adduct from benzene produced 3.5 g. (81%) of 6-methyl-$\Delta^{6,9(10)}$-hexahydronaphthalene-2,3-dicarboxylic anhydride (XI), m.p. 132–133.5°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42; sapn. equiv., 109. Found: C, 71.31; H, 6.28; sapn. equiv., 107.

Acidification of the solution from the determination of the saponification equivalent of XI produced 6-methyl-$\Delta^{6,9(10)}$-hexahydronaphthalene-2,3-dicarboxylic acid, m.p. 226–228°.

6-Methyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic Acid (XII).—A solution of 2.0 g. (0.02 mole) of acetylenedicarboxylic acid in 25 ml. of benzene was heated under reflux in a 50-ml. flask. To this hot solution was added 2.4 g. (0.02 mole) of 4-methyl-1,2-dimethylene-4-cyclohexene (VIII) and the reaction mixture was heated for 3 hours. The benzene was removed by evaporation and the solid residue was purified by dissolving in a sodium carbonate solution, followed by treatment with charcoal and reprecipitation with dilute hydrochloric acid, to yield 3.5 g. (82%) of 6-methyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (XII), m.p. 152–153°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.38; H, 5.76.

Catalytic Isomerization of 4-Methyl-1,2-dimethylene-4-cyclohexene (VIII).—A mixture of 3.0 g. (0.025 mole) of 4-methyl-1,2-dimethylene-4-cyclohexene (VIII) and 0.5 g. of 5% palladium-on-charcoal was heated under reflux for 24 hours. The catalyst was removed by filtration to yield 2.8 g. (93%) of pseudocumene (XIII), $n^{25}D$ 1.5050. The liquid pseudocumene was identified by conversion to two solid derivatives.

Addition of an alcoholic solution of picric acid to a few drops of the sample of XIII produced a yellow precipitate of pseudocumene picrate, m.p. 95–97° (reported[13] m.p. 97°). A mixed melting point with an authentic sample of pseudocumene picrate also occurred at 95–97°.

A few drops of the sample of pseudocumene was added to a mixture of 1 ml. of fuming nitric acid and 2 ml. of concentrated sulfuric acid. The solution was heated to boiling for 1 minute and then poured into ice-water. The resulting precipitate was removed by filtration and recrystallized from alcohol to yield 3,5-dinitropseudocumene (XIV), m.p. 170–172° (reported m.p.[14] 171–172°). A mixed melting point with an authentic sample of XIV showed no depression.

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[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 218.

[14] G. Schultz, *Ber.*, **42**, 3607 (1909).

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

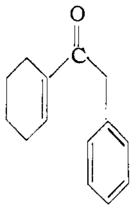
12-Alkyloctahydrophenanthrenes Related to Dehydroabietic Acid

BY WILLIAM E. PARHAM, EDWARD L. WHEELER[1,2] AND R. M. DODSON

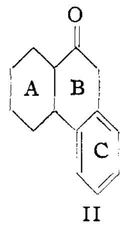
RECEIVED APRIL 26, 1954

The synthesis is described of octahydrophenanthrenes with angular alkyl groups at C-12, especially 1,12-dimethyl-1-carboxy-1,2,3,4,9,10,11,12-octahydrophenanthrenes related to dehydroabietic acid.

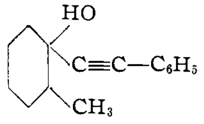
Gutsche and Johnson[3] found that when the α,β-unsaturated ketone I was treated with dry hydrogen chloride and aluminum chloride in refluxing benzene,[4] a mixture of *cis-* and *trans*-10-keto-1,2,3,4,9,10,11,12-octahydrophenanthrene (II) was formed in about 5% yield. This paper describes an extension of this reaction to the synthesis of octahydrophenanthrenes containing angular alkyl groups at C-12, with particular reference to 1,12-dimethyl-1-carboxy-1,2,3,4,9,10,11,12-octahydrophenanthrenes related to dehydroabietic acid.



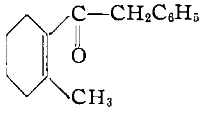
I



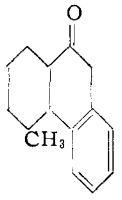
II



III



IV



V

The action of formic acid on III, prepared in 68% yield from 2-methylcyclohexanone and phenylacetylene, gave a liquid ketone (IV) in 68% yield. The ultraviolet spectrum of this ketone showed a maximum in agreement with that calculated[5] for IV, but a molar extinction coefficient of one-half that of I. The ultraviolet spectrum of the semicarbazone of IV showed a pronounced hump on the benzenoid absorption, and there was a point of inflection between 233 and 240 mμ. By subtracting the absorption due to the benzene ring, an estimated maximum at 240 mμ (ε 10,000) was obtained. These results agree closely with the data reported by Turner and Voitle[6] for 1-acetylcyclohexene and 2-methyl-1-acetylcyclohexene, and there can be little doubt that the same explanation obtains for these two cases. Absorption due to the carbonyl group in I is found at 1670 cm.$^{-1}$. In IV the carbonyl band is at 1690 cm.$^{-1}$, with a hump at 1705 cm.$^{-1}$, indicating that a small amount of the unconjugated β,γ-unsaturated ketone was present.[6] In view of the steric hindrance in IV, the observed shift in carbonyl absorption in the infrared spectrum is consistent with the interpretation given for the ultraviolet spectrum.[6] A single semicarbazone was obtained from IV, which is further

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[1] From the Ph.D. Thesis of Edward L. Wheeler, University of Minnesota, 1953.

[2] Parke, Davis Fellow, 1952–1953. Part of this work was sponsored by the Greater University Fund of the University of Minnesota.

[3] C. D. Gutsche and W. S. Johnson, THIS JOURNAL, **68**, 2239 (1946).

[4] These conditions are not those normally employed for the Bogert–Cook reaction.

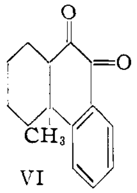
[5] R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 76 (1952).

[6] R. B. Turner and D. M. Voitle, *ibid.*, **73**, 1403 (1951).

evidence that there is only a small amount of unconjugated ketone present.

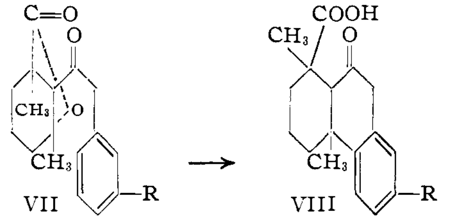
The preparation of 10-keto-1,2,3,4,9,10,11,12-octahydrophenanthrene (II) by the procedure previously described by Gutsche and Johnson[3] was repeated, and results essentially identical to those reported were obtained.[7] 2-Methyl-1-phenylacetylcyclohexene (IV) was subjected to the same cyclization reaction, and 10-keto-12-methyl-1,2,3,4,9,10,11,12-octahydrophenanthrene (V) was obtained in 72% yield. The semicarbazone of V was prepared in good yield, and only one isomer was evident; m.p. 220–221°. It would appear that the energy difference between the *cis* and *trans* form of V has been increased, relative to II, so that at equilibrium a single isomer predominates.

The ketone V was oxidized very slowly by air to a compound $C_{15}H_{16}O_2$, which has been formulated as VI or the corresponding enol. The infrared spectrum of this product showed a moderately strong hydroxyl band at 3400 cm.$^{-1}$, a strong carbonyl band at 1650 cm.$^{-1}$, and strong bands at 1605 and 1575 cm.$^{-1}$. These data are more consistent with the enol formulation.



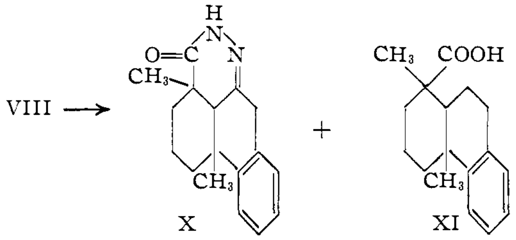
VI

When the ketolactone VII[8] (R = H) was cyclized using the conditions previously described for I and IV, a 56% yield of a solid ketoacid (VIII) was obtained, which did not isomerize by reaction with base. Although the cyclization of VII or its stereomer could lead to four racemic keto acids, the isolation of a single[9] keto acid was not unexpected, for the presence of the carbonyl group at C-10 should permit facile epimerization at C-11 to the sterically favored isomer.



VII VIII

Reduction of the keto acid obtained from VII, by the Wolff–Kishner procedure, gave one neutral product (m.p. 230–231°, 40–55% yield) and small amounts of two acids (m.p. 205–207° and 186–187.5°, respectively). The neutral product has been assigned the structure of the expected pyridazone X, on the basis of its composition and spectra. Of the two acids, XI the higher melting one was the major product. That these acids were not isomorphic mixtures was not established, but it is evident that there must have been at least two isomeric acids formed. The formation of two acids can be rationalized by admitting epimerization at C-11 during the reduction. The composition, neutralization equivalent and spectra of these acids are consistent with structure XI; the spectra of these acids are quite similar to that of dehydroabietic acid.



X XI

When the isopropyl ketolactone VII (R = isopropyl)[10] was cyclized under the same conditions described for VII (R = H), a 70% yield of a ketoacid VIII was obtained which proved to be identical to the acid obtained from VII (R = H). Thus, the action of aluminum chloride and hydrogen chloride in boiling benzene caused a reverse Friedel–Crafts reaction with elimination of the isopropyl group. When the cyclization of VII (R = isopropyl) was carried out at room temperature, using just aluminum chloride as catalyst, the same keto-acid was obtained, although in only 40% yield. Reduction of the product by the Wolf–Kishner procedure gave the same three products previously obtained from the keto acid derived from VII (R = H).

When dehydroabietic acid was treated under conditions similar to those used for the cyclization of VII, the isopropyl group was cleaved from the molecule and an acid (m.p. 159–160°) was obtained which has been assigned structure XI on the basis of its composition, neutralization equivalent, and spectra. This acid differed from the two acids derived from VIII; however, no definite conclusion can be drawn concerning its structure.[11]

Preliminary attempts have been made to effect cyclization of VII (R = isopropyl) to VIII with retention of the isopropyl group. When the lactone was treated with polyphosphoric acid, a neutral product with the empirical formula $C_{20}H_{24}O_2$ was obtained in 66% yield. The analysis and spectra of this product indicated it to be the enol lactone XII.

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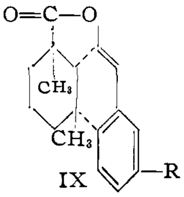
[7] In addition to the principal semicarbazone (5% yield, m.p. 219–220°), there was obtained two isomeric products (m.p. 199–200° dec. and 209–210° dec.); however, owing to the small quantities available, the purity of these products was not established.

[8] W. E. Parham, E. L. Wheeler, R. M. Dodson and S. W. Fenton, THIS JOURNAL, **76**, 5380 (1954).

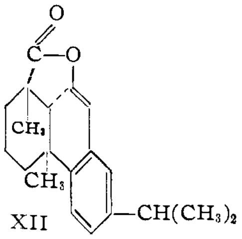
[9] A small amount of a second product was obtained from this reaction. The composition and spectra of this material suggest that it is the enol lactone IX derived from VIII. The low molar extinction coefficient (λ_{max} 270, ϵ 6900) would be evidence that the carbon–carbon double bond has been forced out of the plane of the benzene ring (compare with XII), and this would occur when there is a *cis* fusion of the A and B rings. The formation of an enol-lactone from the other racemic keto acid with *cis* ring fusion of the A and B rings is sterically improbable. The infrared spectrum of this lactone shows a lactone-carbonyl absorption at 1825 cm.$^{-1}$ and another strong band at 1705 cm.$^{-1}$, which is probably due to the carbon–carbon double bond.[8]



IX

[10] *Cf.* ref. 8 for a discussion of the stereochemistry of the lactone VII (R = H, isopropyl).

[11] The acid obtained by R. D. Haworth and R. L. Barker (*J. Chem. Soc.*, 1299 (1939)), which was assigned structure XI, melts at 233°.



XII

The ultraviolet spectrum of this lactone showed a maximum at 272 mμ (ε 12,200), and the infrared spectrum showed strong bands at 1830 and 1700 cm.$^{-1}$. The high extinction coefficient for the carbon–carbon absorption is evidence that the double bond is less strained (more in the plane of the benzene ring) than would be possible[12] in XII with a *cis* ring fusion between rings A and B. The formation of an enol-lactone from the other racemic keto acid VIII with rings A and B fused *trans* is sterically improbable.

Experimental

2-Methyl-1-(1-phenylethynyl)-cyclohexanol (III).—A solution of 2-methylcyclohexanone[13] (56.8 g., 0.50 mole, b.p. 71–73° (32 mm.), n^{20}D 1.4499) in anhydrous ether (50 ml.) was added over a two-hour period to a cold (15°), well stirred, solution of potassium phenylacetylide, prepared from potassium (19.6 g., 0.50 g. atom), *t*-butyl alcohol (350 ml.), phenylacetylene (51 g., 0.50 mole) and ether (200 ml.). The mixture was heated at the reflux temperature for 90 minutes, then cooled, and cold 10% hydrochloric acid was added until the solution was just acid to litmus. The ether and aqueous layers were separated, and the ether extracts were dried over sodium sulfate. The ether and *t*-butyl alcohol were removed by distillation and the residual solid was recrystallized from petroleum ether (60–68°) to give 73 g. (68%) of III, melting at 85.5–87°. The product melted at 87–87.5° after further recrystallization from petroleum ether.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.40. Found: C, 84.2; H, 8.48.

2-Methyl-1-phenylacetylcyclohexene (IV).—A mixture of III (69 g., 0.32 mole) and formic acid (87–90%, 350 ml.) was heated at the reflux temperature for 75 minutes. The mixture was then cooled and neutralized with 10% aqueous sodium hydroxide. The water-insoluble oil was extracted with ether, dried (sodium sulfate) and distilled to give 43.7 g. (63%) of IV (b.p. 110–112° (0.3 mm.), n^{20}D 1.5490).

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.40. Found: C, 84.0; H, 8.64.

The semicarbazone of IV (m.p. 175–175.5°) was recrystallized from ethanol–water.

Anal. Calcd. for $C_{16}H_{21}ON_3$: C, 70.8; H, 7.70. Found: C, 70.75; H, 7.85.

10-Keto-12-methyl-1,2,3,4,9,10,11,12-octahydrophenanthrene (V).—The procedure used was essentially the same as that described by Gutsche and Johnson[3] for the cyclization of 1-phenylacetylcyclohexene (I). The oil obtained from 10 g. of IV was fractionally distilled to give 7.2 g. of V (n^{20}D 1.5600–1.5616) boiling at 110–115° (0.2 mm.). A sample boiling at 111 (0.2 mm.), n^{20}D 1.5602, was analyzed.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.06; H, 8.46. Found: C, 83.80; H, 8.66.

The semicarbazone of V, prepared from the product (n^{20}D 1.5600–1.5616), semicarbazide hydrochloride and sodium acetate in ethanol–water, was fractionally crystallized from ethanol–water. A single semicarbazone (m.p. 220.5–221°) was obtained.

Anal. Calcd. for $C_{16}H_{21}ON_3$: C, 70.85; H, 7.85. Found: C, 71.00; H, 7.61.

Samples of V, that had been allowed to stand for one year, solidified with some apparent decomposition. Sublimation of the solid, followed by recrystallization of the sublimate from ethanol, gave a white solid, m.p. 117–118°, which had the composition calculated for 9,10-diketo-12-methyl-1,2,3,4,9,10,11,12-octahydrophenanthrene (VI).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.79; H, 7.47.

A discussion of the spectrum of this product is found in the text of this report.

10-Keto-1,2,3,4,9,10,11,12-octahydrophenanthrene (II).—II was prepared from 1-(1-keto-2-phenylethyl)-cyclohexene[14] by the method previously described by Gutsche and Johnson.[3] The product was distilled and two fractions were obtained (fraction 1, 2.75 g., b.p. 130–145° (1 mm.); fraction 2, 2.30 g., b.p. 145–160° (1 mm.)). Each fraction was treated with semicarbazide hydrochloride in pyridine and methanol. The product obtained from the first fraction was crystallized from ethanol and water and two solids were obtained in low yield.

Anal. Calcd. for $C_{15}H_{19}ON_3$: C, 70.0; H, 7.43. Found: (solid m.p. 199–200° dec.): C, 69.8; H, 7.70. Found: (solid m.p. 209–210° dec.): C, 70.3; H, 7.56.

The principal semicarbazone (m.p. 219–220° dec., reported m.p. 221–222° dec.[3]) was obtained from the second fraction.

1,12-Dimethyl-1-carboxy-10-keto-1,2,3,4,9,10,11,12-octahydrophenanthrene (VIII).—The cyclization of VII (R = H,[8] 8.0 g., 0.03 mole) was carried out with freshly sublimed aluminum chloride and hydrogen chloride under the same conditions employed for the cyclization of IV. Hydrolysis of the complex with ice and hydrochloric acid afforded a solid keto-acid (4.5 g., 56% yield, m.p. 234–237°) that was insoluble in water and in benzene. The solid melted at 241–242° after sublimation (0.1 mm.), and subsequent recrystallization of the sublimate from acetic acid–water.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40; neut. equiv., 272. Found: C, 74.69; H, 7.71; neut. equiv., 271.

The ultraviolet spectrum showed two maxima: 267 mμ (ε 710) and 274 mμ (ε 770). The infrared spectrum showed two carbonyl bands: 1690 and 1710 cm.$^{-1}$.

Attempts to isomerize this keto-acid with hot 10% aqueous sodium hydroxide (2.5 hours) were unsuccessful; only unchanged starting material was recovered.

The methyl ester of the keto-acid (diazomethane method) was purified by crystallization from methanol–water; m.p. 87–87.5°.

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.21; H, 7.91.

The benzene layer from which VIII had been removed was extracted with alkali, and the alkaline extract acidified with hydrochloric acid and extracted with ether. The oil (*ca.* 3 g.) obtained by evaporation of the dry ether extract, contained a small amount of a solid. The solid was sublimed (0.1 mm.), and sublimate was recrystallized from acetic acid and water. The purified solid (m.p. 111–112°) was insoluble in 5% aqueous sodium hydroxide (room temperature). This product has been tentatively assigned the structure of the enol-lactone IX. The spectrum of this product is discussed in footnote 9.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.02; H, 7.10.

The Wolf-Kishner Reduction of VIII.—A mixture of the keto-acid VIII (1 g., 0.0037), obtained from VII, potassium hydroxide (0.75 g., 0.0134 mole), 95% hydrazine (2.5 ml.) and diethylene glycol was heated at 125° for two hours. The excess hydrazine and water were distilled from the reaction mixture, and the resulting solution was heated at 200° for four hours.

The reaction mixture was cooled and poured into a mixture of ice and water. A neutral product (0.4 g.) was separated by filtration and purified by recrystallization from acetic acid–water, sublimation (0.1 mm.), and recrystallization of the sublimate from acetic acid–water. The pure product X melted at 230–231°.

Anal. Calcd. for $C_{17}H_{20}ON_2$: C, 76.08; H, 7.51; N, 10.44. Found: C, 76.35; H, 7.21; N, 10.48.

The ultraviolet spectrum of X showed a maximum at

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[12] *Cf.* ref. 9 for comparison of the spectra of XII to the analogous compound with rings A and B fused *cis*.

[13] G. G. Smith, Ph.D. Thesis, University of Minnesota, 1949.

[14] P. S. Pinkney, G. A. Nesty, D. E. Pearson and C. S. Marvel This Journal, **59**, 2666 (1937).

249 mμ (ε 8400). The infrared spectrum showed a strong band at 1690 cm.$^{-1}$ and two medium bands at 3125 and 3220 cm.$^{-1}$.

The basic solution, from which X had been removed, was acidified with 10% hydrochloric acid, and the resulting precipitate (150 mg.) was separated. Fractional crystallization of this acidic product from acetic acid–water gave two isomeric 1,12-dimethyl-1-carboxy-1,2,3,4,9,10,11,12-octahydrophenanthrenes (XI).

Anal. Calcd. for $C_{17}H_{22}O_2$ (acid, m.p. 205–207°): C, 79.03; H, 8.58. Found: C, 78.97; H, 9.05.

The ultraviolet spectrum of this acid showed maxima at 265 mμ (ε 440) and 272 mμ (ε 404).

Anal. Calcd. for $C_{17}H_{22}O_2$ (acid, m.p. 186–187°): C, 79.03; H, 8.58. Found: C, 78.73; H, 8.55.

The ultraviolet spectrum of this acid showed maxima at 265 mμ (ε 478) and 272 mμ (ε 440). The infrared spectra of the two acids were almost identical and were similar to the spectrum of dehydroabietic acid.

The Cyclization of VII (R = Isopropyl).—The cyclization of VII (R = isopropyl, 14.5 g., 0.046 mole) was carried out under conditions identical to those described above for VII (R = H). The product (10 g., 70% yield, m.p. 239–241° (crude) or 242–243.5° pure) was shown to be identical to VIII, obtained from VII (R = H) by: (1) comparison of ultraviolet and infrared spectra, (2) mixed melting point studies, (3) composition, (4) reduction (Wolff–Kishner) to the same three products originally obtained from VII (R = H).

Reaction of Dehydroabietic Acid with Aluminum Chloride.—A solution of dehydroabietic acid (2 g., 0.0067 mole, m.p. 171°, $\lambda^{\max}_{268\ m\mu}$ (ε 682), $\lambda^{\max}_{272}$ (ε 722)) in thiophene-free benzene (30 ml.) was added, with stirring, to a suspension of freshly sublimed aluminum chloride (2.7 g., 0.02 mole) in thiophene-free benzene (50 ml.). The mixture was heated (reflux) and stirred for three hours, and then stirred at room temperature for one hour. The reaction mixture was hydrolyzed with ice and hydrochloric acid, and the benzene layer was separated and extracted with 5% aqueous sodium hydroxide. The basic solution was acidified and extracted with ether. The oily acid obtained from the ether extract was sublimed (0.1 mm.) to give a white glass, which eventually crystallized. Fractional crystallization of this solid gave a small amount of a pure compound as colorless plates melting at 159–160°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58; neut. equiv., 258. Found: C, 79.07; H, 8.61; neut. equiv., 260.

The infrared spectrum of this isomer was quite similar to the acids obtained from VIII. The band in the carbonyl region was at 1700 cm.$^{-1}$. The ultraviolet spectrum was almost identical to the acids obtained from VIII, and showed maxima at 265 mμ (ε 422) and at 272 mμ (ε 413).

The acidic residue obtained, after the 159–160° isomer had been removed, melted over a range of 125–135°. Attempts to obtain a second pure product by recrystallization (methanol–water or petroleum ether) and chromatography (silica gel) failed. A mixture of isomers (m.p. 138–140° with sublimation starting at 136°) was obtained from the chromatogram.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.70; H, 8.88.

Reaction of VII (R = Isopropyl) with Polyphosphoric Acid.—A mixture of polyphosphoric acid (prepared from 24.9 g. of phosphorus pentoxide in 16 ml. of 85% orthophosphoric acid) and VII (R = isopropyl, 1.5 g.) was heated on a steam-bath for two hours. The reaction mixture was poured onto ice and water and the amorphous solid that precipitated was removed by filtration. The solid darkened rapidly to a brown gummy substance when exposed to air. This material was dissolved in ether and extracted with 200 ml. of 5% aqueous sodium hydroxide and 100 ml. of water. No product was obtained from the alkaline extracts. The ether solution contained 1.0 g. of residual oil which solidified after standing for three days. The product melted at 95.5–96.5° after recrystallization from ethanol–water.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16; sapn. equiv., 296. Found: C, 81.24; H, 8.33; sapn. equiv., 290.

The infrared and ultraviolet spectra of this product, which has been assigned structure XII, are discussed in the text of this report.

Acknowledgment.—The authors would like to thank Dr. Stuart W. Fenton for discussions concerning the infrared spectra.

Minneapolis 14, Minn.

[Contribution from the School of Chemistry of the University of Minnesota]

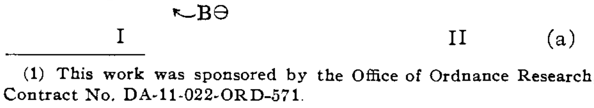
Heterocyclic Vinyl Ethers. VIII.[1] The Acid-catalysed Reaction of α-Haloacetals with Mercaptans

By William E. Parham, Jack Heberling[2] and Hans Wynberg

Received August 4, 1954

The spontaneous loss of hydrogen halide (ε-1 elimination) from α-halomercaptals ($R{-}\overset{X}{\overset{|}{C}}H{-}CH(SR)_2$) has been shown to result in the formation of 1,2-bis-(alkylmercapto)-ethylenes (R—S—CR=CH—S—R). There is no unequivocal evidence that ketenemercaptals are formed directly in such reactions. A new synthesis for heterocyclic vinyl sulfides is reported. The compound previously reported to be acrolein diethylmercaptal (III) has been shown to be 1,3-bis-(ethylmercapto)-propene-1 (IV).

Rothstein[3] has postulated that the formation of 1,1-bis-(ethylmercapto)-propene-1 (II), by reaction of β-chloropropionaldehyde diethylmercaptal (I) with alkali, occurs as shown in equation (a).



$$\underset{\text{I}}{Cl\,CH_2{-}\underset{H}{\underset{|}{C}}H{-}\underset{H}{\underset{|}{C}}{-}(S{-}C_2H_5)_2} \quad (B^\ominus) \longrightarrow \underset{\text{II}}{CH_3CH{=}C(SC_2H_5)_2} \qquad \text{(a)}$$

An alternate reaction path, shown in equation (b), was rejected on the basis that acrolein diethylmercaptal was not isomerized by action of alkali. A

$$\text{I} + B^\ominus \longrightarrow \underset{\text{III}}{CH_2{=}CH{-}CH(SC_2H_5)_2} \xrightarrow{B^\ominus} \text{II}\text{(b)}$$

re-examination of the structure of the product previously designated by Rothstein as acrolein diethylmercaptal (III) has now been made, and it is believed that this product is actually 1,3-bis-(ethylmercapto)-propene-1 (IV).

$$C_2H_5{-}S{-}CH_2CH{=}CH{-}S{-}C_2H_5 \qquad \text{IV}$$

Rothstein assigned structure III to the compound

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[2] From the Ph.D. Thesis of Jack Heberling, University of Minnesota, 1954.

[3] E. Rothstein, *J. Chem. Soc.*, 1550 (1940).