°; oxidation in 60% AcOH gave but 8-15% and in Ac_2O 18-20%. Pure I is bright yellow, m. 66.5-7.0°, and irritates the mucous membranes; it can be kept for several weeks in a desiccator. Heated with *o*-$C_6H_4(NH_2)_2$ it forms the *quinoxaline*, m. 253-4°. I.*HCl*, colorless, m.



(IIA)

79-80°, is made in C_6H_6 with dry HCl; H_2O causes rapid hydrolysis. I with Ac_2O-KOAc gave the *diacetate* (II), m. 146-7°, corresponding to the *dimer diketone* (IIA), while the mother liquor yields the diacetate, *3,5-diacetoxy-2,4-dimethyl-2-cyclopentene-1-one*, (III), $b_{1.5}$ 124-5°, n_D^{20} 1.4760, d_4^{20} 1.153. Hydrogenation of I over Pd-$CaCO_3$ gave after addn. of II a product that is probably the *keto-enol* *3,5-dimethyl-2-cyclopenten-2-ol-1-one* (IV), m. 87-8°, whose *bis(2,4-dinitrophenylhydrazone)* m. 196-8° (decompn.), while IV itself gives a violet color with $FeCl_3$, but does not form a quinoxaline deriv. nor an enolate in a soda soln. but gives a yellow soln. in 5% KOH. IV with Ac_2O gave the *2-AcO analog* (V), b_5 115°, n_D^{20} 1.4775, d_4^{20} 1.0771, hydrogenated over Adams Pt catalyst to the *satd. analog* (VI), b_5 94-6°, n_D^{20} 1.4442, d_4^{20} 1.0355, hydrolyzed with 10% KOH to the ketol, *3,5-dimethylcyclopentan-2-ol-1-one* (VI), b_5 77-9°, n_D^{20} 1.4621, d_4^{20} 1.0300, which does not give a solid semicarbazone or dinitrophenylhydrazone. Hydrogenation of III over Adams Pt catalyst gave a mixt. of V and VI. Hydrogenation of IV falls with Pd-C or Adams Pt in dioxane or AcOH, but with 30% Pt-C and a trace of chloroplatinic acid in dry Et_2O, 3.4 moles H was absorbed in 10 hrs. and gave: *1,3-dimethylcyclopentane* (VII), b_{750} 90°, n_D^{20} 1.4105, d_4^{20} 0.7460, *2,4-dimethylcyclopentanol* (VIII), b_{50} 68-70°, n_D^{20} 1.4457, d_4^{20} 0.8990 (*dinitrobenzoate*, m. 70-3°), and *3,5-dimethyl-1,2-cyclopentanediol*, b_5 98-9°, n_D^{20} 1.4657. If the hydrogenation is stopped after addn. of 1 mole H, the products include VII, crude 2,4-dimethylcyclopentanone, (IX), and VI, b_5 65°, n_D^{20} 1.4589, d_4^{20} 1.021. IX with EtOH-Na gave VIII, b_{50} 76°, n_D^{20} 1.4442, d_4^{20} 0.8925; *dinitrobenzoate*,

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m. 72.7-4.6°. I with 5% MeONa in EtOH yields IIA, decomp. 200°; pyridine has the same effect. IIA normally m. 199-201° (decompn.) on rapid heating, decomp. 215°, is readily sol. only in pyridine or hot dioxane and AcOH, and gives a violet color with $FeCl_3$. IIA and o-$C_6H_4(NH_2)_2$ form the *quinoxaline*, m. 168-70°; dry HCl yields with IIA its *HCl salt*, decomp. 190.5-1.5°, which is readily hydrolyzed by warm H_2O. Satn. of II soln. in MeOH with HCl yields the *chloroacetal*, probably with OMe and Cl on the symmetrically located carbonyl group; the product m. 164-6° (crude), m. 167-7.5° (pure). IIA with KOAc-Ac_2O gave II, m. 147°, which gives no color with $FeCl_3$ and is not hydrogenated over Adams catalyst. IIA with BzCl in pyridine gave the *benzoate*, with the location of the BzO probably at (a) in formula IIA, m. 152-3°. IIA treated 2 hrs. with 20% KOH in a N atm., then rapidly acidified with cooling, formed a *hydiate* (?) of IIA, decomp. 195-8°, giving a violet color with $FeCl_3$, which with Ac_2O yielded II, m. 147°. IIA hydrogenated over Pd-C in dry dioxane at 100-10° and 85 atm. yielded the *enediol analog* of IIA(X), m. 186-90°, also obtained over Pt-C. This product with Ac_2O-pyridine gave the *diacetate*, m. 130-9.5°, giving no color with $FeCl_3$ and showing no active H by the Zerewitinov method; this diacetate did not react with EtMgBr, while hydrogenation of the diol over Raney Ni gave an oil, which on acetylation gave apparently *Ac deriv.* of *tetramethylbicyclodioxadodecanol*, $C_{16}H_{28}O_4$, a viscous oil, and methylation of the glycol with Me_2SO_4 of X gave the *di-Me ether* of X, m. 65.5-6.5°. IIA by the Clemmensen method gave *1,4,7-trimethylbicyclo[3.3.0]octane*, b. 85-7°, n_D^{20} 1.4760, d_4^{20} 0.8818. G. M. Kosolapoff

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Organic Chemistry

CA

Acetylene derivatives. CXXX. Synthesis of polycyclic compounds. 8. Condensation of 1-vinylcyclohexene with cyclohexen-1-one. I. N. Nazarov, I. V. Torgov, and M. V. Kuvarzina. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 22, 220-7(1952); cf. *C A.* 46, 8021g; 10098g; preceding abstr.—Dehydrohalogenation of 2-bromocyclohexanone gave *2-cyclohexen-1-one*, b_{20} 71°, n_D^{20} 1.4840. This (16 g.) and 7 g. *1-vinylcyclohexene* (from 1-vinylcyclohexanol with P_2O_5 in Me_2CO at 35-50°), b_{100} 142-4°, b_{20} 63-5°, n_D^{20} 1.4910, heated in a metal ampul with 0.1 g. pyrogallol 3 hrs. at 200-5°, gave 14 g. unreacted materials and 6 g. *cis-Δ^bis-dodecahydro-4-phenanthrone* (I), b_5 127°, m. 63° (from EtOH); *semicarbazone*, m. 188° (from EtOH); *2,4-dinitrophenylhydrazone*, m. 167° (from EtOH). Hydrogenation over Adams' Pt catalyst in EtOH gave *cis-perhydro-4-phenanthrone*, m. 110-12° (from EtOH); *semicarbazone*, m. 91-2° (from 50% MeOH); *2,4-dinitrophenylhydrazone*, m. 140° (from EtOH). I with MeMgI gave 60% *4-methyl-Δ^bis-dodecahydro-4-phenanthrol*, b_5 140-2°, m. 117-18° (from 75% EtOH). This stirred 3 hrs. at 75° with 70% H_2SO_4 gave *mixed 4-methyldecahydrophenanthrenes*, b_5 114-27°. The 1st fraction, b_5 114-17°, n_D^{20} 1.5425, d_4^{20} 0.9081; 2nd fraction, b_5 125-7°, n_D^{20} 1.5200, d_4^{20} 0.9776. Heating the 2nd fraction with Se 3 hrs. at 300-10° gave some 50% product, b_5 127-35°, yielding a little picrate, m. 87-94°; dehydrogenation for 15 hrs. failed to yield distillable products. Dehydrogenation with 30% Pt-C at 330-50°, gave a mixt. b_5 133-50°, the higher-boiling portion of which yielded a picrate, m. 132-5°. Dehydrogenation with Raney Ni in C_6H_6 3.5 hrs. at 350-60° and 0.5 hr. at 370-80° gave largely a mixt. b_5 80-130°, whose higher-boiling portion formed a picrate, m. 141-2°, which with NaOH gave a small amt. of *4-methylphenanthrene*, m. 41°. Dehydrogenation of I with Se directly failed to give any identifiable products. Refluxing I (0.5 g.) 3 hrs. with MeOH contg. 0.5% MeONa gave the *trans-isomer*, m. 76°; *semicarbazone*, m. 188-9°; *2,4-dinitrophenylhydrazone*, m. 189° (from EtOH). This, hydrogenated over Adams' Pt catalyst, gave *trans-perhydro-4-phenanthrone*, m. 74-5°; *2,4-dinitrophenylhydrazone*, m. 210-12° (from EtOH).

CXXXI. Synthesis of polycyclic compounds. 9. Condensation of [bi-1-cyclohexen-1-yl] with α,β-unsaturated cyclic ketones. I. N. Nazarov and I. V. Torgov. *Ibid.* 228-44.—To 200 ml. hot C_6H_6 and 25 g. Al granules are added at once 12 g. $HgCl_2$ and 100 g. cyclohexanone, the mixt. is cooled intermittently to control the vigorous reaction, then refluxed 2 hrs. with stirring, treated with cooling with 80 ml. H_2O, heated to boiling, filtered hot, and the filter cake extd. twice with hot C_6H_6; cooling the exts. yields 38 g. *[bicyclohexyl]-1,1'-diol*, m. 123-4° (from C_6H_6-ligroine). This (40 g.) stirred 4 hrs. at 100° with 200 ml. 10% H_2SO_4 gave 29 g. (89%) *[bi-1-cyclohexen-1-yl]* (I), b_5 95-6°, n_D^{20} 1.5335. I (6.1 g.) and 3.5 g. 2-cyclohexen-1-one heated in an ampul in CO_2 6 hrs. at 200° (at a lower temp. almost no reaction takes place) yielded 1 g. *Δ^bis-hexadecahydro-1-triphenylenone*, b_5 150-8° (crude), m. 99-100° (from petr. ether); *2,4-dinitrophenylhydrazone*, m. 211-12° (from C_6H_6). Reduction of 3.2 g. of the ketone with 10 g. amalgamated Zn, 40 ml. fuming HCl, and 30 ml. AcOH in 25 ml. MePh gave in 7 hrs. 2.1 g. *Δ^bis-hexadecahydrotriphenylene*, $b_{1.5}$ 140-5°, m. 87-90° (from petr. ether), which, dehydrogenated with Raney Ni in C_6H_6 8 hrs. at 350-80°, gave some 25% *triphenylene*, m. 194-5°; *picrate*, m. 222-3°. Heating 15.0 g. I with 11.2 g. 2-methyl-2-cyclohexen-1-one in an ampul in

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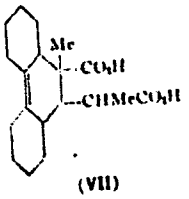
CO_2 27 hrs. at 200° gave 2.3 g. *12b-methyl-Δ^{2a}-hexadecahydro-1-triphenylenone*, $b_{1.5}$ 150-5°, b_2 160-3°, n_D^{20} 1.5440, d_4^{20} 1.064; *2,4-dinitrophenylhydrazone*, m. 162-5° (from petr. ether). Similarly, 10.1 g. I and 21 g. 2,4-dimethyl-2-cyclopenten-1-one (IA) in 6 hrs. at 190-5° gave 6.5 g. mixed *stereoisomers* of *3,7a-dimethyl-Δ^{1}-dodecahydro-4,5:6,7-dibenzindan-1-one*, b_2 150-3°, sepd. into the high-melting, m. 102-3°, and low-melting isomer, m. 72-3° (both from Et_2O-petr. ether), yielding *2,4-dinitrophenylhydrazones*, m. 246-7° (from C_6H_6), and 207-8° (from EtOH), resp. Heating 5.6 g. I with 4.3 g. 3,5-dimethyl-3-cyclopentene-1,2-dione (II) 6 hrs. at 100° in an ampul with 10 ml. C_6H_6 gave 62% *3,7a-dimethyl-Δ^{1}-dodecahydro-4,5:6,7-dibenzindan-1,2-dione* (III), m. 130-1° (from EtOH); the ketone does not give a color with $FeCl_3$ and does not evolve CH_4 with MeMgI. I (1.8 g.) and 1.4 g. II heated in CO_2 in an ampul 4.5 hrs. at 120° formed 0.1 g. III, m. 125-7° (crude), and 0.3 g. colorless keto-enol, *3,8-dimethyl-Δ^{2,3}-decahydro-4,5:6,7-dibenzindan-2-ol-1-one* (IV), m. 149-51°. III can be isomerized to the keto-enol by heating 7 hrs. at 125° in C_6H_6; the pure IV, forms colorless needles, m. 150-1° (from EtOH), and gives a violet color with $FeCl_3$. III forms a *quinoxaline deriv.*, m. 185-6°, on heating with o-$C_6H_4(NH_2)_2$. III can also be isomerized to IV by shaking a few min. with 10% KOH in aq. dioxane, or by letting it stand in dioxane with a little piperidine. IV heated with Ac_2O, cooled, treated with a little pyridine, and let stand overnight yields the *monoacetate*, m. 64-5° (from 75% EtOH). IV does not hydrogenate over Pd, Adams' Pt, Pt-C, but does react in the presence of Raney Ni at 120° (90 atm. H), yielding in 5 hrs. the *1,2-diol*, m. 150-1° (from MeOH), which gives no color with $FeCl_3$. III (6 g.) hydrogenated with Adams' Pt catalyst in dioxane gave 4.3 g. *1-hydroxy-2-oxo*, (V), m. 159-62°, and 1 g. more sol. *2-hydroxy-1-oxo analog* (VI), m. 117-18°, forming *2,4-dinitrophenylhydrazones*, m. 193-4°, m. 187-91°, resp., which do not depress each other's m.p., indicating interconvertibility of V and VI. This is confirmed by conversion of VI into V the low-m. form by heating with HCl-MeOH; MeONa also acts as a similar catalyst. Acetylation of V with Ac_2O-pyridine gave a *monoacetate*, m. 124-4.5°, with KOH-EtOH-H_2O to V, m. 157-61°, while the mother liquor yielded a small amount of the acid (VII), m. 199-201° (from



(VII)

AcOH). Acetylation of VI as above gave the *monoacetate*, m. 108-9° (from MeOH). Oxidation of V by aeration in 20% KOH-EtOH gave VII, m. 200-3°, and a small amt. of its *anhydride*, m. 99-100° (from Et_2O); the anhydride forms readily on warming VII with Ac_2O. Similar air-oxidation of VI gave VII. Reduction of 10 g. *3,4-dihydro-1(2H)-naphthalenone* with 4 g. granular Al and 0.3 g. $HgCl_2$ in C_6H_6 at reflux gave 4.8 g. of the corresponding *pinacol*, m. 178-9° (from C_6H_6), dehydrated by hot AcOH to *3,4,3',4'-tetrahydro-1,1'-binaphthyl* (VIII), m. 138-9°, which, refluxed in xylene with maleic anhydride, gave the *adduct*, m. 234-7°. VIII could not be satisfactorily condensed with IA at 200°, as considerable tar formed and much initial material could be recovered. Condensation with II also failed. Reduction of 6-methoxy-3,4-dihydro-1(2H)-naphthalenone with Al, as above, gave a low yield of the pinacol, m. 140-5° (crude), which heated with AcOH gave a viscous mass from which a very small amt. of a solid, m. 60-70°, was isolated; attempts to isolate the desired diene from this material failed.

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LIMANOV, V.Ye.; ANANCHENKO, S.N.; TORGOV, I.V.

Synthesis of d,l-D-homoestrone,d,l-8-iso-D-homoestrone, and corresponding estradiols. Izv. AN SSSR. Ser. khim. no.10: 1814-1819 O '64. (MIRA 17:12)

1. Institut khimii prirodnykh soyedineniy AN SSSR.

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RZHEZNIKOV, V.M.; ANANCHENKO, S.N.; [illegible], I.V.

Reduction of some D-homosteroids with an aromatic ring A by alkali metals under conditions of Birch's process. Part 1. Khim.prirod.soed. 1:7-15 '65. (MIRA 18:6)

1. Institut khimii prirodnykh soyedineniy AN SSSR i Vsesoyuznyy institut eksperimental'noy endokrinologii Ministerstva zdravookhraneniya SSSR.

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ZAKHARYCHEV, A.V.; ANANCHENKO, S.N.; TORGOV, I.V.

Cyclization of 3-methoxy-1,3,5(10),9(11)-8,14-secoestratetraenee-14,17-dione to D-homoestrone derivatives. Izv. AN SSSR. Ser. khim. no.8:1413-1416 '65. (MIRA 18:9)

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ZAKHARYCHEV, A.V.; LIMANOV, V.Ye.; ANANCHENKO, S.N.; PLATONOVA, A.V.; TORGOV, I.V.

1-Vinyl-1,2,3,4-tetralin-1,6-diol and its condensation with 2-methyl-1,3-cyclohexanedione and 2-methyl-1,3-cyclopentanedione into estrone derivatives. Izv. AN SSSR.Ser.khim. no.10:1809-1814 '65. (MIRA 18:10)

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LAGIIGE, D.R.; ANANCHENKO, S.N.; TORGOV, I.V.

Preparation of 2-alkyl-1,3-cyclopentanediones. Izv. AN SSSR.Ser. khim. no.10:1899-1901 '65. (MIRA 18:10)

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USSR/Chemistry - Acetylene Derivatives Feb 52

"Acetylene Derivatives. 131. Synthesis of Polycyclic Compounds. IX. Condensation of Di-Δ^1-Cyclohexenyl With α, β-Unsaturated Cyclic Ketones," I. N. Nazarov, I. V. Torgov, Inst of Org Chem, Acad Sci USSR

"Zhur Obshch Khim" Vol XXII, No 2, pp 228-244

In order to study possibility of applying method of diene condensation with α, β-unsatd cyclic ketones for synthesis of polycyclic systems to bi- and tetracyclic dienes with both double bonds in rings, conducted a series of reactions starting from

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condensation of di-Δ^1-cyclohexenyl with 5- and 6-membered cyclic ketones. Describes the tetracyclic ketones and ketoenols obtained.

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TORGOV, I. V.

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TORGOV, I.V.

Torgov, I.V. --"Synthesis of Polycyclic Compounds, Related to Steroids, By the Method of Diene Condensation." DrChem Sci, Inst of Organic Chemistry Acad Sci USSR, MOSCOW 1953. (REFERATIVNYY ZHURNAL --KHIMIYA, No 1, Jan 54.)

Source: SUM 168, 22 July 1954

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TORGOV, I. V.

7. Synthesis of polycyclic compounds related to steroids

I. I. Zorevskaya, G. P. Verkhovetova, S. N. Ananchenko

Chem. Sci. 1953, 60-80 (Engl. translation). —See C.A. 48, 3224h.

H. L. H.

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TORGOV, I. V.

1/8

Synthesis of polycyclic compounds related to steroids. XVII. Preparation of α,β-unsaturated cyclic ketones (2-cyclenones). I. N. Nazarov, L. D. Bergelson, I. V. Torgov, and S. N. Ananchenko (Inst. Org. Chem., Acad. Sci., U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 889–900; cf. *C.A.* 39, 1620*; 46, 2088; 48, 3324*h*; Kötz, *et al.*, *C.A.* 7, 3748. A general method of prepn. of conjugated unsatd. cyclic ketones was developed on the basis of halogenation (bromination) of cyclic ketones in the presence of $CaCO_3$ or $MgCO_3$ and dehydrohalogenation with $PhNEt_2$. It was shown that bromination of 2-methylcyclohexanone and 2-methylcyclopentanone leads to introduction of Br at the tertiary C atom, rather than a secondary C atom. *o*-MeC_6H_4OH (500 g.) hydrogenated in 20 ml. EtOH with 15 g. Raney Ni at 120 atm. and 120° initially, then at 160–70° gave 92% *2-methylcyclohexanol*, b_{22} 78–80°, n_D^{20} 1.4610. This (350 g.) in 250 ml. Et_2O treated with cooling (−3°) over 6 hrs. with 350 g. $Na_2Cr_2O_7$ in 455 g. H_2SO_4 and 1.5 l. H_2O, kept overnight in the cold and stirred 3 hrs. longer, gave after extn. with Et_2O 87% *2-methylcyclohexanone* (I), b_{11} 51–2°, n_D^{20} 1.4482. This (224 g.) and 220 ml. H_2O treated with 112 g. powd. $CaCO_3$ and stirred with illumination with a 1000-watt lamp 0.5 hr. then treated at 30° dropwise with 320 g. Br in 260 ml. $CHCl_3$; the org. layer was then combined with an Et_2O ext. of the aqueous layer and the soln. was washed with $NaHCO_3$ and $Na_2S_2O_3$, treated with 320 g. $PhNEt_2$, dried with Na_2SO_4 and slowly concd. in slight vacuum over 5–6 hrs. to remove the solvents after which the residue was kept 3 hrs. on a steam bath with increasing vacuum [illegible] distillate of 173 g., which on redistn. gave 58% [illegible] [illegible], b_{12} 56°, n_D^{20} 1.4865, d_{20} 0.9667; [illegible] [illegible] Ozonolysis of the ketone gave AcOH [illegible] no HCO_2H could be detected. I (56 g.) [illegible] was treated over 2 hrs. in small portions [illegible] 125 g. dioxane-Br complex at 22–3°; the resulting soln. was washed with NaOH and $Na_2S_2O_3$, and the org. soln. was treated as above with $PhNEt_2$ yielding 47% unsatd. ketone identical with the above; addn. of $CaCO_3$ during the bromination failed to improve the yield. Passage of dry air into 250 ml. liquid NH_3, 1.5 g. Na, and 0.15 g. $Fe(NO_3)_3$ until the soln. became colorless, followed by addn. of 10 g. Na and stirring until the blue color faded out, addn. of 200 ml. Et_2O, removal of the cooling bath, and evapn. of NH_3 spontaneously at room temp. gave a residue of $NaNH_2$; when the temp. of the mixt. approached room temp. it was treated with 42 g. cyclopentanone over 5 min. after preliminary cooling to −70°, after which 85 g. MeI was added (despite the cooling, temp. rose to 15°); after stirring

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15 min. the mass was treated with NH_4Cl (40 g.) followed by 250 ml. H_2O; distn. of the org. layer gave a mixt. of methylation products, which could not be satisfactorily resolved into pure components by distn. To 245 ml. HNO_3 (d. 1.4) heated to 108° was added 0.25 g. NH_4 vanadate and a few drops 2-methylcyclohexanol; the mixt. was cooled to 60° and 50 g. 2-methylcyclohexanol was then added over 1 hr. at 60–70°; after 1 hr. on a steam bath the mixt. was chilled overnight yielding 9 g. adipic acid; the filtrate on evapn. gave 3 g. adipic acid and 50 g. *α-methyladipic acid*, m. 60–7° (from Et_2O). The latter (42 g.) and 2.1 g. $Ba(OH)_2$ heated to 285–95° 2 hrs. gave about 12% *o-methylcyclopentanone* (II), b. 135–6°, n^{20}_D 1.4365; *semicarbazone*, m. 170–1°. Di-Et adipate, b_{15} 127–8°, n^{20}_D 1.4280, was prepd. in 97% yield by azeotropic esterification of the acid with EtOH in C_6H_6 with concd. H_2SO_4 catalyst. The ester (303 g.), 15 ml. abs. EtOH, 1260 ml. MePh, and 49.5 g. powd. Na were stirred on a steam bath 4 hrs. yielding a ppt. of the Na deriv.; on the following day the mass was treated with 7% HCl yielding 89% *2-carbethoxycyclopentanone*, b_{20} 110–13°, n^{20}_D 1.4525. This (300 g.) was added in 0.5 hr. at −13° to 44.2 g. Na in 1 l. abs. EtOH, stirred 1 hr., treated at once with 275 g. MeI and allowed to rise to room temp. over 5–6 hrs., then left overnight, concd. *in vacuo*, dild. with H_2O and extd. with Et_2O, yielding 286 g. crude product, b_{16} 106–18°; for removal of the starting material this product was treated in Et_2O at 0° with cold soln. of 32 g. KOH in 800 ml. H_2O and stirred 3 min., then extd. with Et_2O, yielding 67% pure *2-methyl-2-carbethoxycyclopentanone*, b_{16} 116–19°, n^{20}_D 1.4465 (this gave no color with $FeCl_3$). This (255 g.) in 1020 ml. H_2O and 510 ml. concd. H_2SO_4 was heated 9 hrs. on a steam bath (the reflux condenser was provided with a trap for retention of volatile product); after extn. with Et_2O there was obtained 69% II, b. 136–7°, n^{20}_D 1.4360; *semicarbazone*, m. 170–1°. Alkaline hydrolysis gave but 50–4% yields. II (93 g.), 50 ml. $CHCl_3$, 52 g. $MgCO_3$, and 150 ml. H_2O were treated over 2 hrs. at 22° with 152 g. Br (addn. of 1 ml. HCl at the beginning is advisable); the org. layer combined with Et_2O ext. of the aqueous layer was concd. and the residue treated with 160 g. $PhNEt_2$, dried and heated as described above, yielding 51% *1-methyl-1-cyclopenten-5-one*, b_{15} 52–3°, n^{20}_D 1.4770; *semicarbazone*, decomp. 218°; oxime, m. 123°. Use of $CaCO_3$ gave but 40% yield, while replacement of $CHCl_3$ by CCl_4 gave even lower yield. Ozonolysis of the ketone gave CO_2 and succinic acid. To 26 g. cyclohexanol, 70 g. $CaCO_3$, and 80 g. cyclohexanone was added at 35° over 4 hrs. 182 g. Br; after stirring 0.5 hr. longer the layers were sepd. and the aq. layer was extd. with Et_2O; combined org. layers after concn. were treated with $PhNEt_2$ (it is best to use small portions of 50 g. crude bromo deriv. and 50 g. amine) and the mixt. rapidly heated to 150–5° at 100 mm. yielding 35% *1-cyclohexen-6-one*, b_{15} 63.5°, n^{20}_D 1.4872 *semicarbazone*, m. 161°. Similarly, 45 g. cyclopentanone, 5 g. cyclopentanol, 100 ml. H_2O and 30 g. $CaCO_3$ treated with 80 g. Br at 35° 3 hrs., gave 28% *1-cyclopenten-5-one*, b_{15} 45°, n^{20}_D 1.4720; *semicarbazone*, m. 214–15°; this ketone on ozonolysis gave suc-

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cinic acid, while ozonolysis of the cyclohexenone gave glutaric acid. To 180 ml. H_2O was added 11 g. H_2SO_4, followed by 15 g. $HgSO_4$, followed by 800 g. vinylisopropenylacetylene and 1800 g. MeOH; the mixt. was stirred at 60° 6 hrs. with addn. every hr. of 1 g. $HgSO_4$; on the following day heating was resumed for 6 hrs. with addn. of 7 g. and 1 g. $HgSO_4$ in 2 portions; after concn. at 35° the residue was neutralized with 10 g. Na in 200 ml. MeOH, dild. with Et_2O, treated with 50 g. Zn dust and shaken occasionally for 4-5 hrs. After filtration the soln. was mixed with 5-6 ml. PhMe, concd. in vacuo, and distd. in slight vacuum yielding 600-650 g. mixed methoxy ketones, b_{10} 70-100°. This mixt. (540 g.) treated with 580 ml. H_3PO_4 (d. 1.77) slowly (temp. rise to 50-55°) with occasional cooling below 70°, heated 2 hrs. at 70°, dild. with H_2O and treated with 400 g. Na_2CO_3 with cooling, gave after extn. with Et_2O 49-53% *1,2-dimeth-4-1 cyclopenten-5-one*, b_{14} 61-2°, n_D^{25} 1.4675-1.4685. If the ketone mixt. (1050 g.) is cyclized with 2160 g. 18% HCl 4 hrs. at 80-5°, a 55-9% yield of the cyclic ketone is obtained; pure product b_9 62-2°, n_D^{20} 1.4670. **XVIII. Condensation** of 1-vinyl-9-methyl-6-octahydronaphthalenone and 1-vinyl-9-methyl-7-octahydronaphthalenone with 1,3-dimeth-4-1 cyclopenten-5-one. I. N. Nazarov and I. V. Torgov *Ibid.* 931-19.—Total synthesis of steroidal ketones of the series was accomplished in 60% yield. Regardless of the existence or position of substituents in ring A, all diketones formed by diene condensation have so-called inverted structure, i.e. ring D contains the angular Me group in position 14, and the carbonyl group in position 15. The difference between isomers is detd. by spatial distribution of A-B and C-D rings relative to each other; in other substances the difference lies in position of H at position 8. The double bond in tetracyclic steroidal diketones migrates readily under influence of HCl from 9-11 to 8-9 position. The keto group in ring D is quite resistant to Clemmensen reduction. 1-Vinyl-9-methyl-1,6-octahydronaphthalenone (12.3 g.) and 36 g. 1,3-dimeth-4-1-cyclopenten-5-one [illegible] tube under CO_2 13 hrs. at 170° gave 55% [illegible] 15 [illegible] 17 isomers *d-3-carbinterone 3,17 trione* [illegible] 27% [illegible] Crystallizat. from petr. ether [illegible] isomer IIA, m. 166-7°, and 0.15 g. [illegible] IIA. IIB, m. 150-6.5°. IIA has been des[illegible] (*C.A.* 45, 7583c). The mixture of both isomers [illegible] 40°. Fractional crystallization of a middle [illegible] mg. 8-iso-isomer of IIA (IIC), m. 203-5° (from MeOH-C_6H_6). Refluxing IIA in AcOH with HCl in the presence of MePh 10 hrs. gave the Δ^8 isomer of IIA (IID), m. 114-15°. treatment in AcOH with HCl in the cold led to no change in IIA, nor did mere heating in xylene. Similarly treated IIB gave the Δ^8 isomer of IIB (IIE), m. [illegible] (from EtOH). [illegible] IIF, m. 112-13° (from EtOH). IIC similarly isomerized to IID, although the reaction was much slower than with IIA. Clemmensen reduction of 2 g. IIA in AcOH and concd. HCl over Zn-Hg in MePh gave 52% *10,14,17-trimethyl-8-cardosterone-15-one* (IV), m. 103-4° (from petr. ether); *2,4-dinitrophenylhydrazone*, m. 212-3° (from EtOH). The same sub-

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stance was obtained after Clemmensen reduction of IIC. The product (1.7 g.) in 5 ml. dioxane was treated with 1.2 ml. $N_2H_4.H_2O$ and 5 ml. diethylene glycol and heated on a steam bath briefly, then treated with 1.4 g. Na in 36 ml. diethylene glycol and heated in N_2 15 hrs. to 205–10°; after diln. with H_2O the mass was extd. with Et_2O, the ext. was shaken with 10% HCl and distd. yielding 1.3 g. *10,14,17-trimethyl-9-cardosterene*, b_4 130–5°, n^{20}_D 1.5200. This (1.1 g.) heated with 10% Pd-C in dry C_6H_6 under 30 atm. N 0 hrs. at 350° then chromatographed on Al_2O_3 from petr. ether gave a range of fractions, after elution with petr. ethe. and C_6H_6, yielding 10 mg. Diels hydrocarbon, *3'-methyl-1,2-cyclopentanophenanthrene* m. 121.5–2.0°, whose *trinitrobenzoate*, m. 148–9°. The mother liquor gave some 40 mg. more of the same substance. Clemmensen red. ion of IIB gave the 13-iso-14α,17α-isomer of IV (V), m. 129–2° (from hexane). To 0.8 g. IV in 40 ml. MeOH was added Simultaneously 2.1 g. iodine in 25 ml. MeOH and 4 g. KOH in 8 ml. H_2O and 15 ml. MeOH, keeping iodine in excess, after stirring 2 hrs., MeOH was removed in vacuo, the residue treated with 10 ml. H_2O, acidified to Congo red, extd. with Et_2O, the ext. washed with $Na_2S_2O_3$, concd., treated with 5 ml. MeOH and 4 ml. 30% NaOH, heated 4 hrs. on a steam bath, dild. with H_2O, extd. with Et_2O and acidified, gave 41% VI, m. 199–202° (from AcOH), which heated with 10% Pd-C in C_6H_6 11 hrs. at 150° under N gave 1-methyl-2-ethylphenanthrene, m. 95–6°, the latter oxidized with CrO_3 in AcOH to 1-methyl-2-ethylphenanthrenequinone m. 155–7°, whose reaction with o-$C_6H_4(NH_2)_2$ gave the quinoxaline, m. 108–9° (from MeOH). Similar oxidation of V with iodine in alkaline medium gave 1-methyl-2-ethylphenanthrene, which gave the quinone and quinoxaline identical with the above specimens. Hydrogenation of IIA over Adams Pt catalyst in AcOH does not proceed; IIB, IIC and IID gave only uncrystallizable mixts. which could not be resolved chromatographically. However, hydrogenation of 1 g. IIA in AcOH shaken in H with 0.5 g. Pt-$BaSO_4$ 1 hr. was made to proceed by addn. of a little H_2PtCl_6 and after completion of H uptake there was isolated 110 mg. *10,14,17-trimethyl-3-cardosterene-3-ol-15-one*, as an equimolar complex with *Hg acetate*, m. 147–0°. Heated with aq. alc. KOH (10%) 5 min. the complex yielded the pure *ketone*, m. 131–2°. The latter oxidized with CrO_3 in AcOH to IID, m. 111–13°. Heating 12 g. 1-vinyl-9-methyl-1,2,3,4-tetrahydronaphthalen-7-one with 66 g. I in N in sealed tube 10.5 hrs. at 170° gave after the usual treatment 10.1 g. crude [illegible] of *10,14,17-trimethyl-9(11)-cardosterene-2,15-dione* (VII), m. 130–50° or higher. Fractional crystn. from petr. ether–C_6H_6 gave in all: 4.86 g. VIIA, m. 187–9°, 2.57 g. 13-iso-14α,17α-isomer (VII3) of VIIA, m. 177–8°, 0.25 g. 8-iso-isomer (VIIC) of VIIA, m. 199–200°, and 0.16 g. unstated isomer (VIID), m. 163–4°. Heating VIIA in AcOH at [illegible] with concd. HCl in the presence of $MeOH$ 1 hr. gave same

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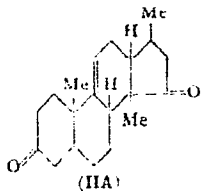
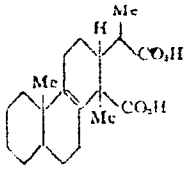
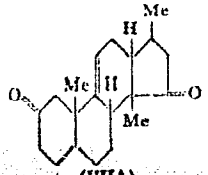
80% unchanged material and a 15% yield Δ^8 isomer (VIIE) of VIIA, m. 139–41°; mere heating of VIIA in xylene gave no change. VIIB similarly isomerized (10 hrs. heating) to about 10% yield Δ^8-isomer (VIIF) of VIIB, m. 111–12°. Clemmensen reduction of VIIA gave 14% IV, also obtained similarly from VIIC. Clemmensen reduction of VIIB gave 10% V; 2,4-dinitrophenylhydrazone, m. 215–17°. Clemmensen reduction of VIID gave noncrystg. oil, which after chromatography on Al_2O_3 gave a very low yield of *material*, m. 78–80°, above *2,4-dinitrophenylhydrazone* m. 198–201°. This [illegible] VIIA, VIIB [illegible] VIIC are not hydrogenated over Adams Pt catalyst in EtOH or AcOH. XIX. Condensation of 1-



(IIA)



(VI)



(VIIA)

vinyl-9-methyl-1-octahydronaphthalen-6-one and 1-vinyl-9-methyl-1-octahydronaphthalen-7-one with 1-cyclohexenones and citraconic anhydride. I. N. Nazarov, I. I. Zaretskaya, G. P. Verkholetova, and I. V. Torgov. *Ibid.* 920–3.—It was shown that in diene condensation for synthesis of D-homosteroidal diketones of cis-cis series the double bond in position 9–11 can shift to 8–9 position [illegible] Clemmensen reduction of the steroidal diketones [illegible] reduce only the carbonyl in ring A, yielding a 15-monoketone. Heating 12 g. 1-vinyl-9-methyl-1-octahydronaphthalen-6-one and 120 g. 1-methyl-1-cyclohexen-3-one in sealed tube in CO_2 10 hrs. at 170–5° gave after concn. *in vacuo* and treatment with petr. ether (the unreacted material was again reused) the following isomers of *10,14-dimethylcardochrysanene-3,15-dione* (I): IA, 1.2 g., m. 157–8°; 13-iso-14α-isomer (IB) of IA, 0.35 g., m. 159–60°; 8-iso isomer (IC) of IA, 0.17 g., m. 166–7°; and the Δ^8-isomer (ID) of IA, 10 mg., m. 149°. Heating any of these alone 1 hr. at 200° resulted in tar formation and only ID gave crystalline material which was the unchanged starting material. Refluxing IA in AcOH with concd. HCl in the presence of MeOH 9 hrs. gave ID, m. 146–7°, in 80% yield. C similarly treated gave 15% ID, while IB gave 20% Δ^8-isomer (IE) of IB, m. 128–9°. ID failed to isomerize. Clemmensen reduction of IA gave 63% *10,14-dimethyl-8-cardochrysanen-15-one* (II), m. 136–7° (from petr. ether). The same II was obtained in Clemmensen reduction of IC and ID. Clem-

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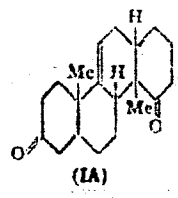
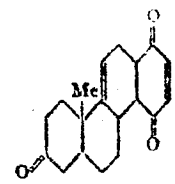
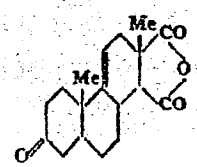
mensen reduction of IB however gave a 30% yield of the 13-iso-14α-isomer (III) of II, m. 75–80°, contaminated with a hydrocarbon which could not be removed. Treatment of 0.23 g. II with MeMgI (from 1.2 g. MeI) in Et_2O-C_6H_6 gave no reaction, and repetition at 100° gave some unchanged II and much unerystallizable matter; LiMe gave the same result. Heating 2 g. 1-vinyl-9-methyl-1-octahydronaphthalen-7-one with 5 g. 1-methyl-1-cyclohexen-6-one in CO_2 in sealed tube 13 hrs. at 170–5° gave after treatment with MeOH 3 *isomers* of *10,14α-dimethyl-13-isocardochrysan-9-ene-2,15-diene* (III) in a 15:12:1 ratio: IIIA, 130 mg., m. 143–4°; IIIB, 100 mg., m. 203–5°; and IIIC, 8 mg., m. 182–3°. Heating 5.5 g. 1-vinyl-9-methyl-1-octahydronaphthalen-6-one and 40 g. 1-cyclohexenone in CO_2 in sealed tube at 150° 10 hrs. gave after treatment with petr. ether 2 isomers of *10-methyl-9-cardochrysanene-3,15-diene* (IV) in a 6:1 ratio: IVA, m. 150–1°, and IVB, m. 181–3° (from petr. ether-C_6H_6). Similar condensation with benzoquinone 4.5 hrs. at 60° gave 55% pure isomer of *10-methyl-9,16-cardochrysadiene-3,15,17a-trione* (V), m. 185–6° (from petr. ether). Similar condensation with *citraconic anhydride* 6 hrs. at 100° (a trace of methylene blue was added to the mixture) gave some 10% either VIA or VIB, m. 175–6°, and a mixt., m. 150–60°, which was not resolved. Refluxing 5.2 g. 1-vinyl-9-methyl-1-octahydronaphthalen-6-one in 50 ml. *M* (iso-PrO_3)Al soln. in iso-PrOH with slow distn. 3 hrs. gave 0.1 g. sub[illegible] 208–9°, $C_{11}H_{12}O_2$, and a more sol. substance of [illegible] composition, m. 160–1°. The structures of these are unknown. The filtrate gave 50% *1-vinyl-9-methyl-1-octahydronaphthalenol*, b. 120–1.5°, n_D^{20} 1.5293. This (VI) heated with benzoquinone in dioxane in sealed tube under [illegible] at 60° gave 32% *10-methyl-9,16-cardochrysadiene-3,15-diene*, m. 130–1°. Condensation of VI with 1,3-dimethyl-1-cyclopentene-5-one gave only an unerying [illegible] which could not be resolved chromatographically. XX. Con



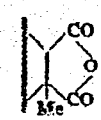
(IA)



(V)



(VIA)



(VIB)

cont.

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"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001756320009-8

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densation of 1-vinyl-9-methyl-1-octahydronaphthalen-6-one and 1-vinyl-9-methyl-1-octahydronaphthalen-7-one with 1-cyclopentenone, 1-methyl-1-cyclopenten-5-one and 1,3-dimethyl-1-cyclopentene-4,5-dione. I. N. Nazarov, G. P. Verkholetova, I. V. Torgov, I. I. Zaretskaya, and S. N. Ananchenko. *Ibid.* 929–40.—In diene condensations reported below the formation of steroidal diketones results in isolation of predominantly the substances with "inverted" ring disposition. Heating 6.9 g. 1-vinyl-9-methyl-1-octahydronaphthalen-6-one and 13.8 g. 1-methyl-1-cyclopenten-5-one in CO_2 in sealed tube 6 hrs. at 150° gave after concn. and treatment with petr. ether 6.9 g. solid mixt. of isomers of *10,14-dimethyl-9-cardosterene-3,15-dione* (I): IA, m. 131–3°, the 13-iso-14α-isomer (IB) of IA, m. 155–5°; and an isomer of unstated structure (IC), m. 127–8°. Refluxing IA with AcOH, concd. HCl and MePh 9 hrs. gave *10,14-dimethyl-8-cardosterene-3,15-dione* (ID), m. 100–103.5° (from petr. ether) in 75% yield. IB similarly gave 24% yield of the 13-iso-14α-isomer (IE), of ID m. 91–3° (from EtOH and petr. ether). Clemmensen reduction of IA gave 35% *10,14-dimethyl-8-cardosteren-15-one* (II), m. 53–4°; *2,4-dinitrophenylhydrazone*, m. 193–4°. Similar reduction of IB gave 35% 13-iso-14α-isomer (III), of II m. 94–5°; *2,4-dinitrophenylhydrazone*, m. 191–3°. Dehydrogenation of II with Pd-C in C_6H_6 at 350° under N 6 hrs. gave some 10% 1-methyl-2-ethylphenanthrene, m. 100–2°, contaminated with high m. wt. substances. Similar treatment of III gave an oil, which after chromatographing on Al_2O_3 gave mainly liquid materials, and a low yield of 1-methyl-2-ethylphenanthrene. Heating 4.9 g. 1-vinyl-9-methyl-1-octahydronaphthalen-7-one with 10.9 g. 1-methyl-1-cyclopenten-5-one as above 6 hrs. at 150° in N gave after concn. and treatment with EtOH 38% of a mixt. of 3 isomers of *10,14-dimethylcardosterene-2,15-dione*, (IV); these were sepd. by crystn. from EtOH and yielded 1.45 g. 13-iso-14α-isomer (IVA) of IV, m. 184–6°, 0.42 g. normal isomer (IVB) of IV, m. 154–4.5°, and 0.06 g. isomer of unstated structure (IVC), m. 192–3°. IVA heated [illegible] hrs. with AcOH, concd. HCl, and MePh gave a low yield [illegible] *10,14-dimethyl-13-isocardoster-8-ene-2,15-dione* [illegible] 124–5°. Clemmensen reduction of IVA gave 6% [illegible] III. Clemmensen reduction of IVB gave 6% II [illegible] 2.5 g. 1-vinyl-9-methyl-1-6-octahydronaphthalenone [illegible] g. 1-cyclopentenone in CO_2 11 hrs. at 130° in sealed tube similarly gave 11% mixed isomers of *10-methyl-9-cardosterene-3,15-dione* (V), sepd. into 0.1 g. VA, m. [illegible] and 20

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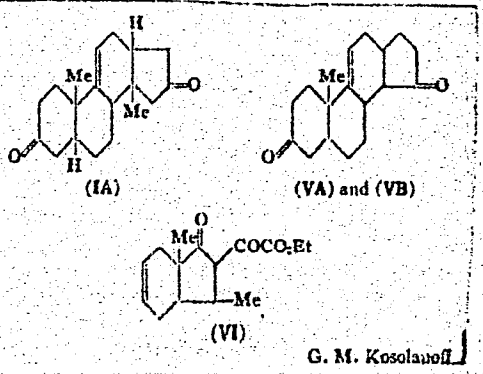
mg. more sol. VB, m. 156-7°; condensation run at 160° gave much tar. Heating 1.1 g. 1-vinyl-9-methyl-1-octahydronaphthalen-6-one and 0.6 g. 1,3-dimethyl-1-cyclopentene-4,5-dione in dry C_6H_6 under CO_2 in sealed tube 6 hrs. at 100° similarly gave 140 g. *10,14,17-trimethyl-9-cardosterene-3,15,16-trione*, m. 108-10°, resolidifying at 112-15° and again m. 167-8°. The mother liquor was chromatographed on Al_2O_3 from petr. ether and eluted with C_6H_6, yielding 0.1 g. enol of the trione, *10,14,17-trimethyl-9,16-cardosteradien-16-ol-3,15-dione*, m. 107-8°, which gives a violet color with $FeCl_3$. The same enol is formed from the trione on treatment with pyridine in dioxane soln. If the original diene condensation is run at 120° it is no longer possible to isolate the trione, since only the enol can be obtained. To 11 g. powd. EtONa was added 10.5 g. di-Et oxalate and 80 ml. C_6H_6, under N_2, heated 10 min. on a steam bath, cooled and treated slowly with 14.6 g. 3,8-dimethyl-Δ^5-hydrindanone (b_7 90-2°, n^{20}_D 1.4875) in C_6H_6; after 5 hrs. at 20° the mixt. was dild. with H_2O, the org. layer was sepd., neutralized by shaking with dil. HCl and distd. yielding 11.2 g. VI, b_1 142-3°, n^{20}_D 1.5070, which failed to lose CO even at 180-200° in the presence of glass and Fe powder.



(IA) (VA) and (VB)

(VI)

G. M. Kosolapoff

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TORGOV, I. V.

USSR/Chemistry - Synthesis

Card 1/1 : Pub. 40 - 17/22

Authors : Nazarov, I. N., and Torgov, I. V.

Title : Synthesis of steroid compounds and their substances. Part 18.-

Periodical : Izv. AN SSSR. Otd. khim. nauk 5, 901-919, Sep-Oct 1953

Abstract : A complete synthesis of steroid diketones of the cis-cis series was accomplished by the condensation of 1-vinyl-9-methyl-Δ^1-6-octalone and 1-vinyl-9-methyl-Δ^1-7-octalone with 1,3-dimethyl-Δ^1-cyclopentene-5-one. A mixture of three or four isomeric steroid diketones in which the A-B and C-D rings are connected in cis-position, was obtained in both instances. All steroid diketones, synthesized by the diene-condensation method, were found to have a so-called inverted structure regardless of the presence and position of substituents in the A-ring. Twenty-one references: 4-USSR; 9-USA; 2-Swiss and 6-German (1927-1953). Tables.

Institution : Academy of Sciences USSR, Institute of Organic Chemistry

Submitted : October 7, 1952

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"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001756320009-8

TORGOV, I. V.

USSR/Chemistry - Synthesis

Card 1/1 : Pub. 40 - 18/22

Authors : Nazarov, I. N.; Zaretskaya, I. I.; Verkholetova, G. P.; and Torgov, I. V.

Title : Synthesis of steroid compounds and their substances. Part 19.-

Periodical : Izv. AN SSSR. Otd. khim. nauk 5, 920-928, Sep-Oct 1953

Abstract : The realization of a complete synthesis of D-homosteroid diketones of the cis-cis series (with keto-group in position 15), through the condensation of 1-vinyl-9-methyl-Δ^1-6-octalone with 1-methyl-Δ^1-cyclohexene-6-one, is described. The four isomeric tetracyclic ketones, formed as result of condensation and their physico-chemical properties, are also described. The displacement of the double bond from positions 9 to 11 and 8 to 9 was observed during the process of diene condensation. By reducing the steroid ketones, according to the Clemmens method, only the keto-group in the A-ring is eliminated and diketone converts into 15-monoketone. Eight references: 4-USSR; 2-USA and 2-German (1929-1953).

Institution : Academy of Sciences, USSR, Institute of Organic Chemistry

Submitted : October 7, 1952

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TORGOV, I. V.

USSR/Chemistry - Synthesis

Card 1/1 : Pub. 40 - 19/22

Authors : Nazarov, I. N.; Verkholetova, G. P.; Torgov, I. V.; Zaretskaya, I. I.; and Ananchenko, S. N.

Title : Synthesis of steroid compounds and their substances. Part 20. -

Periodical : Izv. AN SSSR. Otd. khim. nauk 5, 929-940, Sep-Oct 1953

Abstract : The synthesis of steroid diketones of the cis-cis series is described. The formation of three isomeric diketones, two of which have an inverted structure and are distinguished by a spatial position of substitutes, is explained. The products derived from the condensation of 1-vinyl-9-methyl-Δ^1-6-octalone with Δ^1-cyclopentenone and with 1,3-dimethyl-Δ^1-cyclopentene-4,5-dione and their characteristics, are described. Nine references: 7-USSR and 2-USA (1935-1953).

Institution : Academy of Sciences USSR, Institute of Organic Chemistry

Submitted : October 7, 1952

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TORGOV, L.V.

Synthesis of polycyclic compounds related to steroids. [illegible]

XXI. Condensation of [illegible]

[illegible]

hrs at 245–50° gave 543 g. [illegible] and [illegible] g. (45% conversion) *cis-9-methyl-Δ¹-octahydro-1-oxonaphthalene* (I), b_1 82–4°, n_D^{20} 1.5050 [*semicarbazone*, decomp. [illegible] (cf. Nudenberg and Butz, *C.A.* 37, 5399[4])], hydrogenated over Pt in EtOH to *cis-9-methyldecahydro-1-oxonaphthalene* (II), b_1 84–6°, n_D^{20} 1.4950 [*2,4-dinitrophenylhydrazone* [illegible]

[illegible]

[illegible] gave 39% mixed anhydrides, [illegible] was isolated the more abundant form, *2,4,5-methyl-1,2-decahydro-1,2-phenanthrenedicarboxylic anhydride*, m. 16g 2° (from hexane); the other isomer, presumably the *1,4-dihydro analog*, was not [illegible]

[illegible]

63° apparently a [illegible] this acid mixt. with Raney [illegible] in C_2H_5 [illegible]

[illegible]

[illegible] over PtO_2 to the corresponding *dihydro analogs* [illegible] (III) and 12 × 3° (IV) resp. in which [illegible]

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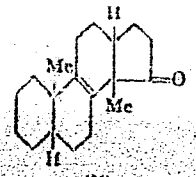
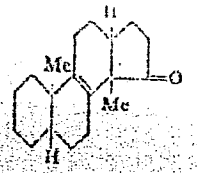
remained. Further hydrogenation in AcOH over PtO_2 of the former, m. 114–15°, gave $C_{14}H_{22}O$, the sat. analog, which was the 1st instance of hydrogenation of the [illegible] link in this group. Reducing III with AcOH [illegible] Pt for hrs. gave an isomer, m. 72–[illegible], which [illegible] as V, which had been [illegible] not be hydrogenated [illegible] also gave the isomer VI [illegible] under scribed earlier (cf. *loc. cit.*). Shaking IV [illegible] isomer



(V)



(VI)

H in AcOH gave 50% yield VI. Heating 6 g. vinylmethylhexahydronaphthalene (above) with 24 g. 1,3-dimethylcyclopenten-5-one under CO_2 10 hrs. [illegible] gave a mixt. of isomers which [illegible] (m. 111–[illegible]) and 1.6 g. low [illegible] of [illegible] and 2.9 g. [illegible] [illegible] with toluenesulfonic acid, [illegible] 49, TsOH); the latter was not isomerized [illegible] with AcOH-HCl, nor could this ketone be hydrogenated further. Similar hydrogenation of VII gave the corresponding *dihydro analog*, m. 127–8°, which does not isomerize with AcOH nor hydrogenate further. However, treatment of VII with iodine in aq. MeOH in the presence of KOH gave a *diketo deriv.*, m. 128–9°, while Kishner reduction of VII with $N_2H_4.H_2O$ in $O(CH_2CH_2OH)_2$ gave 81% hydrocarbon (VIII), b_5 145–7°, n_D^{20} 1.5230, dehydrogenated under N in C_6H_6 in the presence of Pd-C in 6 hrs. at 350°/30 atm. to *Diels hydrocarbon* (IX), m. 119–21° ($C_{14}H_8(NO_2)_3$ adduct, m. 148–7°), which was isolated after chromatographic purification on Al_2O_3. Thus VII has the "inverted" configuration of the cyclopentane ring relative to the main nucleus. Heating the vinylmethylhexahydronaphthalene [illegible]

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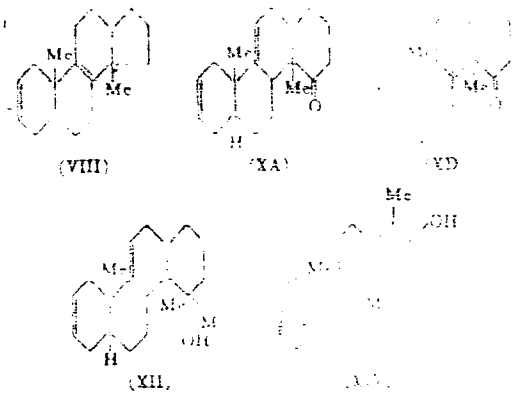
[illegible]

gave XD, m. 137-8°, described earlier ([illegible] 49, [illegible]); the same isomerization took place in AcOH in contact with PtO_2 and H. XB heated with HCl-AcOH as above gave an *isomer*, m. 121-1.5°, whose structure was not detd.; XC failed to isomerize under these conditions. Treatment of XI with MeMgBr, finally in boiling C_6H_6, gave the tetracyclic alc. (XII), m. [illegible] (from MeOH), dehydrated over $KHSO_4$ in xylene to a crude product, which after chromatographic treatment gave a low yield of *chrysene*, m. 243-5°; normally the product expected in this case would have been 4-methylchrysene. Heating the vinylmethylhexahydronaphthalene (2.1 g.) with 13 g. 2-methyl-2-cyclohexenone 10 hrs. at 170° under CO_2 gave 1.7 g. mixed *isomeric* ketones, $C_{17}H_{22}O$ (XIII), $b_{0.05}$ 137-8°, n_D^{20} 1.5[illegible], *semicarbazone*, m. 237-7.5°. XIII could not be crystal. or sepd. into individual stereoisomers. Similar reaction with *p*-benzoquinone gave after 3 hrs. at [illegible] *10-methyl-2,9,16-cardochrysatriene-15,17a-dione*, [illegible] m. 108-18° (from MeOH), with evidence of change of the substance on melting; the compd. failed to yield a semicarbazone or dinitrophenylhydrazone ([illegible] and Fatz, *C.A.* 41, 4789*d*). Similar condensation with 1,3-dimethyl-1-cyclopentene-4,5-dione in dioxane 6 hrs. at 100° under CO_2 gave 30% *10,1*[illegible]*,17-trimethyl-2,9-cardosteradiene-1*[illegible]*,16-dione*, m. 100-10° (from EtOH); the wide m. range is caused by ready isomerization at elevated temp. [illegible]



(VIII) (XA) (XD) (XII) (XI)

Semiester of *cis*- and *trans*-1-methylcyclohexane- and -4-cyclohexene-1,2-dicarboxylic acids and their transformations. I. N. Nazarov and V. F. Kucherov, [illegible] 1954 [illegible]; cf. *C.A.* 48, [illegible]

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I. N. NAZAROV

4355°; 38, 92°; 46, 1018g.—Refluxing 25 g. *cis-1-methyl-4-cyclohexene-1,2-dicarboxylic anhydride* (I) 6 hrs. in 75 ml. abs. MeOH gave after evapn. and treatment with petr. ether [illegible] (addnl. 1.2 g. obtained by chilling the mother liquor) [illegible] *methoxy-4-cyclohexene-1-carboxylic acid* [illegible] reaction product failed to crystallize (n_D^{20} 1.4875) and on attempted distn. gave I; hydrolysis with alc. NaOH gave *cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acid*, m. 167–8°. The latter (4 g.) re- [illegible] ml. abs. MeOH with 2.6 ml. concd. [illegible] to 25 ml., treated with H_2O, extd. [illegible]

with HCl, followed by extn. with Et_2O, 5.2 g. *cis-1-methyl-1-carbomethoxy-4-cyclohexene-2-carboxylic acid*, a viscous oil, [illegible] this was also formed in 1.8-g. yield when 2 g. [illegible] methyl-4-cyclohexene-1,2-dicarboxylate was re- [illegible]

cis-1-methyl-2-carbomethoxycyclohexane-1-carboxylic acid (III) [illegible] Refluxing 3 g. *cis-1-methyl-* [illegible] MeOH 5 hrs. gave [illegible] in 25 ml. abs. MeOH was added [illegible] g. IV and the mixt. refluxed 3 hrs., gave, after usual treatment [illegible] *cis-1-methyl-1-carbomethoxycyclohexane-2-carboxylic acid* (IVa), m. 59–60° (from petr. ether), which also formed on hydrogenation of the 4-cyclohexene analog. To 10 g. II was added 10 ml. CO_2Cl_2 and the mixt. allowed to stand 1 hr., heated 0.5 hr. [illegible] evapd. and distd., gave 10.6 g. *cis-1-methyl-2-carbomethoxy-4-cyclohexene-1-carbonyl chloride* (V), b. [illegible] III gave 5.7 g. *cis-1-methyl-2-carbomethoxycyclohexane-1-carbonyl chloride* (VI), $b_{1.4}$ 110.5–11°, n_D^{20} 1.4780. Similarly 13 g. *cis-1-methyl-1-carbomethoxy-4-cyclohexene-2-carboxylic acid* gave 13.3 g. corresponding acid chloride (VII), $b_{1.4}$ [illegible]–7°, n_D^{20} 1.4865. IVa [illegible] gave the corresponding acid chloride (VIII) [illegible]

[illegible] with 7 ml. 40% KOH and 5 ml. MeOH, yielded after acidification and extn. with Et_2O 0.35 g. *cis-1-methyl-2-carboxy-4-cyclohexene-1-acetic acid*, m. 141–3° (from Me_2CO-petr. ether). Similarly 2.1 g. VI gave 0.28 g. *cis-1-methyl-2-carbomethoxycyclohexane-1-acetic acid*, m. 174–5°, which was [illegible] analog over [illegible] VII gave [illegible] *1-methyl-2-carboxy-4-cyclohexene-1-acetic acid*, m. 162–6° (even after [illegible] from various solvents), hydrogenation of [illegible] gave [illegible] *methyl-2-carboxycyclohexane-1-acetic acid* [illegible] and a small amt. of the [illegible] analog, m. 175–7°, since the original acid chloride

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was a pure cis isomer, the result indicates an unexpected isomerization during the Arndt-Eistert reaction. Similar reaction of VIII

PCl_5, heated until soln. took place, then treated with PhNH, and

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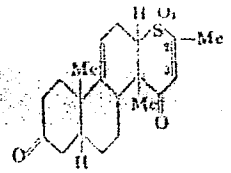
the form of a colorless resinous mass. Oxidation of XII with CrO_3-AcOH gave X m. 214-15°. XXIV Condensa-



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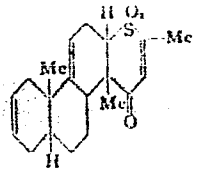

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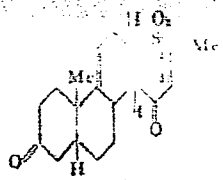

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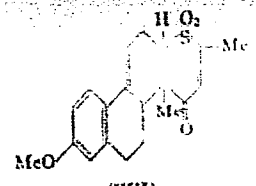

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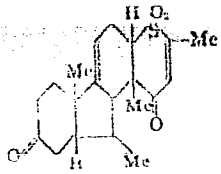

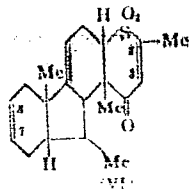

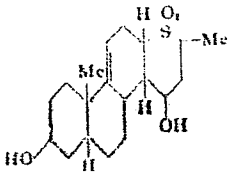

(XII)

tion of 3,8-dimethyl-1-vinyl-$\Delta^{1,3}$-tetrahydroindene with α,β-unsaturated cyclic ketones I. N. Nazarov and M. S. [illegible]

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Into 0.2 g. Na in 350 ml. liquid NH_3 was passed C_2H_2 3 hrs. at 20 l./hr. and the mixt. was then treated, with continued passage of C_2H_2 with [illegible]

Me_2NPh 10 hrs. at 170° gave 2.5 g. isomers of 7,10,14-trimethyl-8-nor-iridochrysa-1,9-dien-15-one [illegible]

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hydronaphthalene (by hydrogenation of 2-C_6H_5OH) in 800 ml AcOH was added over 5 hrs at 3° [illegible] AcOH and 80 ml [illegible]

[illegible] an [illegible] gave about 30% [illegible]

at −70°, warmed to 10°, and stirred 1 hr, then [illegible] at [illegible] (2-3 atm.), evapn of the org layer gave [illegible]

[illegible] as above with MeMgI and the [illegible] at 170° gave an [illegible]

[illegible] gave an [illegible] heated with

(over)

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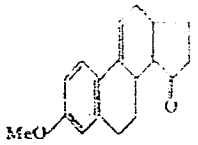
199–203°. Heating 2.7 g. II and 8 g. 1,3-dimethyl-1-cyclopenten-5-one 6 hrs. at 155–60° gave 0.8 g. mixed *isomers* (VIII), $b_{0.1}$ 205–8°, which, refluxed with AcOH–48% HBr 6 hrs., extd. with NaOH and acidified, gave mixed isomers of IX, $b_{0.01}$ 215–20°. VIII over Pt in EtOH added H_2 and yielded mixed dihydro ketone derivs. (X), $b_{0.1}$ 195–200°, demethylated as above in 3 hrs. to the mixed *isomers* of XI, $b_{0.01}$ 215–20°. Heating 4 g. II with 12 ml. 1-cyclohexen-1-one 20 hrs. at 120° gave 2 g. product, b_1 160–70°, which with EtOH yielded 2 g. XII, m. 132° (from EtOH), hydrogenated over Pd in EtOH to *compd.* XIII, m. 147° (from EtOH). Heating 0.1 g. XII with 6 ml. AcOH and 3 ml. 48% HBr 3 hrs. gave 50 ml. *8-methoxy-1,2,3,4-tetrahydrochrysene*, m. 183°. Similar treatment of XIII gave *8-methoxy-1,2,3,4,4a,12a-hexahydrochrysene*, m. 219–20°. The structures of the last 2 products are tentative.



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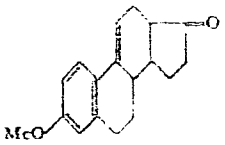

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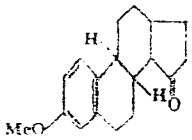

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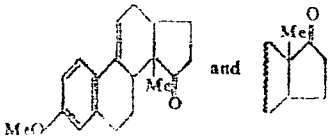

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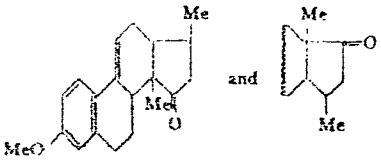

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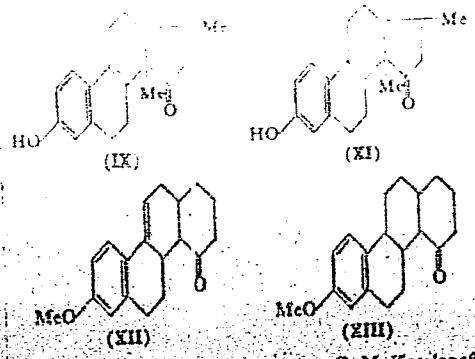
(VIII)



G. M. Kosolapoff

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[redacted] TORGOV, I. V.

Synthesis of polycyclic compounds related to steroids. XXI. Condensation of 1-vinyl-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene with α,β-unsaturated cyclic ketones. Synthesis of steroid ketones with hydrogenated skeletons of cyclopentanophenanthrene and chrysene [illegible]

[illegible] Moscow [illegible] *Otdel. Khim. Nauk* 1953, 1074-90, cf. C.A. 49, [illegible] — Heating steroidal ketones with [illegible] $\Delta^{1,4}$-OH serves to shift the double bond from the 9 [illegible] to the 8,5-position. Heating 582 g. 1-methyl-1-cyclohexen-6 one with 75 g. $(CH:CH_2)_2$ and 2.5 g. Et_3NPh in an autoclave 2 hrs. at 245–50° gave 543 g. unchanged ketone and 20.5 g. (45% conversion) *cis-9-methyl-$\Delta^{1,4}$-octahydro-1-oxonaphthalene* (I), b_1 82–4°, n_D^{20} 1.5050 [*semicarbazone*, decomp. 220° (cf. Nudenberg and Rutz, *C.A.* 37, 5399[4])], hydrogenated over Pt in EtOH to *cis-9-methyldecahydro-1-oxonaphthalene* (II), [illegible]

[illegible]

treated with [illegible] g. [illegible] Pt gave [illegible] n_D^{20} 1.5060, which slowly solidified and m. 62–3°; the product was probably a mixt. of 2 *stereoisomers* which differ in configuration at C-1. Hydrogenation of the ethynylalc. over [illegible]

[illegible] b_1 74–4[illegible], n_D^{20} 1.5250, which, warmed with [illegible] *decahydro-1,2-phenanthrenedicarboxylic anhydride*, m. 119–20° (from hexane). Citraconic anhydride in a similar condensation (24 hrs. at room temp. and [illegible] at 100°) gave 30% mixed anhydrides, [illegible] was isolated the more abundant [illegible] *decahydro-1,2-phenanthrenedicarboxylic anhydride* [illegible] (from hexane); the other isomer, presumably the *1,4-Me analog*, was not purified; if the [illegible]

[illegible] (III) and [illegible] (IV) [illegible]

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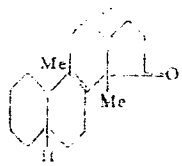
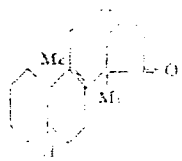


V



[illegible] in 127 [illegible], which [illegible] Act. H not hydrogenate further [illegible] of VII with iodine in aq. MeOH in the presence of KOH gave a *diiodo deriv.*, m. 128–9°, while Kishner reduction of VII with N_2H_4 H_2O in $O(CH_2CH_2OH)_2$ [illegible] (VIII), b_2 145–7°, [illegible] C_6H_6 in the presence of [illegible] *Inels hydrocarbon* (IX) [illegible]

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Reducing

MeOH, there was also formed 0.03 g. II, which was sepd. by freezing. Hydrogenation of II in dioxane over Pt gave

2-carboxycyclohexane-1-acetic acid, m. 174–5°, which was also obtained by hydrogenation of the unsatd. analog over

MeOH

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was a pure cis isomer, the result indicates an unexpected isomerization during the Arndt-Eistert reaction. Similar reaction of VIII [illegible]

[illegible] added 0.6 g. powd. PCl, the mixt. was heated until soln. took place and was then treated with 4 g. PhNH₂ then refluxed 0.5 hr. after dilu [illegible] there was obtained [illegible] 1,2-dicarboxylic acid N-phenylimide, m. 103-4° (from EtO-petr. ether); the same product formed from cis-1-methyl-1-carbomethoxy-4-cyclohexene [illegible] the similar treatment, the same [illegible] V or VII on treatment [illegible] X was refluxed [illegible] the same phenylimide was again obtained [illegible] formed on similar treatment of the [illegible] VII [illegible] III with [illegible] PCl [illegible] PhNH₂ gave 0.96 g. [illegible] methyl- [illegible]

[illegible] MeOH [illegible] with H₂O, and [illegible] XII [illegible] ether) This [illegible] in EtO was treated with 0.75 g.

PCl, heated until soln. took place, then treated with PhNH₂ and [illegible] to stand [illegible]

[illegible] m. 103-5° (from dil. MeOH [illegible] trans-1-Methylcyclohexane 1,2-dicarboxylic [illegible] XIII [illegible] give 77% satd. analog of XII, m. 91-3° identical with the above described [illegible] refluxing [illegible] KOH [illegible] XI [illegible] petr. [illegible] XII [illegible] XIV [illegible] XIV [illegible] treatment of the [illegible] analog of XII with (COCl)₂ gave the

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corresponding *acid chloride* (XVII), $b_{1.5}$ 96–7°, n_D^{20} 1.4770, which with $PhNH_2$ gave the *anilide*, m. 104–5°, identical with the above described specimen. XVI treated with CH_2N_2 as described above gave 85.5% *trans-2-methyl-2-carboxy-4-cyclohexene-1-acetic acid*, m. 205–6° (from Me_2CO). Similarly, XVII gave *trans-2-methyl-2-carboxycyclohexane-1-acetic acid*, m. 175–7° (60% yield); pure product, m. 176–7° (from Me_2CO-petr. ether), is also obtained by hydrogenation of the unsatd. analog over Pd in MeOH. In this series the trans isomers give stable anilides and enter the Arndt-Eistert reaction more readily than do the cis analogs. **XXIII. Synthesis of sulfur analogs of steroidal compounds by diene condensation of cyclic γ-keto sulfones with bicyclic dienes.** I. N. Nazarov, I. A. Gurvich, and A. I. Kuznetsova. *Ibid.* 1953, 1691–9.—Heating 4.8 g. 1-vinyl-9-methyl-$\Delta^{1,9}$-octahydro-5-oxonaphthalene (I) and 4.3 g. 2,7-dimethyl-4*H*-1-thiapyran-4-one 1,1-dioxide (II) in dioxane with 0.05 g. pyrogallol under N 6 hrs. at 170°, then 7 hrs. at 170° on the next day, gave 6.5 g. crude tetracyclic diketo sulfone, which after fractional crystn. from MeOH and chromatography on Al_2O_3 gave 3 g. low-melting form (III), m. 212–13°, and high-melting isomer, m. 225–6°. Similar reaction of 1 g. 1-vinyl-9-methyl-$\Delta^{1,9}$-hexahydronaphthalene and 0.98 g. II gave 1.3 g. mixed isomers, sepd. by treatment with EtOH into compd. IV, m. 205–9.5°, and a low-melting isomer of IV, m. 182–3°. Heating 0.75 g. 1-vinyl-3,8-dimethyl-Δ^1-hexahydro-5-indenone and 0.75 g. II similarly in the presence of pyrogallol in dioxane 6 hrs. at 170–5° gave about 0.25 g. high-melting V, m. 235–6° (from EtOH and Me_2CO), and the low-melting *isomer*, m. 170–1°. Similarly 2 g. 1-vinyl-3,8-dimethyl-$\Delta^{1,4}$-tetrahydroindene and 1.8 g. II after 4.5 hrs. at 170° gave 1.4 g. mixed isomeric product, which was sepd. into the low-melting VI, m. 155–9°, and the high-melting *isomer*, m. 172–3° (from EtOH). I (1.5 g.) and 1.2 g. 2-methyl-4*H*-1-thiapyran-4-one 1,1-dioxide, similarly heated 6 hrs. at 143–6°, gave 2 g. crude product, m. about 200°, which after chromatography on Al_2O_3 gave 1.7 g. VII, m. 215–15.5°, which is unaffected by refluxing 0.25 hr. with MeOH contg. 0.1% Na, but which forms a tar after 2 hrs. refluxing. Heating 1.2 g. 1-vinyl-6-methoxy-3,4-dihydronaphthalene with 1 g. II similarly 6 hrs. at 170–5° gave about 1 g. product, which was sepd. into 0.2 g. starting material and about 0.8 g. VIII, m. 221–1.5° (from C_6H_6). The low-melting isomer of III hydrogenated in dioxane over Pd-$CaCO_3$ gave the 2,3-dihydro deriv. (IX) of III, m. 246–7°, which could not be hydrogenated further; similar hydrogenation of the high-melting III gave the other *isomer* of IX, m. 231–2° (from EtOH). Hydrogenation of VII gave the 2,3-dihydro deriv. (X), m. 216–16.5° (from MeOH), which was unchanged on short boiling with a dil. soln. of Na in MeOH but which formed a tar after 2 hrs. reflux. The hydrogenation could be run either in Me_2CO or dioxane (the latter at 60 atm. at 100–20°). The low-melting isomer of VI was hydrogenated in dioxane over Pd to the 2,3,7,8-tetrahydro deriv. (XI), m. 159–60° (from EtOH). X hydrogenated in AcOH over PtO_2 and H_2PtCl_6, then chromatographed on Al_2O_3, gave XII, m. 245–6° (from C_6H_6), contg. 0.5 mole C_6H_6, along with its *diacetate*. Heating XII with AcCl–AcOH 1.5 hrs. at 110° yielded the diacetate in

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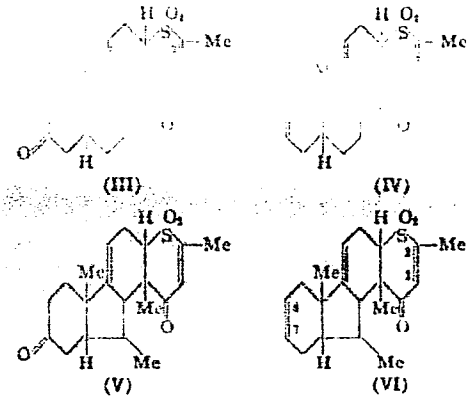
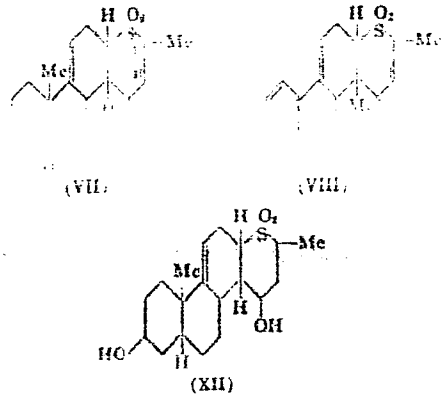
the form of a colorless resinous mass. Oxidation of XII with CrO_3-AcOH gave K. m. 214–15°. XXIV. Condensa-



(III) (IV) (V) (VI)



(VII) (VIII) (XII)

tion of 3,8-dimethyl-1-vinyl-$\Delta^{1,6}$-tetrahydroindene with α,β-unsaturated cyclic ketones. I. N. Nazarov and M. S. Burmistrova. *Ibid.* 1954, 56–62; cf. *C.A.* 48, 12759a.—

(C.A.)

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Into 9.2 g. Na in 350 ml. liquid NH_3 was passed C_2H_2 [illegible] hrs. at 20 l./hr. and the mixt. was then treated, wit[illegible] continued passage of C_2H_2, with 33 g. 3,8-dimethyl-[illegible] tetrahydroindan-1-one in 75 ml. Et_2O, after which the mix[illegible] was treated with C_2H_2 1 hr. longer and kept in the cold [illegible]

[illegible] Heating [illegible] g. I with 50 g. [illegible] at [illegible] g. isomers of [illegible] which hydrogenated in dioxane over Pt [illegible] 7,10-dimethyl-B-norcardocarysan-[illegible] n_D^{20} 1.5215, d_{20} 1.0433. Heating 4 g. I with 45 g. 2-methyl-2-cyclohexen-1-one in sealed ampul in the presence of 0.5 g.

7 "

Me_2NPh 10 hrs. at 170° gave 2.5 g. *isomers* of *7,10,14-trimethyl-B-norcardocarysan-2,9-dien-15-one* [illegible] n_D^{20} [illegible] d_{20} [illegible], which on standing deposited [illegible] *solid isomer*, m. 139-42°. Hydrogenation of the mixed isomers over Pt in dioxane gave [illegible]

[illegible] of compounds related to estrone [illegible] condensation, I. N. Nazarov and I. I. Kotlyarevskii. *Ibid.* 1953. 1100-10.—To 140 g. 2-methoxy-6,6,7,8-tetra-

(Cont)

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I. N. NAZAROV

hydronaphthalene (by hydrogenation of 2-$C_{13}H_{11}OH$ in 800 ml. AcOH was added over 5 hrs. at 3° 140 g. [illegible] in 400 ml. AcOH and 60 ml. H_2O, the mass concd. in vacuo the following day at 40-50° and the [illegible]

[illegible]

[illegible] methoxy-1,4-dihydro[illegible] from C_6H_6); heating the mother liquor in a high vacuum to 140° (much foaming) gave 7.2 g. 6-methoxy-1-ethynyl-1,4-dihydro[illegible] unstable and cannot be satisfactorily distd. again owing to [illegible] 6798r). Hydrogenation of a fresh sample over Pd $CaCO_3$ in MeOH gave 75% *6-methoxy-1-vinyl-3,4-dihydronaphthalene* (II), $b_{1.4}$ 118-24°, n_D^{18} 1.5865, *maleic acid adduct*, m. [illegible] II [illegible]

an ampul gave about 30% [illegible] 210-15°, which yielded 1.5 g. [illegible] from [illegible] II [illegible]

[illegible]

with [illegible] *methoxy-1,2-cyclopentanophenanthrene* [illegible] *benzene adduct* m. 136.5-7° [illegible] II [illegible] ampul gave about [illegible] the eluted product with Na EtOH [illegible] with $KHSO_4$ 1 hr. at 180°, gave an oil, $b_{0.1}$ 180-[illegible] which, heated with Se 7 hrs. at 320-30°, gave a low yield of a solid product, $C_{13}H_{10}O$ [illegible] EtOH gave [illegible]

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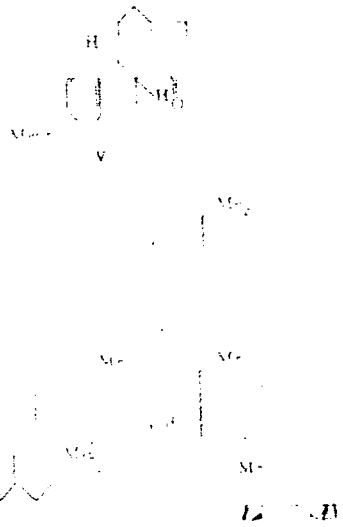
I. N. NAZAROV

160–203°. Heating 2.7 g. II and 8 g. 1,3-dimethyl-1-cyclopentan-5-one 6 hrs. at 155-60° gave 0.8 g. mixed isomers VIII [illegible] which, refluxed with AcOH-48% HBr 8 hrs., [illegible] with NaOH and acidified, gave mixed isomers of IX, b. 215-20°. VIII over Pt in EtOH added H_2 [illegible] dihydro ketone derivs. (X), b. [illegible] the mixed isomers of XI [illegible] heating [illegible] gave [illegible] product [illegible] XII [illegible] XIII [illegible] Heating 0.1 g. XII [illegible]



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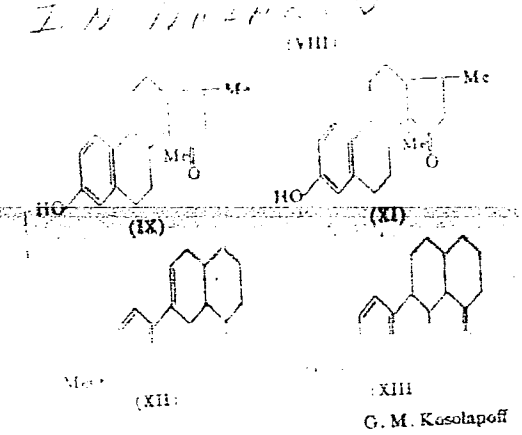

G. M. Kosolapoff

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TORGOV-I.V.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Organic Chemistry

Synthesis of polycyclic compounds related to steroids. XVI. Condensation of 1-methyl-1-cyclohexen-6-one with 2-methoxy-1,3-butadiene. Synthesis of 8a-methyl-1-vinyl-Δ^1-octahydro-6-naphthalenone and 8a-methyl-1-vinyl-Δ^1-octahydro-7-naphthalenone. I. N. Nazarov, I. V. Torgov, I. I. Zaretskaya, G. P. Verkholetova, S. N. Ananchenko, and V. N. Andreev. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 78–90; cf. *C.A.* 45, 7583*c*; 47, 10515*d*.—To the catalyst prepd. from 4.5 ml. $BF_3.Et_2O$, 15 g. yellow HgO, 2 g. Cl_3CCO_2H, and 10 ml. abs. MeOH was added 480 g. abs. MeOH and the mixt. treated over 9 hrs. with 280 g. $CH_2:CHC:CH$ at about 40°, let stand overnight, stirred 4 hrs. at 40°, cooled, and neutralized with 16 ml. 6% MeONa; distn. gave 67% *1,3,3-trimethoxybutene*, b_{10} 60–2°, n^{20}_D 1.4112. If near the end of the reaction some 1 ml. $BF_3.Et_2O$ and 5 g. HgO are added, the yield is raised 5–7%. The product was slowly added to 10 g. Ph_2O and 0.6 g. powd. $KHSO_4$ heated to 150° at such a rate that the vapor temp. remained below 62°, yielding a distillate of *2-methoxy-1,3-butadiene* (I), $MeOCH_2CH_2C(OMe):CH_2$, and MeOH; redistn. gave 65–70% I pure enough for further work, b. 72–5°, n^{20}_D 1.4430–1.4450. I (15 g.) and 120 g. 1-methyl-1-cyclohexen-6-one heated in a metal ampul in CO_2 with 1%

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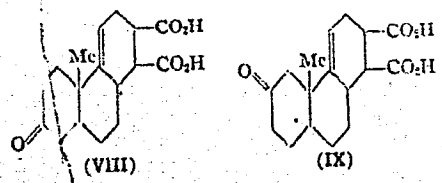
PhNEt$_2$ 2.5 hrs. at 260–70° yielded after repeated distn. 44% *mixed 8a-methyl-6-methoxy-Δ^8-octahydro-1-naphthalenone* (IA) and *8a-methyl-7-methoxy-Δ^8-octahydro-1-naphthalenone* (II), b$_1$ 92–6°. IA *semicarbazone* (provisionally characterized), m. 208–9.5°. Hydrogenation of mixed IA-II over Pd in dioxane gave *8a-methyl-7-methoxydecahydro-1-naphthalenone*, b$_{0.5}$ 89–91°, n^{20}_D 1.4892, d$_{20}$ 1.039; *semicarbazone*, m. 199–202° (decompn.). To 7 g. Na in 300 ml. liquid NH$_3$ was added over 2 hrs. C$_2$H$_2$ at 20 l./hr., then 10.7 g. mixed IA-II in Et$_2$O, the C$_2$H$_2$ flow continued 9 hrs., 20 g. NH$_4$Cl added, and the mixt. allowed to stand overnight; treatment with H$_2$O and extn. with Et$_2$O gave 2 g. *1-ethynyl-8a-methyl-6-methoxy-Δ^8-octahydro-1-naphthol* (III), m. 123–3.5° (from CHCl$_3$). The mother liquor gave 6 g. mixed III and its *7-MeO isomer*, b$_1$ 119–21°, n^{20}_D 1.5203. The use of K or Li failed to give better results. Shaking III in Et$_2$O 2 hrs. with 8% HCl gave 100% *1-ethynyl-8a-methyl-1-hydroxydecahydro-6-naphthalenone* (IV), m. 155–6°. To 17 g. Na in 850 ml. liquid NH$_3$ was added 40 l. C$_2$H$_2$ in 1 hr., and, with a reduced rate of C$_2$H$_2$ flow, the mixt. was treated with 80 g. mixed IA-II in 250 ml. Et$_2$O, the passage of C$_2$H$_2$ continued 6 hrs., and the mixt. kept overnight at −70°, treated with C$_2$H$_2$ 5 hrs., allowed to warm to −35°, treated with 60 g. powd. NH$_4$Cl, allowed to evap.; the residue, after addn. of Et$_2$O, was treated with ice H$_2$O, and the concd. org. layer treated with 100 ml. 1% HCl and stirred 3 hrs., yielding 34–9 g. IV, m. 158° (from EtOH or C$_6$H$_6$). The mother liquor treated with petr. ether gave 6–8 g. *7-oxo isomer* of IV, m. 144° (from EtOH); the residue (13–16 g.) was a mixt. of the 2 substances, b$_{1.5}$ 134–6°, n^{20}_D 1.5280. Hydrogenation of IV over PtO$_2$ in EtOH gave the *1-Et analog*, m. 127–8°; the other isomer similarly gave *1-ethyl-8a-methyl-1-hydroxydecahydro-7-naphthalenenone*, m. 86°. Hydrogenation of IV in dioxane over Pd (1 mole H absorbed) gave a viscous mass, crystg. very slowly; the pure *1-vinyl analog* of IV m. 111–12° (from petr. ether). The *1-vinyl-8a-methyl-1-hydroxydecahydro-7-naphthalenone* (V), m. 114–15°, crystd. rapidly. Dehydration of these over KHSO$_4$ in the presence of pyrogallol at 140–5°/40–5 mm. gave, resp. 67% *1-vinyl-8a-methyl-Δ^1-octahydro-6-naphthalenone* (VI), b$_3$ 114–17°, b$_1$ 100–3°, n^{20}_D 1.5260, d$_{20}$ 1.022 [*semicarbazone*, m. 174.5–6.0° (from EtOH)], and 74% *1-vinyl-8a-methyl-Δ^1-octahydro-7-naphthalenone* (VII), b$_{0.5}$ 91–6°, n^{20}_D 1.5270 (*semicarbazone*, m. 196–7°). Hydrogenation of mixed IV and its 7-oxo isomer over Pd gave some 20% V, and dehydration of the residue gave 40% mixed VI-VII. VI reacted spontaneously with maleic anhydride and treatment of the product with alc. aq. KOH, followed by acidification, gave the previously described dicarboxylic acid (VIII), m. 200–2.5°. VII similarly gave the dicarboxylic acid (IX), decomp. 203°, becoming transparent only at 210°. IX (2 g.), 10 ml. MePh, and 0.05 g. powd. KOH



(VIII) (IX)

heated 0.5 hr. at 110° gave C$_2$H$_2$ and a trace of *8a-methyl-1,6-dioxodecahydronaphthalene*, m. 60–2°. To MeMgBr (from 13 g. MeBr) was added in 10 min. at 5–10° 5 g. VI and the mixt. refluxed 5 min.; after decompn. with ice and 20% HCl, the org. layer gave 90% *1-vinyl-6,8a-dimethyl-Δ^1-octahydro-6-naphthol* (X), b$_{0.5}$ 91–4°, n^{20}_D 1.5260. Similarly was obtained 87% *1-vinyl-7,8a-dimethyl-Δ^1-octahydro-7-naphthol* (XI), b. 92–6°, n^{20}_D 1.5235. Dehydration over KHSO$_4$ in the presence of pyrogallol at 140–50°/45 mm. gave, resp., 60% *1-vinyl-6,8a-dimethyl-Δ^{1,8}-hexahydronaphthalene* (XII), b. 1–2°, n^{20}_D 1.5240, d$_{20}$ 0.940, and *1-vinyl-7,8a-dimethyl-Δ^{1,8}-hexahydronaphthalene* (XIIIa), b$_{0.5}$ 68–70°, n^{20}_D 1.5220. XII (5.8 g.) heated with 15 g. di-Me maleate 6 hrs. at 100°, followed by removal of unused ester in

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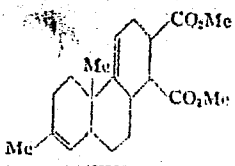
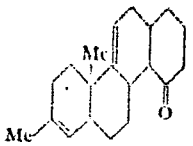
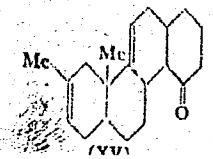
vacuo and heating the residue with $KHSO_4$ and little pyrogallol 0.25 hr. at 160–70°/25 mm. gave 4.3 g. XIII, b_1 165–70°, n_D^{20} 1.5200, which, heated 3 hrs. with aq. alc. NaOH, gave the free *acid*, does not m. 200°. XI treated similarly gave the corresponding *ester* (not characterized) but hydrolysis of the latter gave only a viscous mass. The free acid of XIII heated in a N atm. with Pd-C in C_6H_6 11 hrs. at 370° reacted incompletely and yielded but 50 mg. *2-methylphenanthrene*, m. 57–8.5°; *picrate*, m. 115–17°. Dehydrogenation of the viscous isomeric acid failed to yield a solid product. Heating 1.2 g. XII and 3.1 g. 2-cyclohexen-1-one in CO_2 in an ampul 4 hrs. at 200° gave 0.5 g. crude ketone (XIV), b_1 150–5°, which was used in this form. Similarly XIIIa gave crude ketone (XV), b_1 145–55°, which was used in this state. Heating 0.5 g. XIV in 3 ml. $O(CH_2CH_2OH)_2$ with 0.4 g. $N_2H_4.H_2O$ 5 min., then with 0.4 g. Na. in 10 ml. $O(CH_2CH_2OH)_2$ 10 hrs. at 200° and 3 hrs. at 220°, extn. of the dild. mixt. with Et_2O, evapn. of the washed ext., and heating the residue with Pd-C in C_6H_6 6 hrs. at 350° in a N atm. gave 14 mg. *2-methylchrysene*, m. 222–3° (*picrate*, m. 145.5–6.0°). Similarly 1.2 g. XV gave 0.45 g. crude product, $b_{0.5}$ 120–30°, dehydrogenated as above to 15 mg. *3-methylchrysene*, m. 160–9° (*picrate*, m. 169–1°).



(XIII)



(XIV)



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KARYAKIN, Yuriy Viktorovich; ANGELOV, Ivan Ivanovich; TORGOV, I.V., redaktor; SHPAK, Ye.G., tekhnicheskiy redaktor.

[Pure chemical reagents; manual for the preparation of non-organic reagents and compounds under laboratory conditions] Chistye khimicheskie reaktivy; rukovodstvo po prigotovleniiu neorganicheskikh reaktivov i preparatov v laboratornykh usloviiakh. Moskva, Gos.nauchno-tekhn.izd-vl khim.lit-ry 1955. 583 p. (MLRA 9:1)

(Chemical tests and reagents)

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NAZAROV, I.N.; ANACHENKO, S.N.; TORGOV, I.V.

Synthesis of steroid compounds and related to them substances. Part 32. Stereochemistry of the hydrogenation and reduction of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene. Zhur.ob.khim. 26 no.4:1175-1186 Ap '56. (MLRA 9:8:

1. Institut organicheskoy khimii Akademii nauk SSSR.
(Naphthalene) (Hydrogenation)

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NAZAROV, I. N., ANANCHENKO, S. N., ...

failed. To 6.9 g. [illegible]

the condensation is run [illegible] using H gave [illegible] yield of same [illegible]

[illegible] dine butyrate to 130° in [illegible] The dione heated with $N_2H_4.H_2O$ in EtOH, followed by heating with Na in diethylene glycol to 190° over 2 hrs. and kept at 205° 6 hrs. under N gave about [illegible]

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NAZAROV IN. [illegible] S N

dinitrobenylhydrazone of [illegible]

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NAZAROV, I.N., ANANCHENKO, S.N., ...

... Dir. Chem. SN 1955, 31-4 (Engl. translation)

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NAZAROV, I.N.; VERKHOLETOVA, G.P.; ANANCHENKO, S.N.; ALEKSANDROVA, G.V.; TORGOV, I.V.

Synthesis of polycyclic compounds related testereids. Part 35. Condensation of cyclic allyl halo derivatives with cyclic 2-methyl-1,3-diketones and intramolecular cyclization of resulting compounds into ketones with hydrogenated skeletons of phenanthrene, chrysene, and cyclopentanophenanthrene containing an angular methyl group. Zhur.ob.khim.26 no.5:1482-1495 My '56. (MLRA 9:9)
(Ketones) (Condensation products (Chemistry))

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TORGOV, I.V.

Synthesis of polycyclic compounds related to steroids. XXXV. Condensation

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TORGOV, I.V.

USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311.

Author : Nazarov I. N., Anachenko S.N., Torgov I. V.
Inst :
Title : Synthesis of Steroid Compounds and Relative Substances. XXXII. Stereochemistry of Hydrogenation and Reduction of 6,9-dimethyl-1-keto- Δ4(10) 5, - hexahydronaphthaline.

Orig Pub: Zh. Obshch. Khimiyi, 1956, 26, No 4, 1175-1186.

Abstract: It was shown, that at the hydrogenation of 6,9-dimethyl-keto- Δ 4(10), 5 -hexahydronaphthaline (I) with Pt-catalyst and at the reduction I with Li in liquid NH_3 are formed derivatives of trans-6,9-dimethyldecaline. The addition of the first molecule H_2 to I in the presence of Pt in alcohol or glacial CH_3COOH occurs mainly in the position of the double bond in the position 4-10 on the opposite side from the angular methyl group, whereby is formed a

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya; No 6, 1957, 19311.

trans-6,9-dimethyl-Δ 5-octalon-1 (II) with an admixture (~5%) 6,9-dimethyl-Δ 4(L))-octalon-1 (III). The addition of the second molecule H_2 goes into 5-6 position and leads to trans-6 , 9-dimethyl decalon-1(IV). On the exhaustive hydrogenation I in the presence of Pt are absorbed 3 molecules H_2, and 6 ,9-dimethyldecalolo-1 (V) is obtained. Hydrogenation of I in V is best carried out with Pt in the presence of HCl; at the hydrogenation of I in a solution of alcohol or CH_3COOH without the addition of HCl, adds easily and speedily only 2 molecules of H_2 to the ethylene bonds; however the reduction of the CO group proceeds several times slower. In the presence of Pd-catalyst in alcohol the addition of the molecule H_2 to I occurs in the position 1-4, whereby is formed 6 ,9-dimethyl-Δ 5(10)-octalon-1 (VI), after which the hydro-

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311.

gonation slows down drastically. At further hydrogenation VI with Pt is obtained a mixture of equal amounts of cis-6 ,9-dimethyldecalone-1 (VII) and IV. At the action CH_3MgI on VI is formed 1, 6β,-trimethyl-Δ 5(10)-octalol-1 (VIII), dehydrating $KHSO_4$ in 1, 6β,0-trimethyl-Δ1,5(10)-hexahydronaphthaline (IX). The presence in VI of a double bond in the position 5-10, and not in the position 4-10 is proven by the fact of the formation of IV and VII at hydrogenation of VI and the complete absence of acetic and malonic acids in the ozonization product IX. The hydrogenation of I in the presence of Ni-catalyst proceeds very slowly with the addition of 2 molecules H_2, whereby V is obtained with a yield of ~20%, and a liquid mixture of substances not investigated further. At the reduction of I Li in liquid NH_3, the reduc-

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311

tion of the CO-group only takes place and is formed 6, 9-dimethyl- $\Delta^{4}(10)$,5-hexalole-1 (X) which at further hydrogenation with Pt is converted into V. In the presence of alcohol the reduction of I Li in liquid NH_3 yields trans-6,9-dimethyl- Δ^{5}-octalole-1 (XI), oxidized with CrO_3 into II. In the presence of Pt, XI is hydrogenated into V. At the previously described (RZhKhim, 1956, 16188) diene condensation of isoprene (XII) with 1-methyl- Δ^{1}-cyclohexanone-6 (XIII) are obtained $\Delta^{6(7)}$-6,9-dimethyl-octalone-1(XIV) and $\Delta^{6(7)}$-7,9-dimethyloctalone-1 (XV). The hydrogenation of XIV with Pt yields a mixture of VI. and its 6-epimere (XVI) with a predominant amount of VI. For the determination of the structure XV it was converted by means of interaction with CH_3MgI into 1,7,9-trimethyl- Δ^{6}-octalone-1(XVII), which is dehydrated into 1,

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311.

7,9-trimethyl-$\Delta^{1,6}$-hexahydronaphthaline (XVIII) yielding at the dehydration 1,7-dimethylnaphthaline (XIX). 0.3 g. of I, m.p. 49-50°, is hydrogenated in 8 cc alcohol with Pt, V is obtained, yield 0.24 g. m.p. 94° (from petr. ether); 3,5-dinitrobenzoate, m.p. 128-129° (from petr. ether). The oxidation of 88 mg V with CrO_3 in glac. CH_3--COOH (48 hours at ~20°) yields IV, isolated in the form of 2,4-dinitrophenylhydrazone (DNPH) IV, m.p. 212-213° (from alc.-benzene, 1:1). 0.5 g. of I is hydrogenated in alcohol with Pt until $2H_2$ is absorbed, IV is obtained, yield 0.4 g. b.p. 92-93/1 mm, $n^{18}D$ 1.4854; semicarbazone (SMC), m.p. 215-216° (from alc.-dioxane); DNPH, m.p. 212° (from alc.-benz 1.5 g. I in 15 cc alcohol is hydrogenated with Pt until 1 mole H_2 is absorbed, a mixture of II and III is obtained, 1.4 g. from which at the treatment with

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311.

dinitrophenylhydrazine (XX) and subsequent fractional crystallization are isolated DNPH II, yield 2 g. m.p. 207-208.5° and DNPH III, yield 0.1 g., m.p. 189-190°. 0.22 g. of I in 10 cc alcohol and 3 cc HCl is hydrogenated with Pt until the absorption reaches 3 moles H_2, V is obtained, yield 0.17 g., m.p. 96-98°. 1 g. I is hydrogenated in alcohol with skeleton Ni until the absorption of 2 moles H_2 and V is obtained, yield 0.19 g. 1.8 g. I in 15 cc alcohol is hydrogenated in the presence of Pd/$CaCO_3$ (10% Pd.); after the absorption of 1 mole of hydrogen the hydrogenation is drastically slowed down, VI is obtained, yield 1.5 g., b.p. 85-87°/1.5 mm, $n^{20}D$ 1.5000; DNPH, m.p. 200-201° (doc. from alc.-ethylacetate 1:1). To the cooled off solution CH_3MgI (from 0.8 g Mg, 5 g. CH_3I, and 40 cc ether) is added 2 g. VI in 15 cc ether,

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311.

heated 4 hours at 35-40°, treated with HCl (1:1), and VIII is obtained, yield 1.8 g., b.p. 97-100°/2mm, $n^{20}D$ 1.5070. A mixture of 1.8 g. VIII and 0.6 g. $KHSO_4$ is heated 40 min. at 150-160°, treated with water, extracted with ether, and IX is obtained, yield 1 g., b.p. 63-65°/2 mm, n20D 1.5010. At the hydrogenation of 1 g. VI in alcohol with Pt is obtained 0.9 g. of a mixture of IV and VII, b.p. 90-92°/1 mm, n20D 1.4865, from which by means of XX are isolated equal amounts DNPH IV and DNPH VII, m.p. 182-183°. To 100-120 cc liquid NH_3 is added 0.2 g. Li, stirred 20 min. at -70°, a solution of 1 g. I in 15 cc ether is poured in and stirred for 2 hours more; 5 g. of NH_4Cl is added, and stirred, increasing the temperature gradually to ~20°, treated with water and extracted with ether. X is obtained, yield 0.7 g., b.p. 105-106°/3 mm,

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311.

$n^{20}D$ 1.5410. At the hydrogenation of 0.6 g. of X in alcohol with Pt for 30 min. 2 moles of H_2 is absorbed, and V is formed, yield 0.25 g. m.p. 100°; 3,5 dinitrobenzoate, m.p. 128-129°. Oxidation of V by means CrO_3 in glac. CH_3COOH leads to the formation of IV, with characteristics of the form of DNPH. To 140-150 cc NH_3 is added 0.6 g. Li, stirred 20 min. at -70°, is added a solution 2.1 g. I in 40 cc ether, stirred 35 min., 15 cc of absol. alc. is poured in and stirred 2 hours at -70°. After the usual treatment is obtained XI, yield 0.9 g., m.p. 87-89° (from petr. ether). At the oxidation of 0.3 g. XI CrO_3 in glac. CH_3COOH is formed II, yield 0.1 g. At the hydrogenation of 0.33 g. XI in alcohol with Pt in 1 hour is absorbed 1 mole H_2, and V is formed, yield 0.203 g. at the oxidation of which is obtained IV characteristic of the form of DNPH. A mix-

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Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311

ture of 30g. XII and 135 g. XIII is heated in a metallic ampoule 50 min. at 280-285° (temperature of water bath) and the unreacted XIII is distilled off in vacuum (123 g.). From three experiments is obtained 20 g. of a mixture XIV and XV. From 10 g. of a mixture is obtained DNPH (10.4 g. XX, 50cc alcohol, 50 cc dioxane and 12 cc HCl), and after a fractional crystallization of DNPH mixture from a mixture of ethylacetate and alcohol is isolated DNPH XIV, yield 6 g., m.p. 181-182° and DNPH XV, yield 1.02 g., m.p. 162.5-163°. A mixture of 4 g. DNPH XIV, 8 cc $CH_3COOCOOH$, 9.6 g. CH_3COONa, 100 cc water and 260 cc CH_3COOH is heated 2 hours at 110-120°, CH_3COOH is distilled off in vacuum before the crystallization starts, the remainder is treated with a solution of soda until it reacts slightly alkaline, filtered, the filtrate is

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues.

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311

extracted with ether, and XIV is obtained, yield 1.6 g., b.p. 82-83°, 2 mm, $n^{20.5}D$ 1.5005; SMC, m.p. 218-220° (dec.). At the hydrogenation of 1.6 g. XIV in 25 cc alcohol with Pt in 23 hours is absorbed 3 moles H_2 and a mixture is formed of cis-6,9-dimethyldecalole-1 (XXI), yield 1.2 g., b.p. 94-96°/1 mm, n20D 1.4960, at the oxidation of which (CrO_3 in CH_3COOH) are obtained a mixture of VI and XVI, separated by means of DNPH; DNPH VI, yield 0.3 g. and DNPH XVI, yield 0.1 g., m.p. 152-153.5°. A mixture of 2.1 g. DNPH XV, 4 cc $CH_3COCOOH$, 4.6 g. CH_3COONa, 130 cc CH_3COOH, and 100 cc water is heated 3 hours at 110-115° and after treatment, analogical to the one described above, is obtained XV, yield 0.8 g., b.p. 83-84°/2 mm, n20D 1.5008. To a solution CH_3MgI (from 0.3 g. MG, 2 g. CH_3I and 20 cc ether) is added a solution of 0.8 g. XV in

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USSR/Organic Chemistry. Natural Products and their Synthetic Homologues. E-3

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19311

10 cc ether, is heated 1 hour at 35-40°, treated with 5 cc HCL (1:), extracted with ether, and XVII is obtained, yield 0.6 g., b.p. 96-100°/2 mm, $n^{20}D$ 1.5110. A mixture of 0.6 g. XVII and 0.2 g $KHSO_4$ is heated 1 hour at 150-160°, treated with water, extracted with ether, and XVII is obtained, yield 0.35 g., b.p. 73-65°/1 mm, n20D 1.5030. A solution of 0.35 g. XVIII in 10 cc C_6H_6 and 0.2 g. 10% Pd/C is heated 21 hours at 360-370° in an autoclave, the solvent is distilled off in vacuum, the remainder is treated with a solution 143 mg. picric acid in 3 cc alcohol, and the picrate XIV, is obtained yield 112 mg., m.p. 119-120° (from alcohol). Report XXXI see RZhKhim, 1957, 8180.

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TORGOV, I. V.

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SOV/20-122-1-22/44

AUTHORS: Nazarov, I. N., Member, Academy of Sciences, USSR (Deceased), Nazarova, I. I., Torgov, I. V.

TITLE: Synthesis of Polyene Aldehydes and Ketones by Condensation of Aldehyde Acetals With Vinyl and Isopropyl Ether (Sintez poliyenovykh al'degidov i ketonov kondensatsiyey atsetaley al'degidov s vinilovym i izopropenilovym efirami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 1, pp 82 - 85 (USSR)

ABSTRACT: Polyene aldehydes and ketones are well known. Some of them (citral, farnesal) occur in nature, others are intermediate products in the synthesis of isoprenoids (Ref 1). Polyene carbonyl compounds of unramified structure were, however, less carefully investigated though they may be used as intermediate products in the synthesis of so important natural substances as fatty acids and some types of sugar. It is the aim of this paper to apply the method of aldehyde polycondensation - in practice this is the only possible method - to the substances mentioned in the title with a normal carbon chain. Thus, by

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Synthesis of Polyene Aldehydes and Ketones by Condensation of Aldehyde Acetals With Vinyl and Isopropyl Ether

condensation of crotonic aldehyde (I) with vinyl ethyl ether 3-ethoxy hexene-4-Al-acetal (II) was produced in the presence of zinc chlorine. By saponification the latter compound yields sorbic aldehyde (III). Since sorbic aldehyde (III) is changed to acetal (IV) it may subsequently be condensed by means of vinyl ethyl ether. After saponification octatriene-2,4,6-Al (V) is formed in a 71% yield. By means of such a subsequent lengthening of the chain deca-tetraene-2,4,6,8-Al-(VI) and dodeca-pentaene-2,4,6,8,10-Al (VII) are synthetized. The intermediate acetals were produced in a high yield under the action of tetraethoxy silane on the aldehydes (Ref 5). In all stages high yields are obtained (70-80%). Thus it may be said that the authors' method showed without any doubt advantages as compared to the method of Kuhn (Kun). It could be proved that also isopropenyl ethyl ether reacts with acetals similar to vinyl ethyl ether. Thus a new method of synthesis of polyene ketones was found. The condensation of isopropenyl ethyl ether with crotonic

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Synthesis of Polyene Aldehydes and Ketones by Condensation of Aldehyde Acetals With Vinyl and Isopropyl Ether

aldehyde acetal (I) leads to 4-ethoxy-heptene-5-On-2-ketal (VIII) which, after saponification of heptadiene-3,5-On-2 (IX) yields 51%. According to the same scheme nonatriene-3,5,7-On-2 (X) and undecatetraene-3,5,7,9-On-2 (XI) were synthetized from sorbic aldehyde acetals and octatriene-2,4,6-Al. The structure of the ketones produced was proved by the hydration to the corresponding saturated ketones which were identified as their derivatives. There are 8 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im.N.D.Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N.D. Zelinskiy, AS USSR)

SUBMITTED: May 16, 1958

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SOV/62-59-1-16/38

5(3)

AUTHORS: Nazarov, I. N., Ananchenko, S. N., Torgov, I. V.

TITLE: Condensation of Vinyl Cyclohexene With Propiolic and Tetrolic Acid and Their Esters (Kondensatsiya viniltsiklogeksena s propiolovoy i tetrolovoy kislotami i ikh efirami)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 95 - 102 (USSR)

ABSTRACT: The authors of the present paper tried to investigate the possibility of building polycyclic systems like stereoids by condensation of dienes with acetylene monocarboxylic acids and subsequent prolongation of the chain by means of condensation with sodium acetic (or sodium malonic) ester and cyclization according to the scheme adjoining. The condensation of 1-vinyl-1-cyclohexene with propiolic acid forms, at 100° and with a total yield of 60%, a mixture of $\Delta^{1,4}$-hexahydronaphthalene-1-carboxylic acid (I) and $\Delta^{1,4}$-hexahydronaphthalene-2-carboxylic acid (II) at a ratio of 10:1. The reaction with methyl ester of propiolic acid takes a similar course. The hydrogenation of the isomeric acids (I) and (II) with platinum oxide as a catalyst

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Condensation of Vinyl Cyclohexene With Propiolic and Tetrolic Acid and Their Esters

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in acetic acid takes a space selective course in both cases and leads accordingly to the cis-syn-decalin-1-carboxylic acid (III) and cis-decalin-2-trans-carboxylic acid (IV). The reduction of $\Delta^{1,4}$-hexahydronaphthalene-1-carboxylic acid (I) by lithium aluminum hydride yields 1-oxy-methyl-$\Delta^{1,4}$-hexahydronaphthalene (VI). This was tranformed by the effect of phosphorus tribromide into a corresponding bromide. The authors tried to condense the latter with sodium acetic and sodium malonic ester. The condensation of 1-vinyl-1-cyclohexene with tetrolic acid takes place not earlier than at 130° in a yield of the adduct (VIII) of 4% only, for the basic mass of tetrolic acid is decomposed therein into methyl acetylene and carbon dioxide. Propiolic acid condenses very readily with 1-vinyl-6-methoxy-3,4-dihydronaphthalene (IX) under the formation of a mixture of isomeric acids (X) and (XI) in large yield. There are 1 figure and 10 references, 5 of which are Soviet.

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Condensation of Vinyl Cyclohexene With Propiolic and Tetrolic Acid and Their Esters SOV/62-59-1-16/38

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 16, 1957

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SOV/62-59-1-17/38

5(3)

AUTHORS: Nazarov, I. N., Ananchenko, S. N., Torgov, I. V.

TITLE: Synthesis of Stereoid Compounds and Related Substances (Sintez steroidnykh soyedineniy i rodstvennykh im veshchestv) Communication 41. A New Type of Condensation of Divinyl Carbinols With Cyclic 1,3-Diketones (Soobshcheniye 41. Novyy tip kondensatsii divinilkarbinolov s tsiklicheskimi 1,3-diketonami)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 1o3 - 1o9 (USSR) Submitted 1957

ABSTRACT: In preceding papers it was found that the condensation of allyl bromides with sodium derivatives of cyclic 1,3-diketones and the subsequent cyclization of reaction products leads to the formation of polycyclic ketones, among them also those related to stereoids (Refs 1 and 2). In the present paper these transformations were carried out also with 2 isomers of 2-methyl-1-vinylcyclohexane-1-ol (I). The results were practically the same. By the effect of gaseous hydrogen bromide on both isomers (I) the allyl bromide (II) is produced in vinyl alcohol at 0° in a yield of ~ 60%. The bi-

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Synthesis of Stereoid Compounds and Related Substances. SOV/62-59-1-17/39
Communication 41. A New Type of Condensation of Divinyl Carbinols With Cyclic 1,3-Diketones

cyclic diketone (III) is produced in a yield of 55% by the condensation of (II) with methyl hydroresorcinol in the presence of sodium ethylate. (III) is cyclized with phosphoric anhydride (10-15%) on heating in vacuum. The water is separated and the tricyclic ketone (IV) is formed in a yield of ~ 50%. Furthermore, 1-vinyl-Δ^2-cyclohexene-1-ol (V) and 1-vinyl-2-methyl-Δ^2-cyclohexene-1-ol (VI) were synthesized according to the usual scheme by condensation of Δ^2-cyclohexenone and 2-methyl-Δ^2-cyclohexenone with lithium acetylenide in liquid ammonia and subsequent selective hydrogenation of corresponding acetylene alcohols (VII) and (VIII). The authors failed to carry out this reaction by way of allyl bromides and 1-vinyl-6-methoxy-1-tetralol. It was found, however, that in the presence of sodium ethylate or trimethylbenzyl ammonium hydroxide (Triton B) an addition of methyl hydroresorcinol to vinyl cyclohexenols (V) and (VI) takes place. Thereby bicyclic diketones (IX) and (X) are formed on the separation of water in a yield of ~50%. The structure of (IX) and (X) was confirmed by infra-

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Synthesis of Stereoid Compounds and Related Substances. Communication 41. A New Type of Condensation of Divinyl Carbinols With Cyclic 1,3-Diketones SOV/62-59-1-17/38

red spectra (Table). The cyclization of (IX) and (X) is very difficult and could be carried out only in the case of (X). On its heating in vacuum with 50 wt% phosphoric anhydride the authors suceeded in obtaining the tricyclic ketone (XI) at 150-160° in a small yield. There are 1 table and 7 references, 5 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

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5(3) SOV/62-59-2-16/40

AUTHORS: Nazarov, I. N., Verkholetova, G. P., Torgov, I. V.

TITLE: Synthesis of Steroid Compounds and Related Substances (Sintez stroidnykh soyedineniy i rodstvennykh im veshchestv). Communication 42. Condensation of 1-Vinyl-9-methyl-Δ^1-6-octalone With Quinone (Soobshcheniye 42. Kondensatsiya 1-vinil-9metil-Δ^1-6-oktalona s khinonom)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, Nr 2, pp 283-292 (USSR) Submitted 1957

ABSTRACT: The authors of the present paper tried to synthesize D-homosteroids with a trans-combination of the C- and D-rings and with corresponding position of the functional groups (in position 3 and 17a). By condensation of vinyl cyclohexene with quinone syn-cis-$\Delta^{2,9(14)}$-decahydro phenantrene-1,4-dione (III) (Ref 4) was obtained. On the reduction of it with zinc in acetic acid syn-cis-$\Delta^{9(14)}$-dodecahydrophenantrene-1,4-dione (IV) was formed. The isomerization of (IV) with sodium methylate yielded anti-trans-$\Delta^{9(14)}$-dodecahydrophenantrene-1,4-dione (V) (Ref 5). On

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Synthesis of Steroid Compounds and Related Substances. Communication 42. Condensation of 1-Vinyl-9-methyl-Δ^1-6-octalone With Quinone

heating of (V) with ethylene glycol in the presence of p-toluene sulfo acid the crystalline monoethylene ketal (VI) (40%) was formed. On the reaction of ethylene glycol with (VI) under identical conditions a difficultly decomposable mixture is formed, from which an isomer of (VI) in small yield was separated. (VI) was transformed by means of the Kizhner reduction and following hydrolysis with a mixture of hydrochloric- and acetic acid into the crystalline anti-trans-$\Delta^{9(14)}$-dodecahydro phenantrene-1-one (VIII). At the same time a liquid isomer was separated which was characterized as 2,4-dinitro-phenyl hydrazone. By the action of methylmagnesium iodide on the mixture of the isomers of ketone (VIII) a carbinol mixture was obtained. It was found that the condensation previously described (Ref 2) of the dienone (I) with quinine proceeds more readily in acetic acid at room temperature. As a consequence of the endo-addition 2 isomeric adducts (IIa) and (IIb) are there formed (41 and 3%, respectively). The investigation of the steric model of dienone (I) proved that it can be occurring in two structures. There-

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Synthesis of Steroid Compounds and Related Substances. Communication 42. Condensation of 1-Vinyl-9-methyl-Δ^1-6-octalone With Quinone

fore the choice of the structure between the compounds (IIa) and (IIb) is preliminary and only valid under certain conditions. The reduction of (IIa) with zinc in acetic acid yielded the tetracyclic triketone (XIa) (70%). On a similar reduction of (IIb) the isomeric triketone (XIb) was obtained. Furthermore, the cis-triketone (XI) was isomerized using the better accessible α-isomer (XIa). In all experiments 3 isomers (XII), (XIII), and (XIV) were precipitated. Their behavior to each other is different with alkali or acid isomerization. A further problem was the protection of the 17a-keto group and the elimination of the 15-keto group. On heating of (XII) with excess ethylene ketal of the methylene ketone only the corresponding triethylene ketal (XV) was obtained (30-35%). Under the same conditions from (XIa) two products resulted: (XV) and diethylene ketal (XVI) (3 and 15%, respectively). On the formation of ethylene ketals from (XIa) (under acid conditions) the isomerization takes place in 2 directions, both towards C_{14} and C_{13}. It was proved that there is practically no selective

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SOV/62-59-2-16/40

Synthesis of Steroid Compounds and Related Substances. Communication 42. Condensation of 1-Vinyl-9-methyl-Δ^1-6-octalone With Quinone

protection in tetracyclic ketones of the type (XII) with a trans-position of the C- and D-rings. In the case of cis-ketones of type (XIa) this protection is of complex nature and is accompanied by the isomerization. There are 11 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

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