chloroketone in 50 ml. of ether there was added 0.243 g. (1×10^{-2} mole) of magnesium powder and 10 ml. of 2 *N* *t*-butylmagnesium chloride. The mixture was refluxed for four hours, and carbonated as previously described to give 83 mg. of the acid, m. p. 243°.

3-Carbomethoxy-5-androsten-17-ol.—A solution of 10 ml. of absolute methanol, 110 mg. (3.4×10^{-4} mole) of IV and 6 drops of concd. sulfuric acid was refluxed for twenty-four hours. The mixture was poured into water, extracted with ether and washed free of acid by alkali. Crystallization from methanol–petroleum ether followed by chromatography over alumina from benzene–petroleum ether gave 80 mg., m. p. 141–142°.

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.73. Found: C, 75.20; H, 9.79.

17-Acetoxy-5-androsten-3-carboxylic Acid.—A crude sample, 250 mg., of the acid (IV) was heated at 100° for two hours with excess acetic anhydride in pyridine. The product obtained by pouring into water was dissolved in acetone and filtered to remove some insoluble material. Slow crystallization from acetone gave 110 mg., m. p. 211–213°, $[\alpha]^{23}D$ −40.6 (*C*, 4.90 in chloroform).[9]

Anal. Calcd. for $C_{22}H_{32}O_4$: C, 73.29; H, 8.95. Found: C, 73.00; H, 8.99.

Acknowledgment.—We wish to thank Dr. Wayne Cole of the Soya Products Division of the Glidden Co. for supplying the dehydroisoandrosterone.

Summary

5-Androsten-17-ol-3-carboxylic acid has been prepared by carbonation of a Grignard reagent. Its acetate and methyl ester are described.

(9) The specific rotations of the intermediates and other compounds in this series will appear in a future publication by Dr. Squire.

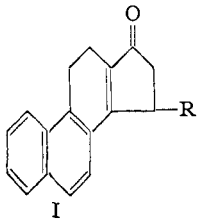
EVANSTON, ILLINOIS RECEIVED NOVEMBER 10, 1948

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

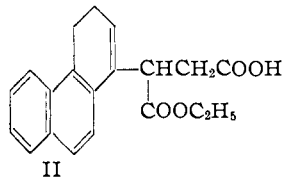
The Stobbe Condensation with 1-Keto-2-methyl-1,2,3,4-tetrahydrophenanthrene. A New Approach to β-17-Equilenone[1]

BY WILLIAM S. JOHNSON, VERNER L. STROMBERG AND JACK W. PETERSEN[2]

A few years ago we described a convenient synthesis of the ketone I (R = H) by the cyclization of the half-ester II produced by a Stobbe condensation with III (R = H), followed by hydrolysis and decarboxylation of the resulting keto ester I (R = $COOC_2H_5$).[3] Since then this scheme has been applied successfully by Riegel, Siegel and Kritchevsky[4] to the synthesis of a number of derivatives of I (R = H) containing alkyl substituents at the 3-position of the phenanthrene nucleus.



I



II

It seemed of particular interest to extend the synthesis to the homologous ketone III (R = CH_3) containing the methyl substituent at the 2-position, since if the cyclization proceeded into the alicyclic ring, a substance IV (R = $COOC_2H_5$) would be produced which is known to be convertible by hydrolysis, decarboxylation and hydrogenation into the 17-equilenones (3-desoxyequilenins).[5] The results of such an investigation are reported in this communication.

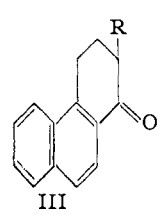
(1) Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(2) W. A. R. F. Research Assistant, 1943–1945. Deceased, January 29, 1948.

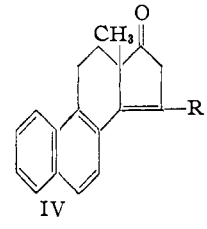
(3) Johnson and Petersen, THIS JOURNAL, **67**, 1366 (1945).

(4) Riegel, Siegel and Kritchevsky, *ibid.*, **70**, 2950 (1948).

(5) Johnson, Petersen and Gutsche, *ibid.*, **69**, 2942 (1947).

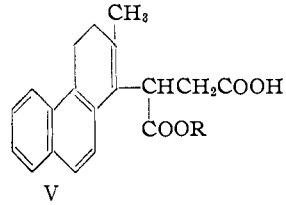


III

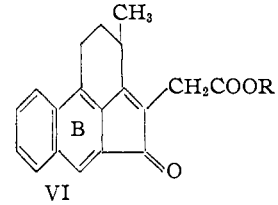


IV

The Stobbe condensation with III (R = CH_3) proceeded less readily than with the unsubstituted ketone III (R = H), but by altering conditions a non-homogeneous half-ester V (R = CH_3)[6] was obtained in excellent yield, from which a pure crystalline isomer was isolated in 61% yield.



V

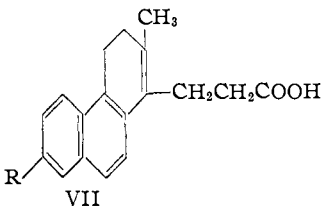


VI

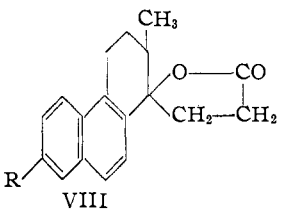
Cyclization of the crude half-ester V (R = CH_3 or C_2H_5) with a mixture of zinc chloride, acetic acid and acetic anhydride gave a neutral crystalline product of the expected composition. Because of its bright yellow color, however, it was presumed to be the indenone derivative VI produced by cyclization accompanied by ester exchange as observed in other studies.[7] That the ring had indeed closed into the aromatic nucleus was proved by oxidative degradation to benzenepentacarboxylic acid evidently arising from ring B (formula VI).

(6) The formulation of the ethylenic bond in the endocyclic position is tentative. *Cf.* the structure of the lower homolog, ref. 3.

(7) Johnson and Goldman, THIS JOURNAL, **67**, 430 (1945).

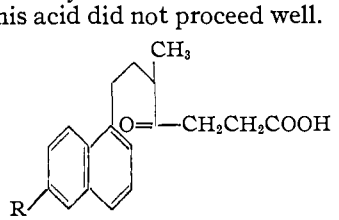


VII

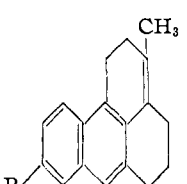


VIII

To circumvent ring closure to VI the carbomethoxy group was removed before cyclization as in previous studies with the lower homolog.[3] Saponification with barium hydroxide gave the crystalline dibasic acid V (R = H)[6] which lost carbon dioxide readily on warming in the presence of an acid catalyst. The product consisted of oily lactonic material and a mixture of unsaturated acids from which a pure isomer VII (R = H)[6] was isolated in 41% yield. This product and the crystalline lactone VIII (R = H) produced by treatment of VII (R = H)[6] with cold hydrogen fluoride[8] proved to be identical (by mixed melting point determinations) with samples prepared from IX (R = H) according to a scheme employed by Haberland[9] for the synthesis of VII (R = OCH_3) and VIII (R = OCH_3) by the cyclization of the keto acid IX (R = OCH_3). For the cyclization of IX (R = H) hydrogen fluoride proved to be much better than sulfuric acid, the lactone VIII (R = H) being obtained in 93% yield. In spite of this improvement the method involving the Stobbe condensation proved to be easier for preparing the unsaturated acid VII (R = H),[6] particularly since the conversion of the lactone into this acid did not proceed well.



IX



X

Even though Haberland's[9] attempts to cyclize the unsaturated acid VII (R = OCH_3) have been shown[5] to give what is most likely the ketone X (R = OCH_3) arising from cyclization into the aromatic nucleus, nevertheless it seemed worth investigating other methods of ring closure of VII (R = H), particularly since in the tetralone series[8] it was discovered that cyclization could take place into either the alicyclic or the aromatic nucleus depending on the conditions. Accordingly VII (R = H) was treated with zinc chloride, acetic acid and acetic anhydride as described for the cyclization of II,[3] but only dark intractable oils were produced. By reducing the amount of zinc chloride to trace quantity, however, a neutral nonsaponifiable oil was obtained from which a ketone crystallized in 21% yield (m. p. 152° after purification). Analysis was compatible with the formula $C_{18}H_{16}O$, and since both 14,15- and 15,16-dehydro-17-equilenone have considerably lower melting points,[5] this substance was presumed to be the product X (R = H) of cyclization into the aromatic nucleus. From the mother liquor a second ketone crystallized in 20% yield. This substance proved to be 14,15-dehydro-17-equilenone, IV (R = H) melting at 135° as shown by comparison of the ketone and semicarbazone with authentic samples. Since reduction of IV (R = H) is known to give β-17-equilenone,[5] the present scheme represents a new synthesis of desoxyequilenin. From previous experience it seems probable that some of the tautomeric 15,16-dehydro-17-equilenone remained in the oily residue.[5] An investigation in the methoxy series which is now in progress is expected to afford a new synthesis of 14,15-dehydroequilenin methyl ether, and hence of equilenin.[9a]

Experimental[10]

The Stobbe Condensation with 1-Keto-2-methyl-1,2,3,4-tetrahydrophenanthrene.—A cold solution of 3.02 g. of potassium in 63 ml. of dry *t*-butyl alcohol was mixed with 12.9 g. of dimethyl succinate and 15 ml. of this mixture was added from a dropping funnel to 2.50 g. of the ketone (m. p. 72–73°) contained in the flask of a special apparatus,[11] the whole operation being conducted under an atmosphere of nitrogen. The flask was immersed in an oil-bath at 50° and the remainder of the solution added slowly with stirring over a period of four hours. After an additional hour at 50° the mixture was cooled, acidified with hydrochloric acid, and the alcohol removed under reduced pressure. The semi-solid residue was taken up in ether, washed with water, then extracted with 1 *N* ammonium hydroxide. Acidification of the alkaline solutions gave 3.57 g. (93% yield) of crude yellow oily half-ester which solidified on standing, m. p. 119–143°. Crystallization from benzene–petroleum ether (b. p. 60–68°) followed by recrystallization from dilute methanol gave 2.37 g. (61% yield) of colorless needles, m. p. 156–159°. Repeated recrystallization from this solvent raised the melting point of this substance, **β-carbomethoxy-β-(2-methyl-3,4-dihydro-1-phenanthryl)-propionic acid,**[6] to 159–160.5°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.78; H, 6.42.

β-Carboxy-β-(2-methyl-3,4-dihydro-1-phenanthryl)-propionic Acid.[6]—To a solution of 10.0 g. of the half-ester, m. p. 156–159°, in 860 ml. of alcohol was added a solution of 126 g. of barium hydroxide octahydrate in 720 ml. of water. The mixture was boiled under reflux for one hour, and most of the alcohol was removed under reduced pressure. The cooled (ice-salt-bath) semi-solid residue was acidified with 1 to 1 hydrochloric acid, the temperature

(8) *Cf.* W. S. Johnson, H. C. E. Johnson and Petersen, THIS JOURNAL, **67**,1360 (1945).

(9) Haberland, *Ber.*, **72**, 1215 (1939); **76**, 621 (1943).

(9a) This expectation has now been realized, the acid VII (R = OCH_3),[6] m. p. 184–185°, giving 14,15-dehydroequilenin methyl ether in low yield. (Added in proof, March 22, 1949.)

(10) Unless otherwise specified, all melting points are corrected.

(11) See the apparatus used in "Step 4" of the synthesis of equilenin, ref. 5.

always being kept below 10° to prevent decarboxylation. The precipitated dibasic acid amounted to 9.51 g. (99% yield), m. p. 190–194° dec. A single recrystallization from acetone-benzene gave colorless prisms melting at 209–211° dec. After repeated recrystallization the m. p. was 209.5–210° dec.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.61, 73.52; H, 5.92, 5.77.

The **anhydride** was produced by the action of boiling acetyl chloride on the dibasic acid. Crystallization from benzene-petroleum ether (b. p. 60–68°) gave colorless prisms, m. p. 147.5–148°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.97, 78.21; H, 5.38, 5.61.

β-(2-Methyl-3,4-dihydro-1-phenanthryl)-propionic Acid, VII (R = H).[6]—Decarboxylation of the dibasic acid (1.000 g.) (m. p. 209–210°) was effected by heating with 18 ml. of pyridine, 30 ml. of concentrated hydrochloric acid and 10 g. of oxalic acid. After twenty-five minutes under reflux the calculated volume of gas was evolved. The mixture was diluted with water and the organic material taken up in ether, washed with water and extracted with 1 *N* ammonium hydroxide. Acidification of the alkaline extracts gave 0.652 g. (76% yield) of colorless acid, m. p. 95–110°. Recrystallization from dilute methanol gave 0.352 g. (41% yield) of fairly pure material, m. p. 125–128°. Further recrystallization gave colorless plates, m. p. 131–132° undepressed on admixture with the sample of VII (R = H) prepared by the Haberland scheme (see below); calcd.: neut. equiv., 266.3. Found: neut. equiv., 265.0.

A sample of the unsaturated acid was lactonized by treatment with cold anhydrous hydrogen fluoride.[8] Recrystallization of the neutral fraction from methanol gave the lactone VIII (R = H), m. p. 155–157°, undepressed on admixture with the sample prepared by the Haberland synthesis (see below).

Cyclization of the Unsaturated Acid VII (R = H).[6]—A solution of 0.400 g. of the above unsaturated acid in 20 ml. of acetic anhydride to which 2 drops of a solution of zinc chloride in acetic acid (20 mg./ml.) had been added was boiled under reflux for eight hours in an atmosphere of nitrogen. The acetic anhydride was decomposed with methanol, and the volatile materials removed on the steam-bath. The red solution was diluted with water, and extracted with ether. The ether solution was washed with 5% sodium hydroxide to remove acidic material, concentrated, and the residue heated on the steam-bath with 20 ml. of 10% potassium hydroxide solution for ten minutes in an atmosphere of nitrogen. The unsaponified material was taken up in ether, washed with 5% sodium hydroxide, 5% hydrochloric acid, and saturated sodium chloride solution. The red glass remaining on evaporation of the ether was evaporatively distilled at 155° (0.1 mm.) giving 0.328 g. of yellow semi-solid distillate. Crystallization from ether gave 0.078 g. (21% yield) of pale yellow needles, m. p. 145.5–150°, probably X (R = H). Repeated recrystallization from alcohol gave yellow needles, m. p. 152.1–152.7°.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.14; H, 6.15.

The **semicarbazone** crystallized from pyridine in the form of pale yellow needles, m. p. (in an evacuated tube) 245.2–246.2° dec. (introduced at 235°).

Anal. Calcd. for $C_{19}H_{19}ON_3$: C, 74.73; H, 6.27. Found: C, 74.82; H, 5.94.

The filtrate from which the 152° ketone separated was evaporated to dryness and crystallized from alcohol to give 0.074 g. (20% yield) of colorless needles, m. p. 118–123°. Recrystallization gave material melting at 134.5–135.5° alone or when mixed with an authentic specimen of 14,15-dehydro-17-equilenone, m. p. 135.5–136°.[5]

The **semicarbazone** crystallized from pyridine in the form of colorless needles, m. p. 248–250° dec., undepressed on admixture with a sample of the derivative (m. p. 248.5–250° dec.) prepared from authentic ketone.[5]

Anal. Calcd. for $C_{19}H_{19}ON_3$: C, 74.73; H, 6.27. Found: C, 74.64; H, 5.97.

Cyclization of the Half-Ester V (R = CH_3).[6]—A mixture of 1.2 g. of the crude half-ester, 6 ml. of acetic acid containing fused zinc chloride (20 mg./ml.), 6 ml. of acetic acid and 12 ml. of acetic anhydride was boiled under reflux for ninety minutes, cooled, treated with water to hydrolyze the acetic anhydride and evaporated under reduced pressure. The residual red oil was taken up in ether, washed with 5% potassium hydroxide solution and, after evaporation of the solvent, crystallized from benzene–ligroin. **Methyl 3-methyl-1,2,3,5-tetrahydro-acephenanthryl-3a,4-ene-5-one-4-acetate, VI** (R = CH_3), was thus obtained as bright yellow prisms, m. p. 134–137°; yield 0.340 g. (30%). A sample prepared for analysis melted at 136.5–138°.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.10; H, 5.98.

Ultraviolet absorption in ethanol: $\lambda_{max.}$ 235 mμ (log *E* 4.30), 279 (4.73), 412 (3.41).

A cyclization with 0.150 g. of pure half-ester, m. p. 156–158°, gave 0.070 g. (49% yield) of crude product, m. p. 124–128°.

The same substance was produced when the cyclization was conducted with phosphorus pentoxide in boiling benzene.

Cyclization of the Half-Ester V (R = C_2H_5)[6] was carried out with the crude acidic material produced by the condensation of 2.10 g. of the ketone III (R = CH_3) with 1.74 g. of diethyl succinate in the presence of potassium *t*-butoxide according to procedures already described.[3] The oily half-ester could not be crystallized and was cyclized directly with 13.5 ml. of acetic acid containing fused zinc chloride (20 mg./ml.), 18.5 ml. of acetic acid and 27 ml. of acetic anhydride as described above for the methyl ester. The crude product, 0.150 g., crystallized from benzene–ligroin in the form of yellow prisms, m. p. 113–118°. Recrystallization raised the m. p. to 115–116.3°.

Anal. Calcd. for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29. Found: C, 78.48; H, 5.98.

Ultraviolet absorption in ethanol: $\lambda_{max.}$ 235 mμ (log *E* 4.30), 279 (4.72), 412 (3.40).

Oxidation of Keto Ester VI (R = CH_3) **to Benzenepentacarboxylic Acid.**—A mixture of 0.340 g. of the keto ester, 2 ml. of concentrated nitric acid and 1.5 ml. of water was heated in a sealed tube at 180–200° for eighteen hours. The residue obtained after evaporation was crystallized once from concentrated nitric acid; yield 0.058 g. of crude colorless acid, m. p. 222–227°, dec. (reported,[12] 232–233°, dec.). The pentamethyl ester prepared with diazomethane melted at 146.5–148.8° (reported,[13] 147–148°).

1-Bromo-3-methyl-5-(1-naphthyl)-2-pentanone.—A solution of 11.40 g. of α-methyl-γ-(1-naphthyl)-butyric acid in 25 ml. of chloroform was treated with 18 ml. of purified thionyl chloride. After refluxing for one hour the mixture was evaporated at 40° under reduced pressure, the thionyl chloride being completely removed by adding small portions of chloroform to the residue and repeating the evaporation. The acid chloride was dissolved in 25 ml. of dry ether and added slowly to a dry ether solution of diazomethane prepared from 20.8 g. of nitrosomethylurea. After one and one-half hours at room temperature 25 ml. of 48% hydrobromic acid was added with shaking. The organic layer was separated, washed with water, then with a saturated solution of sodium bicarbonate, and dried over anhydrous sodium sulfate. Crystallization of the oily residue obtained on evaporation from ether-petroleum ether gave 8.80 g. of brownish product, m. p. 57–60°. An additional 1.65 g. of material, m. p. 52–58° was crystallized from the mother liquor making the total yield 68%. This product was satisfactory for the next step of the synthesis which gave homogeneous material in 86% yield, thus establishing the nature of the bromo ketone which could not be purified satisfactorily for analysis.

(12) Fleischer and Retze, *Ber.*, **56**, 228 (1923).

(13) Ruzicka and Rudolph, *Helv. Chim. Acta*, **10**, 915 (1927).

4-Keto-4-methyl-7-(1-naphthyl)-heptanoic Acid, IX (R = H).—The bromo ketone (5.16 g.) in 20 ml. of dry toluene was added to a solution of sodiomalonic ester prepared from 4.08 g. of diethyl malonate and 0.38 g. of sodium shot in 20 ml. of toluene, whereupon a precipitate formed immediately. After refluxing for four hours, the mixture was evaporated under reduced pressure and the residue saponified by heating for four hours on the steam-bath with 11.5 g. of potassium hydroxide in 15 ml. of water and 5 ml. of alcohol. The substituted malonic acid which was separated by acidification, followed by ether extraction, was decarboxylated by heating at 150–160° for twenty minutes. The brown residue was dissolved in benzene, treated with Norit, and crystallized from benzene–petroleum ether; yield 4.14 g. of slightly brownish needles, m. p. 82–84°. A sample purified for analysis by repeated recrystallization from benzene–petroleum ether was colorless and melted at 89–90°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.80; H, 7.20.

Lactone, VIII (R = H) **of β-(1-Hydroxy-2-methyl-1,2,-3,4-tetrahydro-1-phenanthryl)-propionic Acid.**—Anhydrous hydrogen fluoride (about 40 g.) was added to 1.15 g. of the keto acid contained in a platinum vessel chilled in an ice–salt mixture. After five minutes the reagent was evaporated in a current of air, and the solid residue taken up in ether and washed with sodium bicarbonate solution. The residue obtained on evaporation of the ether was triturated with 5 ml. of cold ether leaving 1.00 g. (93% yield) of tan crystals of the lactone, m. p. 152–155°. Recrystallization from methanol gave colorless prisms, m. p. 155–156°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.16; H, 6.81. Found: C, 81.38; H, 6.92.

The lactone was also produced in high yield when the methyl ester of IX (R = H) was treated with hydrogen fluoride.

β-(1-Hydroxy-2-methyl-1,2,3,4-tetrahydro-1-phenanthryl)-propionic acid was prepared from 0.150 g. of the above lactone by hydrolysis with 0.250 g. of sodium hydroxide in 10 ml. of water. After heating for three hours on the steam-bath the clear solution was chilled and acidified slowly with cold dilute acetic acid. The crystalline hydroxy acid which precipitated (0.145 g.) was recrystallized from methanol giving colorless needles, m. p. 187–188° with dec. (lactonization). Further recrystallization did not raise the melting point.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.97; H, 7.12.

In contrast to the 7-methoxy derivative[9] this hydroxy acid showed no tendency to undergo dehydration to the unsaturated acid, but reverted to the lactone. In order to prepare the unsaturated acid VII (R = H) the procedure of Bachmann, Cole and Wilds[14] for the dehydration of β-hydroxy esters was applied. Thus the hydroxy ester produced from 0.100 g. of the lactone and 2 ml. of methanolic hydrogen chloride, was treated with pyridine (2 drops) and thionyl chloride (3 drops) in 0.5 ml. of benzene for thirty minutes at room temperature, then for ten minutes at 40°. The product was worked up *via* saponification with 45% potassium hydroxide; yield 0.035 g. (35%) of colorless crystals, m. p. 122–126°, soft at 118°. Two recrystallizations from benzene–petroleum ether gave colorless plates, m. p. 131.5–132°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.16; H, 6.81. Found: C, 81.10; H, 7.16.

Summary

A synthetic scheme involving the Stobbe condensation, previously developed for the production of steroid-like structures from 1-keto-1,2,3,4-tetrahydrophenanthrene, has now been applied with some modifications to the 2-methyl derivative to give a homolog containing the 13-angular methyl group. The product, 14,15-dehydro-17-equilenone, is the precursor of β-17-equilenone (3-desoxyequilenin).

(14) Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 824 (1940).

MADISON, WISCONSIN RECEIVED NOVEMBER 13, 1948

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Decarboxylation and Cyclization Reactions of Some Pimelic Acid Derivatives

BY ROBERT L. FRANK AND JAMES B. MCPHERSON, JR.

The cyanoethylation reaction described by Bruson and Riener[1] affords a convenient method for the preparation of pimelic acid derivatives, certain of which suggest themselves as possible intermediates in the syntheses of cyclohexanones related to some of the monocyclic terpenes. In this paper are reported the decarboxylations and ring closures of a group of compounds derived from γ-acetyl-γ-isopropenylpimelonitrile (I), the cyanoethylation product of mesityl oxide. We have been particularly interested in the lability of the unsaturation of the isopropenyl group during these reactions.

Pyrolysis of γ-carboxy-γ-isopropenylpimelic acid (II), a derivative reported by Bruson and Riener,[1] at 285–320° in the presence of barium carbonate resulted in simultaneous decarboxylation and ring closure to give a substituted cyclohexanone. Ozonolysis showed this material to be almost entirely 4-isopropylidenecyclohexanone (VI), since the products isolated were acetone and 1,4-cyclohexanedione. Derivatives of formaldehyde or formic acid were not obtained, although these were detected by faint color tests. Thus this pyrolysis was accompanied by nearly complete isomerization of the double bond of the isopropenyl group. Further evidence for the isopropylidene structure for the cyclohexanone was obtained by reaction with methylmagnesium iodide to give γ-terpineol (VII) rather than β-terpineol. Incidentally, this constitutes a total synthesis for this naturally-occurring terpene.[2]

During the heating of γ-carboxy-γ-isopropenylpimelic acid (II) it was noted that carbon dioxide was evolved at temperatures considerably below 300°. This indicated that simple decarboxylation might be occurring before the cyclization reaction,

(1) Bruson, THIS JOURNAL, **64**, 2457 (1942); Bruson and Riener, *ibid.*, **65**, 18 (1943).

(2) Simonsen, *Ind. For. Rec.*, **10**, 1 (1923).