solvent was distilled, and the warm solution was poured into 2000 g. of ice and water containing 100 ml. of concentrated sulfuric acid. Filtration yielded 61.9 g. (expected, 61.8 g.) of white solid, m.p. 110–184°, infrared absorption (Nujol mull) at 2.90–3.05(s) OH but no band near 5.9. Crystallization of 6.08 g. of the diol from chloroform yielded 3.56 g. of fluffy white needles, m.p. 178–215°, 1.82 g. of light tan solid, m.p. 110–128°, 0.35 g. of light tan solid, m.p. 128–196°, and 0.34 g. of tan oil.[29] Repeated recrystallization of the diol raised the melting point considerably, but no satisfactory carbon–hydrogen analyses were obtained.

The dicarbethoxy derivative[30] of XIII was prepared: to a solution of 1.00 g. of the diol, m.p. 178–215°, in 20 ml. of dry pyridine cooled in an ice-bath was added dropwise with swirling 3 ml. of ethyl chloroformate (distilled Eastman Kodak Co. white label). During the addition the mixture turned from colorless to pink to deep red and a white solid formed. The mixture was allowed to stand at room temperature for five hours and then refluxed gently for one hour. The cooled mixture was poured onto 100 g. of ice and water and stirred well. After having been cooled in the refrigerator overnight, filtered, and dried, the white solid was crystallized from ethanol to yield 1.14 g. (80%) of small colorless plates, m.p. 156–159°. One recrystallization of the first crop from ethanol yielded 1.03 g. (72.5%) of the diester, m.p. 159–160°, infrared absorption (Nujol mull) at 5.72(s) C═O in $ROCO_2R$. The analytical sample, recrystallized several times from ethanol, melted at 159.8–161.3° (cor.).

Anal. Calcd. for $C_{24}H_{25}O_6Br$: C, 58.9; H, 5.1; Br, 16.3. Found: C, 58.8, 58.7; H, 5.1, 5.2; Br, 16.1, 16.2.

Alkaline hydrolysis of 0.150 g. of the diester yielded 0.100 g. of white solid, m.p. 206–222°. Three recrystallizations from warm N-methyl-2-pyrrolidone–water afforded 0.07 g. of XIII as short colorless fibers, m.p. 220–223°.

Anal. Calcd. for $C_{18}H_{17}O_2Br$: C, 62.6; H, 5.0; Br, 23.2. Found: C, 62.5; H, 5.0; Br, 23.3.

1-Bromobenzo[c]phenanthrene (XIV).—A mixture of 1.997 g. of XIII, m.p. 120–193°, 5 ml. of xylene (distilled Mallinckrodt analytical reagent) and 8 mg. of iodine was heated to the reflux temperature. Within a minute after refluxing started, the iodine color disappeared and water began to collect on the sides of the condenser. After 15 minutes all of the diol had dissolved leaving a light yellow solution. After the mixture had refluxed for 24 hours, an additional 4 mg. of iodine was added to the yellow solution. The iodine color again rapidly disappeared. After having been refluxed for a total of 120 hours, the deep red-brown solution was diluted with 1:1 ether benzene, washed with sodium bisulfite solution and treated in the usual manner. The resulting yellow-brown oil was purified by chromatography over alumina using first chloroform and then Skellysolve B. The desired product was contained in the first fractions to be eluted and was characterized by a dark gray-violet fluorescent band on the column when illuminated with ultraviolet light. Crystallization from chloroform–Skellysolve B yielded 1.08 g. of yellow crystals, m.p. 139.0–143.5°, and a yellow oil. Several recrystallizations of the crystals from chloroform–Skellysolve B afforded 0.96 g. (54%) of yellow XIV, m.p. 144–146°. A sample of XIV, purified for analysis by several recrystallizations from chloroform–Skellysolve B and then vacuum sublimation, formed pale yellow crystals, m.p. 146.8–147.3° (cor.); $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ (log E 4.66), 289 (4.76), 323 (3.96), 363 (2.61); $\lambda_{\min}$ 243 (4.00), 318 (3.94), 356 (2.56); points of inflection, 249 (4.03), 259 (4.18), 269 (4.39), 282 (4.66), 338 (3.62), 376 (2.34) and 382 (2.27).

Anal. Calcd. for $C_{18}H_{11}Br$: C, 70.4; H, 3.6; Br, 26.0. Found: C, 70.4, 70.2; H, 3.7, 3.6; Br, 26.2, 26.3.

The 2,4,5,7-tetranitrofluorenone complex[14] of XIV was prepared by mixing a hot solution of 100 mg. of XIV in acetic acid with a hot solution of 130 mg. of the nitro compound in acetic acid, concentrating the solution and cooling. The dark wine-red needles that crystallized were recrystallized several times from acetic acid to a constant m.p. of 192.3–193.5° (cor.). The nuclear magnetic resonance spectrum[16] of XIV showed no non-aromatic hydrogens.

Anal. Calcd. for $C_{31}H_{15}O_9N_4Br$: C, 55.8; H, 2.3; N, 8.4; Br, 12.0. Found: C, 56.1; H, 2.6; N, 8.6; Br, 12.0.

Various other methods of dehydration of XIII were tried. Thermal dehydration, thermal dehydration in the presence of an iodine crystal or thermal dehydration in the presence of potassium bisulfate all led to non-hydroxylic but high melting substances, which could not be converted by standard methods to XIV. Treatment of XIII with phenyl isocyanate, thionyl chloride in pyridine or pyrolysis of the dicarbethoxy derivative gave some non-crystalline dehydrated material but the results did not appear promising.

1-Cyanobenzo[c]phenanthrene.—A mixture of 0.500 g. of XIV, 0.258 g. of dry cuprous cyanide and 2.5 ml. of distilled N-methyl-2-pyrrolidone[17] was refluxed (b.p. 202°) for one hour. During this time the dark red-brown solution became dark brown in color and a brown precipitate formed. The cooled mixture was processed in a standard way to yield an oil which was chromatographed on alumina using benzene as eluent. The first 600 ml. contained the nitrile which had a brilliant violet fluorescence under ultraviolet light. Concentration of the solution and crystallization from benzene–ethanol yielded 0.310 g. of flat cream-colored crystals, m.p. 167–169°. Several recrystallizations from benzene–ethanol afforded 0.292 g. (71%) of flat cream-colored crystals, m.p. 169–171°. The analytical sample, recrystallized several times from benzene–ethanol, melted at 171.2–172.0° (cor.), infrared absorption 4.52-(w-m) CN (KBr wafer).

Anal. Calcd. for $C_{19}H_{11}N$: C, 90.1; H, 4.4; N, 5.5. Found: C, 90.4; H, 4.3; N, 5.5.

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[29] Lithium aluminum hydride reduction of the diketone resulted in the same kind of mixtures.

[30] L. F. Fieser, J. E. Herz, M. W. Kloko, M. A. Romero and T. Utne, THIS JOURNAL, **74**, 3309 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE]

Synthetic Studies on Resin Acids. III.[1] Synthesis of a Stereoisomer of Desisopropyldehydroabietic Acid

BY NARENDRA NATH SAHA, BEJOY KUMAR GANGULY AND PHANINDRA CHANDRA DUTTA[2]

RECEIVED NOVEMBER 20, 1958

The synthesis of an isomer of 1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid is described and the stereochemistry of this substance is discussed.

For the synthesis of the tricarbocyclic resin acids represented by abietic acid and its congeners, the tricyclic ketone I appears to be a potentially useful intermediate. This ketone was first synthesized by Stork, *et al.*,[3] by the cyclization of 2-(β-phenethyl)-3-methyl-Δ^2-cyclohexenone with phosphoric acid.

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[1] (a) N. N. Saha, B. K. Ganguly and P. C. Dutta, *Chemistry & Industry*, 412 (1956). Presented at a symposium at the Forest Research Institute, Dehradun, India, October 6, 1955. (b) Part II, U. Ghatak, N. N. Saha and P. C. Dutta, THIS JOURNAL, **79**, 4487 (1957).

[2] Communications regarding this paper should be sent to this author.

[3] G. Stork and A. Burgstahler, THIS JOURNAL, **73**, 3544 (1951).

We have described a new synthesis of the latter substance[4] and modified the cyclization conditions so as to obtain a product which readily undergoes condensation with ketonic reagents.[5] As a preliminary to exploring the synthetic potentiality of this ketone, we have recently developed two different methods[1b,4] complementary to each other, for converting a carbonyl function to the *gem*-methylcarboxylic acid residue, characteristic of resin acids. To test the stereochemical aspects of these methods, they were extended to 10-methyl-decalin-1-one,[1b] closely related to I, but the presence of the angular methyl group unexpectedly was found to modify the course of the reaction in both the ketones, ascribable to steric factors (*vide infra*). Synthetic studies with the ketone I, particularly the stereochemistry of the products derived therefrom, were complicated as it was present as a mixture of *cis* and *trans* forms.[6] The investigations described in this paper deal with the application of these two methods for the synthesis of an isomer of the acid IX. Moreover the four theoretically possible racemates represented by this structure have already been described,[1,7,8] but the stereochemical aspects have not been clearly defined so far (*vide infra*).

Condensation of the ketone I with ethyl cyanoacetate[9] gave the desired condensation product II in crystalline form in fairly good yield. Repeated attempts to isolate any other solid isomer have failed so far. The dicyano-ester III was obtained in very good yield through the addition of hydrocyanic acid to II and in a high degree of purity despite some initial difficulty due to the sparing solubility of II in ethanol. Here again the isolation of one form strongly suggests that the addition of the cyanide ion takes place from the less hindered side and consequently is stereospecific in nature. Hydrolysis of the dicyano-ester III with a water–sulfuric acid–acetic acid mixture under controlled conditions led to the anhydride IV in almost quantitative yield. The latter substance on treatment with sodium methoxide in methanol solution afforded the half-ester V, m.p. 186°, which was esterified with diazomethane. The partial hydrolysis of the resulting diester led to the isomeric half-ester VI, m.p. 185°. It is interesting to note that there was no depression in melting point on admixture of the two isomeric half-esters. However, the corresponding anilides showed a depression in m.p. on admixture. Their non-identity was further confirmed by their different crystalline forms and the course of reactions described in the sequel.

The sodium salt of the half-ester VI was converted to the silver-salt and subjected to Hünsdiecker degradation. On working up the reaction mixture it was found that the major part of the silver salt was decomposed with regeneration of the free acid. There was also concomitant substitution of bromine in the aromatic nucleus (*vide infra*). The neutral material is evidently the bromo-ester VII admixed with a product brominated in the aromatic nucleus. The neutral material was refluxed with zinc dust and acetic acid to remove aliphatic bromine. Analysis of the resulting material still indicated the presence of brominated material. Since the bromine was in the aromatic nucleus, its removal proved to be difficult. Attempts to remove it by reduction with lithium in liquid ammonia and reoxidation of the crude product with lead tetraacetate did not yield satisfactory results. Clemmensen reduction for a prolonged period was also unsuccessful. Success finally was achieved by refluxing with zinc dust and acetamide[10] whereby the methyl ester VIII was obtained as shiny flakes. The ester VIII also was obtained pure through chromatography, indicating that no rearrangement had taken place during treatment with zinc–acetamide at a high temperature. The over-all yield of the ester VIII was disappointingly poor because of the regeneration of about 50% of the acid during the Hünsdiecker degradation, and because of the formation of other by-products. Hydrolysis under mild conditions failed, and it was therefore possible to discard the remote possibility that the ester possesses structure XII, which would have been expected if VI were identical with V. The ester VIII was hydrolyzed with butyl alcoholic potassium hydroxide,[11] affording the free acid IX, m.p. 146–147°.

Through oxidation with chromic acid, an ingenious method[12] has been developed to determine the nature of the A/B ring-junction in tricarbocyclic diterpenoid resin acids incorporating an octahydrophenanthrene nucleus. On applying this diagnostic procedure, the ester VIII afforded a yellow α-diketo-ester XIII, m.p. 185–187°. This established the *cis* junction of rings A and B in IX. The formation of the anhydride IV on hydrolysis of the dicyano-ester III also can be reconciled somewhat better from consideration of models if rings A and B are *cis* locked. The steric configuration of the carboxyl group in IX must belong to the abietic acid series because it differs from the isomeric acids melting at 232–233°[8] and 206–207° which have been correlated with the podocarpic acid system and which possess the *trans* and *cis* junctions of rings A and B, respectively.[13] The synthetic acid hence is represented by the stereo-formula

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[4] N. N. Saha, P. Bagchi and P. C. Dutta, *Chemistry & Industry*, 1143 (1954); THIS JOURNAL, **77**, 3408 (1955). The intermediate isobutyl enol ether, (2-(β-phenethyl)-3-ketocyclohexenyl isobutyl ether), previously reported as a liquid, has now been obtained as a crystalline solid with m.p. 82°.

[5] The statement of G. Stork, *Chemistry & Industry*, 1429 (1954), particularly the word "identical" needs no comment, as is apparent from the description of our work given in the paper referred to in footnote 4.

[6] (a) N. N. Saha, Thesis, 1953, Calcutta University; (b) J. A. Barltrop and N. A. J. Rogers, *J. Chem. Soc.*, 2566 (1958), and references cited therein. (c) The preponderance of the *cis* form may arise from the combination of two factors operating in the same direction; *viz.* (i) the presence of the aromatic ring fixes the double-bond and hence stabilizes *cis* juncture in substituted octalins (D. A. H. Taylor, *Chemistry & Industry*, 250 (1954)) and (ii) the presence of the angular methyl group lowers to a great extent the energy difference between *cis* and *trans* forms (R. B. Turner, THIS JOURNAL, **74**, 2118 (1952), and F. Sondheimer and D. Rosenthal, *ibid.*, **80**, 3995 (1958)).

[7] W. E. Parham, E. L. Wheeler and R. M. Dodson, *ibid.*, **77**, 1166 (1955).

[8] R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939).

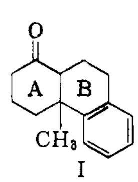
[9] E. J. Cragoe, Jr., C. M. Robb and J. M. Sprague, *J. Org. Chem.*, **15**, 381 (1950).

[10] D. Heyl and A. C. Cope, THIS JOURNAL, **65**, 669 (1943).

[11] W. P. Campbell and D. Todd, *ibid.*, **64**, 928 (1942).

[12] E. Wenkert and B. G. Jackson, *ibid.*, **80**, 211 (1958).

[13] U. R. Ghatak, *Tetrahedron Letters*, 19 (1959).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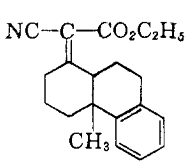
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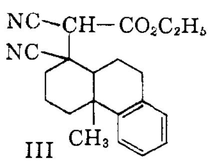
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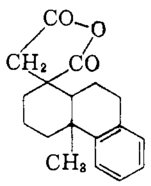
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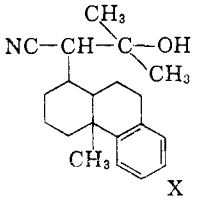
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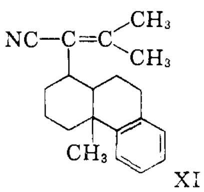
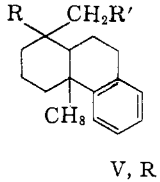
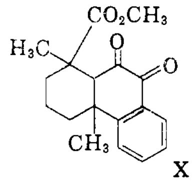
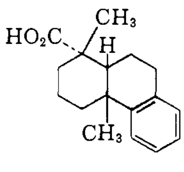

XI




XIII

V, R = CO_2H, R′ = CO_2CH_3
VI, R = CO_2CH_3, R′ = CO_2H
VII, R = CO_2CH_3, R′ = Br
VIII, R = CO_2CH_3, R′ = H
IX, R = CO_2H, R′ = H
XII, R = H, R′ = CO_2H



In order to obtain the C_1-epimer of the above acid, the conjugate addition of methylmagnesium iodide to the unsaturated cyano-ester II in the presence of cuprous iodide was attempted. This reaction led to a crystalline material which was isolated in 37% yield. From the elemental analyses, infrared data and the comparatively high melting point of the compound, the possibility that it was the desired addition product was ruled out. The infrared spectrum of the compound indicated a cyano band (4.4 μ), a weak hydroxyl band (2.9 μ), another weak band (6.2 μ) ascribed to the aromatic ring, but no absorption in the carbonyl region. On the basis of the results available from detailed studies on the unsaturated cyano-ester[1b] from 10-methyldecalin-1-one, X was accepted as the most probable structure, arising through reduction of the double bond and subsequent reaction of the carbethoxyl group with the Grignard reagent. From the percentage composition of carbon it was difficult to decide whether addition of a methyl group across the double bond had taken place, but the corresponding value for hydrogen was more in favor of the accepted formula, originating from simple reduction of the double bond. The compound exhibits strong end-absorption (λ_{max}^{alc} 215 mμ, log ε 4.0), arising mainly from the tetralin moiety. The mechanism of reduction is not clear unless the transition state complex abstracted a proton from ether which was present in the solvent. To have further confirmation of this formula, the substance was dehydrated with phosphorus pentoxide, leading to XI. The latter compound had high intensity absorption in the ultraviolet (λ_{max}^{alc} 215 mμ, log ε 4.25), characteristic of the α,β-unsaturated nitrile,[14] taking into account the absorption due to the tetralin chromophore. Attempts to oxidize XI with ozone or chromic acid so far have failed to afford any recognizable material. Having failed to achieve the desired objective, it appeared that alkylation of appropriate α,β-unsaturated acids and ketones would be more attractive in order to have better control of the stereochemistry at C_1 and investigations are in progress along these lines.

Acknowledgments.—Grateful thanks are due to Prof. F. Sondheimer, Weizmann Institute of Science, Rehovoth, Israel, for kindly reading this manuscript. Micro-analyses have been carried out by Mrs. Chhabi Dutta at the micro-chemical laboratory of the University College of Science and Technology, Calcutta. Infrared measurements were carried out by Dr. N. K. Bhattacharyya at Iowa State College, Ames, Iowa. Thanks are also due to Dr. U. R. Ghatak for his material assistance during this investigation.

Experimental[15]

Ethyl 4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrylidene-1-cyanoacetate (II).—A mixture of the tricyclic ketone I (71.5 g.), ethyl cyanoacetate (75.5 g.), glacial acetic acid (32 ml.), benzene (133 ml.) and ammonium acetate (6 g.) was refluxed in a water separator for 60 hours. During this period, 5-g. lots (total 25 g.) of ammonium acetate were added after every 12 hours. It finally afforded a pale-yellow viscous liquid, b.p. 200–205° (0.4 mm.). The yield was 73 g. (72%). This was dissolved in hot absolute ethanol and was allowed to crystallize in the cold. The separated solid (10 g., m.p. 120–123°) was collected and washed with ethanol to remove any adhering oil. The alcoholic mother liquors were again distilled in high vacuum after removal of the solvent and the distilled oil on crystallization from ethanol in the cold yielded another 7 g. of crystals with m.p. 118–123°. By carrying out this process repeatedly the total yield of the crystalline solid collected was 40 g. (38.8%). A part of the substance was recrystallized from ethanol in which it was slightly soluble in the cold, until the melting point rose to 128–129° (λ_{max}^{alc} 239 mμ, log ε 4.1).

Anal. Calcd. for $C_{20}H_{23}O_2N$: C, 77.6; H, 7.4. Found: C, 77.7; H, 7.3.

Ethyl 4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-cyano-1-cyanoacetate (III).—Sodium cyanide (3.7 g.) dissolved in the smallest quantity of water and diluted with 50 ml. of ethanol was added to the above unsaturated cyano-ester II (7 g.) in ethanol (140 ml.), with thorough shaking at 55–60°. After 5 minutes, concentrated hydrochloric acid (4.5 ml.) was added to the cooled solution. Next it was extracted with chloroform on acidification after standing in the cold for 0.5 hour and the chloroform extract was washed thoroughly with water and dried. After removal of the last traces of the solvent in high vacuum, the gummy residue was treated with ethyl acetate, whereupon shiny needles (4 g.) with m.p. 142° separated on cooling. The mother liquors were concentrated and another crop of crystals (0.8 g.) was obtained. Ethyl acetate was com-

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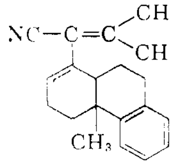
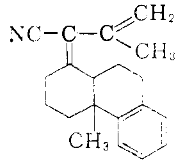
[14] E. A. Braude and O. H. Wheeler, *J. Chem. Soc.*, 320 (1955). If the reduction of the double-bond in II had not taken place during Grignard reaction, XI would have been represented by the following structures and the diene system could be detected easily in the ultraviolet.



or



[15] All boiling points and melting points are uncorrected.

pletely removed from the mother liquor and the gummy residue on trituration with ethanol yielded crystals of the unsaturated cyano-ester II. These crystals and the gummy mass were combined and were treated again with a solution of sodium cyanide (1.3 g.) in the usual way, and further quantity of the dicyano-ester (1.6 g.) was collected. The over-all yield was 6.4 g. (84%). An analytical sample was prepared on repeated crystallization from ethyl acetate, m.p. 144–145°.

Anal. Calcd. for $C_{21}H_{24}O_2N_2$: C, 75.0; H, 7.1. Found: C, 75.3; H, 7.2.

Anhydride of 4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic-1-acetic Acid (IV).—The above dicyano-ester (6.3 g.) was added to a solution of concentrated sulfuric acid (24 ml.), water (24 ml.) and glacial acetic acid (24 ml.). On refluxing slowly in a paraffin-bath, the dicyanoester gradually went into solution and a highly crystalline solid then separated slowly. On further heating, the solution became slightly brown and the crystals went into solution with decomposition. After about 7 hours heating the reaction mixture was cooled and poured into ice-water. The separated solid, 4.4 g. (82.6%), was collected, washed several times with water and dried, m.p. 188–190°. It crystallized from glacial acetic acid as shiny flakes with m.p. 189–190°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.0; H, 7.0. Found: C, 76.3; H, 7.3.

4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbomethoxymethyl-1-carboxylic Acid (V).—The above anhydride (8.4 g.) was added to a solution of sodium methoxide prepared from sodium (1 g.) and absolute methanol (25 ml.). The mixture was refluxed for 3 hours and finally diluted with water. Steam was passed into the aqueous solution to remove methanol, and the filtered solution was acidified with concentrated hydrochloric acid with constant shaking, whereupon a semi-solid mass separated. The latter was collected, washed with water and kept in the cold for some time. The semi-solid mass hardened and was crushed to a powder, 9.3 g. (99.5%), m.p. 172–173°. On crystallization from methanol and finally from ethyl acetate it showed m.p. 186°.

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.1; H, 7.5. Found: C, 71.9; H, 7.2.

The anilide on crystallization from ethanol separated in small flakes, m.p. 191–192°.

Anal. Calcd. for $C_{25}H_{29}O_3N$: C, 76.7; H, 7.4. Found: C, 76.5; H, 7.6.

4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbomethoxy-1-acetic Acid (VI).—The above half-ester (3.2 g.) was dissolved in methanol and esterified with an ethereal solution of diazomethane. On removal of the solvents, the gummy residue was distilled giving a colorless highly viscous mass (3 g.), b.p. 200–205° (0.4 mm.). This was treated with a solution of potassium hydroxide (0.66 g.) in water (0.7 ml.) and methanol (13.2 ml.). The solution was allowed to stand for 2 hours at room temperature and then for 2 hours on the boiling water-bath. Steam was passed through the acidified solution to remove methanol. The reaction mixture then was extracted several times with ether and the ethereal extract was washed with 5% aqueous sodium carbonate solution. On acidification of the alkaline extract, a white crystalline solid (2.7 g., 84%) separated, which on crystallization from ethyl acetate showed m.p. 185°.

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.1; H, 7.5. Found: C, 71.9; H, 7.6.

The anilide, on crystallization from ethanol, gave needles with m.p. 195–196°. The mixed melting point of the two anilides was 185–194°.

Anal. Calcd. for $C_{25}H_{29}O_3N$: C, 76.7; H, 7.4. Found: C, 76.5; H, 7.5.

Methyl 1,4a-Dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (VIII).—The above ester-acid (8 g.) in methanol (180 ml.) was neutralized with *N* sodium hydroxide solution (phenolphthalein). Silver nitrate (4.4 g.) in water (100 ml.) was added with stirring and the silver salt so obtained was washed several times with distilled water until free from nitrate. It then was dried in an air-oven and finally in vacuum (6 mm.) at 90–100° for 3 hours. The silver salt (10 g.) became slightly pasty when hot but resolidified on cooling. It was divided into two portions.

(i) The silver salt (5 g.) was suspended in dry carbon tetrachloride (100 ml.) and bromine (1.2 ml., 2 moles) in carbon tetrachloride (10 ml.) was added to the boiling mixture with vigorous stirring. The mixture was refluxed with stirring until the color of bromine disappeared from the refluxing solvent in the condenser. There was a copious evolution of hydrogen bromide. The reaction mixture was cooled, filtered and the filtrate was washed with water and repeatedly with 5% aqueous sodium carbonate solution until all acidic matter was removed completely. The alkaline extract was acidified and the acidic material was collected and kept for subsequent treatment. On removal of the carbon tetrachloride, a gummy mass was obtained, which on drying in vacuum at 100° weighed 1.8 g. This was dissolved in glacial acetic acid (20 ml.) and refluxed for 7 hours after addition of zinc dust (4 g.). It then was cooled, diluted with a large volume of water and extracted with ether. The ethereal extract was repeatedly washed with 5% aqueous sodium carbonate solution until neutral. On removal of the solvent, a gummy residue (0.9 g.) containing bromine was obtained.

(ii) The degradation of the silver salt (5 g.) was also carried out using bromine (0.75 ml., 1.25 moles). The neutral material (1.5 g.) on subsequent reduction with zinc dust and acetic acid yielded again a gummy residue (0.9 g.) which still contained bromine.

The bromine-containing materials (1.8 g.) from both experiments were mixed with freshly distilled acetamide (3 g.) and heated until a clear mobile liquid was obtained. Zinc dust (1.8 g.) was added and the thoroughly mixed reaction mixture was heated in a metal-bath at 200–205° for 3 hours. It was cooled, decomposed with hydrochloric acid (1:1) and diluted with water. The mixture was extracted with ether, and the ethereal extract was washed successively with 5% aqueous sodium carbonate solution and thoroughly with water. On removal of ether, a viscous liquid was obtained which was distilled at 0.2 mm. (bath-temperature 130–140°). The colorless viscous distillate was triturated with petroleum ether (40–60°), whereupon a white crystalline solid separated which showed m.p. 84–86°. This on careful fractional crystallization from methanol afforded two successive crops of crystals with m.p. 88–89° and 85–86°, respectively. The total yield was about 250 mg. This was recrystallized from methanol whereupon shiny flakes with m.p. 90–91° were obtained.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.4; H, 8.5. Found: C, 79.1; H, 8.6.

The recovered total acidic material (4.4 g.) from the bromine–silver salt reaction described above was dissolved in methanol and esterified with diazomethane. The residue after the removal of solvent was dissolved in acetic acid (20 ml.) and refluxed for 3 hours with zinc dust (4 g.) to remove bromine in the tetralin nucleus, if any. The neutral material was isolated in the usual way and was hydrolyzed partially as before. The dried silver salt (3.7 g.) finally afforded a gummy product (*ca.* 500 mg.), which yielded a further 100 mg. with m.p. 89–90°.

The recovered acidic material (1.9 g.) was again recycled as before and finally a small amount of the methyl ester (15 mg., m.p. 88–89°) was obtained. The over-all yield was 365 mg. (5.3%).

1,4a-Dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic Acid (IX).—The above methyl ester (300 mg.), recovered from an unsuccessful attempt at hydrolysis with 10% methanolic potassium hydroxide, was refluxed with a solution of potassium hydroxide (0.62 g.) in *n*-butyl alcohol (6.2 ml.) for 8 hours. The light yellow solution was diluted with water and steam was passed in to remove most of the butanol. The neutral material was removed by extraction with ether. The clear alkaline filtrate on acidification gave a white crystalline material (250 mg., 88%), m.p. 132–133°. The pure acid was obtained after repeated recrystallizations from absolute methanol as thick needles, m.p. 146–147° (previously[1a] reported m.p. 135–136°).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.0; H, 8.5. Found: C, 79.16, 79.09; H, 8.44, 8.54.

β-Hydroxy-β-methyl-α-(4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1)-butyronitrile (X).—Methylmagnesium iodide (prepared from 3 g. of magnesium and 8 ml.

of methyl iodide in 50 ml. of ether) was diluted with thiophene-free benzene (50 ml.) and most of the ether then was distilled off. Dry cuprous iodide (0.75 g.) now was added with vigorous stirring to the hot solution. The mixture was cooled in ice and a solution of the unsaturated cyanoester V (9 g.) in benzene (60 ml.) was gradually added with stirring. After being allowed to stand in an ice-bath for 0.5 hour, the reaction mixture was refluxed for 2 hours and finally decomposed with ice-cold dilute hydrochloric acid. On working up and removal of the solvent, the residue was crystallized from ethyl acetate, affording needles, 3.2 g. (37%), m.p. 169–170°. On recrystallization from the same solvent, the substance showed m.p. 171–172°. The sample was dried at 100° (0.01 mm.) for 6 hours.

Anal. Calcd. for $C_{20}H_{27}ON$: C, 80.8; H, 9.1; N, 4.7. $C_{21}H_{29}ON$ (methyl-addition compound): C, 81.0; H, 9.3; N, 4.5. Found: C, 80.7, 80.8; H, 8.7, 8.6; N, 4.9.

β,β-Dimethyl-α-(4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1)-acrylonitrile (XI).—The above hydroxy-compound (300 mg.) was dissolved in benzene (20 ml.) and the last traces of moisture were removed through distilling off 15 ml. of the solvent. Phosphorus pentoxide (400 mg.) was added and the reaction mixture was refluxed for 2 hours. The benzene extract was washed with a solution of sodium hydroxide, dried and evaporated. The residue crystallized on trituration with ethyl acetate. An oily impurity was removed on a porous plate and the resulting solid was crystallized repeatedly from the same solvent to yield 50 mg. (17.7%), m.p. 128–129°.

Anal. Calcd. for $C_{20}H_{25}N$: C, 86.0; H, 8.9. $C_{21}H_{27}N$ (methyl-addition compound): C, 86.0; H, 9.3. Found: C, 86.3; H, 8.6.

Methyl 1,4a-Dimethyl-9,10-diketo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (XIII).—To a solution of the ester VIII (310 mg.) in glacial acetic acid (3 ml.) was added a solution of chromic anhydride (390 mg.) in water (1 ml.) and acetic acid (3.5 ml.). The mixture was left, with occasional swirling, for 18 hours at room temperature (28–30°). The light-green reaction mixture was diluted with water (25 ml.), the solution was saturated with sodium chloride and extracted with chloroform (3 × 20 ml.). The light-yellow chloroform extract was washed with water, cold sodium hydroxide solution (5%; 2 × 10 ml.) and finally with water until neutral. The chloroform extract was dried over sodium sulfate and evaporated. Trituration of the residue with ethyl acetate–petroleum ether (40–60°), yielded shiny yellow crystals, m.p. 178–179°, contaminated with some oily material. After three recrystallizations from the same solvent mixture, yellow prisms, 75 mg. (22%), with m.p. 185–187° were obtained.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.6. Found: C, 72.2; H, 6.8.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Oxetanes. VIII. Synthesis and Reactions of 2-Oxaspiro[3,2]hexane[1,2]

BY SCOTT SEARLES, JR., AND EUGENE F. LUTZ

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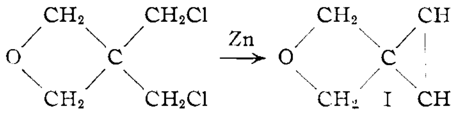
The preparation of the highly strained oxetane, 2-oxaspiro[3,2]hexane, is described. In its reactions with lithium aluminum hydride, hydrochloric acid, hydrogen bromide, oxygen and bromine enhanced reactivity of both rings appeared to be shown.

Few simple spiro compounds consisting of two small, strained rings, are known and practically nothing is known of their chemical reactivity. Considerable attention has been devoted to the synthesis of spiropentane,[3,4] the most strained such spiro compound, but only one reaction has been reported, catalytic hydrogenation to (mainly) 1,1-dimethylcyclopropane.[5] This result suggests that the additional strain of the spirane structure enhanced the ease of hydrogenolysis.

2-Oxaspiro[3,2]hexane (I) would be expected to be almost as strained as spiropentane but would have the advantage of a reactive ether linkage for study of reactivity. This compound has been synthesized now and some of its chemical reactions studied.

It was prepared in 25% yield by the reaction of 3,3-bis-(chloromethyl)-oxetane with zinc dust in molten acetamide according to a procedure similar to that used by Murray and Stevenson for the synthesis of spiropentane.[3] The product is a volatile, water-soluble liquid, boiling at 97°.



The main cause for low yield was undoubtedly the intermolecular condensation of 3,3-bis-(chloromethyl)-oxetane, but two side products resulting from ring enlargement were obtained in low yield. Cyclopentanone (II) was identified positively by its characteristic infrared absorption[6] and by isolation of its 2,4-DNP derivative. 1-Cyclobutenemethanol (III) also appeared to be present, as judged by the infrared spectrum containing absorption bands characteristic of a primary hydroxyl group and a double bond (unfortunately, a strong broad band at 902 cm.$^{-1}$ obscured any possible cyclobutane absorptions[7] that may have been present) and practically identical to those found in another preparation of this compound (see below).

It is believed that these products were formed from the Lewis acid-catalyzed rearrangement of the initially formed 2-oxaspiro[3,2]hexane by a sequence such as shown in I–II–III.

Although sodium carbonate was used to remove the zinc chloride as it was formed in the reaction, it seems likely that there could be some opportunity for zinc chloride or $ZnCl^{\oplus}$ to act on the molecule from which it was formed before interacting with

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[1] A portion of a dissertation presented by E. F. Lutz (1958) in partial fulfillment for the degree of Doctor of Philosophy in Chemistry at Kansas State College. Presented at the Southwest Regional Meeting American Chemical Society, December 5, 1957.

[2] (a) Supported in large part by a research grant from the National Science Foundation for which grateful acknowledgment is made. (b) The preceding paper in the series was S. Searles, K. A. Pollart and F. Block, THIS JOURNAL, **79**, 952 (1957).

[3] M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944).

[4] V. A. Slabey, *ibid.*, **68**, 1335 (1946).

[5] V. A. Slabey, *ibid.*, **69**, 475 (1947).

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 128.

[7] *Ibid.*, p. 28.