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,

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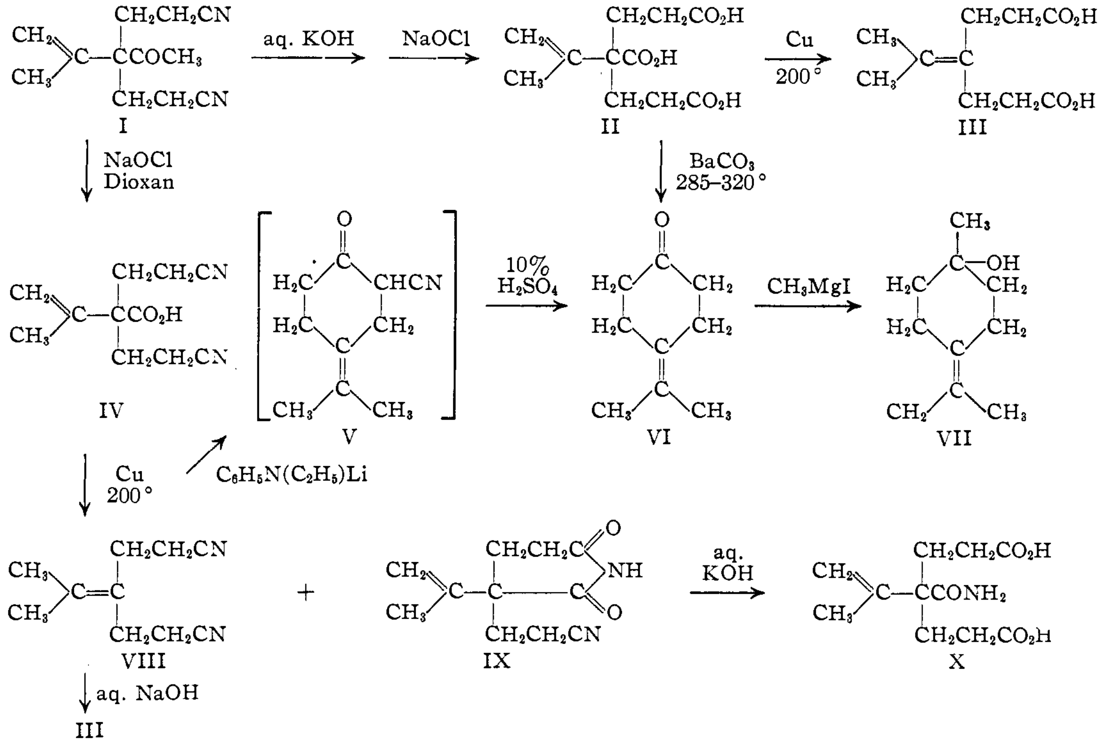
[1] Bruson, This Journal, **64**, 2457 (1942); Bruson and Riener, *ibid.*, **65**, 18 (1943).

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



a conclusion confirmed by heating the triacid (II) with copper-bronze at 200° to give 32% of a dicarboxylic acid. Further work as described below showed the latter to be γ-isopropylidenepimelic acid (III). Thus even under these milder conditions there was isomerization of the isopropenyl group.

Similar decarboxylation of γ-carboxy-γ-isopropenylpimelonitrile (IV), obtained in 81% yield by the haloform reaction on γ-acetyl-γ-isopropenylpimelonitrile (I), also resulted in shifting of the double bond. The product (VIII), obtained in 34% yield, gave acetone on ozonolysis; no formaldehyde was detected. Hydrolysis of the dinitrile gave the same dicarboxylic acid obtained from γ-carboxy-γ-isopropenylpimelic acid (II). We therefore believe the dibasic acid to have the isopropylidene structure represented by III.

As a by-product in the decarboxylation of the dinitrile (IV) there was also obtained an equal amount of a crystalline solid. This was shown by analysis and molecular weight determination to be isomeric with the starting material (IV), although not subject to similar decarboxylation. Further pyrolysis gave only tar. A neutral equivalent showed the presence of no free carboxyl group, although the compound was soluble in aqueous sodium hydroxide. It was insoluble in sodium bicarbonate solution. A saponification equivalent indicated two saponifiable groups; the product of this determination was isolated as a crystalline dicarboxylic acid having the composition $C_{11}H_{17}NO_5$. To this has been assigned the structure γ-formamido-γ-isopropenylpimelic acid (X) and to the by-product itself the structure α-cyanoethyl-α-isopropenylglutarimide (IX). Supporting evidence is the infrared absorption spectrum of the latter and its comparison with the spectrum of glutarimide in the CO (1705 cm.$^{-1}$) and NH (3000–3200 cm.$^{-1}$) regions (Fig. 1). The failure of complete saponification of α-cyanoethyl-α-isopropenylglutarimide (IX) to a tricarboxylic acid is to be expected because of the tertiary nature of the γ-formamido grouping (X).

The formation of an imide by interaction of a cyano and a carboxyl group has been known since 1869[3] and has recently been studied by Wiley and Guerrant.[4]

A further reaction of 4-isopropylidenepimelonitrile (VIII) has been its ring closure by the Thorpe reaction to 2-cyano-4-isopropylidenecyclohexanone (V). Hydrolysis of the latter with 10% aqueous sulfuric acid gave a low yield of a ketone, the 2,4-dinitrophenylhydrazone of which gave no depression in mixed *m. p.* with that of 4-isopropylidenecyclohexanone (VI). A semicarbazone was also obtained; this was different from but isomeric with that formed by the 4-isopropylidenecyclohexanone (VI) derived from γ-carboxy-γ-isopropenylpimelic acid (II). Its formation indicates the possible presence of the isopropenyl analog of the ketone (VI).

Infrared absorption spectra have also been studied because it was hoped they might provide a method for differentiating isopropenyl and isopropylidene groups in this series. As indicated by

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[3] Gautier, *Z. Chem.*, **5**, 127 (1869).

[4] Wiley and Guerrant, THIS JOURNAL, **71**, 981 (1949).

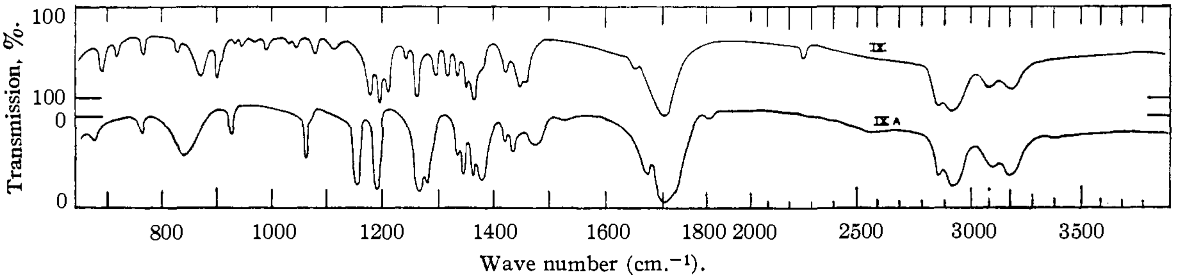

Fig. 1.—Infrared spectra of glutarimides: IX is α-cyanoethyl-α-isopropenylglutarimide; IXA is glutarimide.

Thompson and Torkington,[5] however, both terminal and non-terminal double bonds produce absorption maxima in the region 890–970 cm.$^{-1}$. In this region particularly the absorption depends not only on the position of the double bond, but also on the complete molecular structure. As shown in Fig. 2, all of our compounds, isopropenyl and isopropylidene, exhibit maxima between 890 and 918 cm.$^{-1}$.

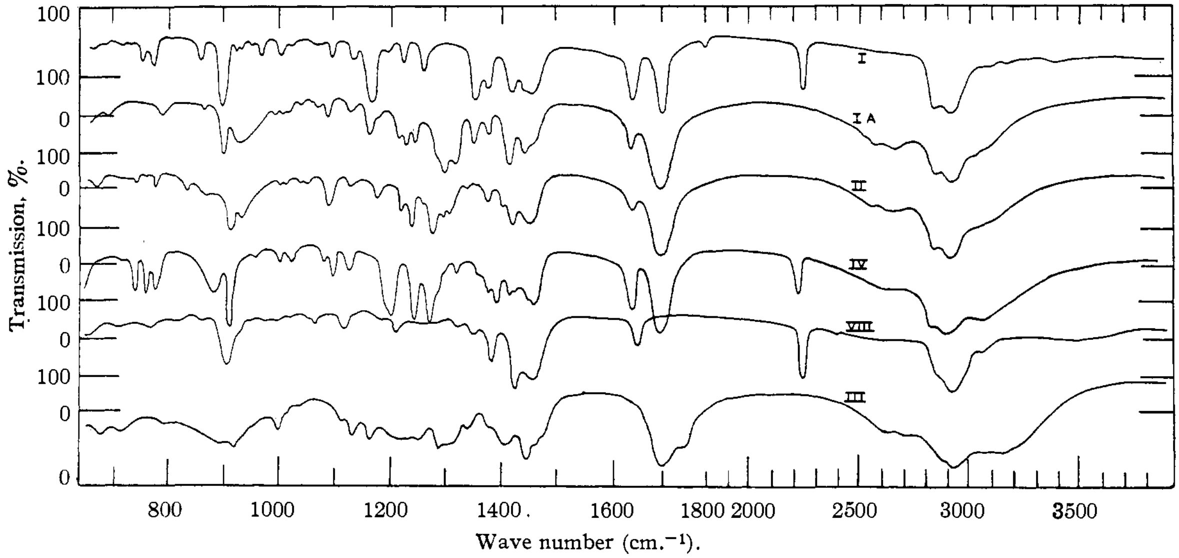

Fig. 2.—Infrared spectra: the Roman numerals correspond to those of the manuscript; IA is γ-acetyl-γ-isopropenylpimelic acid.

Experimental

γ-Acetyl-γ-isopropenylpimelonitrile (I).—The method of Bruson and Riener[1] was employed using 98.0 g. (1.00 mole) of purified mesityl oxide, 106.0 g. (2.00 moles) of acrylonitrile, 100 ml. of *t*-butyl alcohol and 5 g. of Triton B (40% aqueous benzyltrimethylammonium hydroxide). The yield of product was 72 g. (35%), m. p. 115–117°; saponification equiv. calcd.: 102.1; found: 98.0. The purity of the mesityl oxide is critical, and the commercial product generally results in low yields. Purification is accomplished by washing with aqueous sodium carbonate and with water, drying over calcium chloride, and distilling.

γ-Acetyl-γ-isopropenylpimelic Acid and γ-Carboxy-γ-isopropenylpimelic Acid (II).—The procedures of Bruson and Riener[1] were used. Saponification of 28.6 g. (0.14 mole) of γ-acetyl-γ-isopropenylpimelonitrile by means of 20.8 g. (0.37 mole) of potassium hydroxide in 230 ml. of water gave 24.4 g. (72%) of γ-acetyl-γ-isopropenylpimelic acid, m. p. 137.5–138.5°; neutral equiv. calcd., 121.1; found, 120.1. The haloform reaction with 38.6 g. (0.159 mole) of this acid dissolved in 84 ml. of 20% aqueous sodium hydroxide and 512 ml. of 9.5% sodium hypochlorite solution, prepared by the method of Newman and Holmes,[6] yielded 26.0 g. (67%) of colorless crystalline tricarboxylic acid, m. p. 158–160°; neutral equiv. calcd., 81.4; found, 81.5.

4-Isopropylidenecyclohexanone (VI).[7]—An intimate mixture of 46.7 g. (0.191 mole) of γ-carboxy-γ-isopropenylpimelic acid and 1.51 g. (0.0076 mole) of barium carbonate was heated in three separate batches in a 50-ml. distilling flask fitted with a thermometer which extended to the bottom of the flask. Strong effervescence began at 285°, causing the temperature to drop to 275°. The temperature was ultimately increased to 320° as a mixture of water and yellow oil distilled. The distillates from the three batches were combined, the water separated, the oil dissolved in ether, washed with aqueous sodium bicarbonate and with water, and dried over calcium sulfate. Distillation gave 12.0 g. (45%) of colorless liquid product having a cedar-like odor, which on redistillation had the constants: b. p. 54° (1 mm.); $n^{20}{}_{\mathrm{D}}$ 1.4817; sp. gr.$^{20}_{20}$ 0.959; *MR* calcd. 41.1; *MR* found 41.2.

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(5) Thompson and Torkington, *Proc. Roy. Soc.* (*London*), **184A**, 3 (1945).

(6) Newman and Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 428.

(7) Preliminary work on this reaction was performed by Mrs. Blossom Katz.

Anal.[8] Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.07, 77.36; H, 10.10, 10.10.

The semicarbazone, prepared by the directions of Shriner and Fuson,[9a] melted at 196–198° after six crystallizations from ethanol.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78. Found: C, 61.63; H, 8.67.

The 2,4-dinitrophenylhydrazone, prepared by the method of Shriner and Fuson,[9b] recrystallized three times from ethanol and seven from methanol to form orange platelets, melted at 130.5–132°.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.78; H, 5.75.

Ozonolysis of 4-Isopropylidenecyclohexanone (VI).—A stream of 4% ozone was passed at a rate of 88 ml. per minute through a solution of 1.01 g. (0.0072 mole) of 4-isopropylidenecyclohexanone in 15 ml. of methylene chloride in a Dry Ice-bath for two and one-half hours. The ozonide solution was then added dropwise at room temperature with stirring to a mixture of 1.7 g. of 30% hydrogen peroxide, 0.1 ml. of concentrated sulfuric acid, and 35 ml. of water. The mixture was stirred at room temperature for forty-five minutes and then gradually heated to boiling and refluxed for one hour. The methylene chloride escaping through the condenser was collected in a Dry-Ice trap and tested for formaldehyde by means of methone.[10] No formaldehyde was detected. The condenser was set downward for distillation and 24 ml. of aqueous distillate collected. Testing of this distillate with methone[10] failed to detect formaldehyde, but aqueous resorcinol and concentrated sulfuric acid gave an orange-red ring, indicating a trace of formaldehyde.[11a] Heating with mercuric oxide gave a faint gray precipitate of mercury, a weak indication of formic acid.[11b] The haloform reaction[9c] gave a copious precipitate of iodoform, and acetone was further identified by the formation of its 2,4-dinitrophenylhydrazone,[9b] m. p. 120–123°, and mixed m. p., 121–125°, with an authentic sample.

The aqueous pot residue from the above distillation was neutralized with sodium carbonate, extracted with ether, acidified with sulfuric acid, and saturated with ammonium sulfate. A brown oil separated and was removed. The aqueous solution was extracted with chloroform, the chloroform solution washed with water, dried over magnesium sulfate, and evaporated to dryness. The residual oil was dissolved in 95% ethanol and the solution evaporated to yield white crystalline 1,4-cyclohexanedione, m. p. 68–73°. This was sublimed at 60° and 28 mm. pressure to give about 50 mg. of colorless needles, m. p. 77–78°. A mixed m. p. with an authentic sample, prepared by the method of Baeyer,[12] melted at 77–78°.

γ-Terpineol (VII).—The method was based on that of Perkin[13] for β-terpineol. A solution of 3.98 g. (0.029 mole) of 4-isopropylidenecyclohexanone in 10 ml. of anhydrous ether was added slowly with stirring to the Grignard reagent from 15.6 g. (6.84 ml., 0.118 mole) of methyl iodide, 2.64 g. (0.109 gram-atom) of magnesium, and 70 ml. of anhydrous ether. The reaction mixture, after standing overnight, was decomposed by pouring into a mixture of 8 g. of ammonium chloride in 125 g. of ice and water. The solution was barely acidified with hydrochloric acid, the ether layer removed, and the aqueous layer extracted with three 25-ml. portions of ether. The combined ether solutions were washed with dilute aqueous sodium bicarbonate and with water, dried over magnesium sulfate, evaporated, and the oily residue steam distilled. The crude yellow liquid product, separated from the distillate, weighed 1.76 g. Distillation (65° (1 mm.)) gave 0.77 g. of oil which crystallized on chilling, m. p. 57–66°. Sublimation at 45–50° (15 mm.) yielded 0.16 g. (3.6%) of white tabular crystals, m. p. 63–67° (lit.[14] 69–70°), having an odor reminiscent of lilacs.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 76.85; H, 11.97.

γ-Isopropylidenepimelic Acid (III).—Five grams (0.0205 mole) of γ-carboxy-γ-isopropenylpimelic acid mixed with 0.5 g. of copper-bronze powder was heated under a stream of nitrogen to 195–205°. Formation of carbon dioxide was evidenced by a white precipitate when the evolved gases were passed through aqueous calcium hydroxide. The mixture was cooled, dissolved in acetone, filtered and the filtrate evaporated to a brown oil. This, after solution in 10% aqueous sodium hydroxide and acidification with concentrated hydrochloric acid, yielded 1.3 g. (32%) of crystalline product, m. p. 102–105°. An additional 0.3 g. (7%) was obtained by extraction of the acidified solution. Recrystallization of the combined product gave shiny white platelets, m. p. 104.5–106° (lit.[15] 97°); neutral equiv. calcd., 100.1; found, 101.1.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 60.05; H, 8.29.

γ-Carboxy-γ-isopropenylpimelonitrile (IV).—To a stirred solution of 2.68 moles of sodium hypochlorite in *ca.* 2300 ml. of water in a 5-l., three-necked flask was added 850 ml. of peroxide-free dioxane and the mixture was cooled to 0–10°. A solution of 121.6 g. (0.596 mole) of γ-acetyl-γ-isopropenylpimelonitrile in 810 ml. of dioxane was then added dropwise, and the cold reaction mixture stirred for four additional hours. The excess hypochlorite was decomposed by the addition of aqueous sodium bisulfite, the reaction mixture filtered, and the filtrate washed with two 200-ml. portions of ether. The aqueous filtrate was acidified with concentrated hydrochloric acid and allowed to stand for twelve hours at 0°. The white solid then present was collected on a filter, washed with cold water, and dried at 90°. It was digested in 900 ml. of hot water to dissolve inorganic salts, precipitated by chilling, collected on a filter, and dried at 100° to yield 99.9 g. (81%) of white powder, m. p. 164–166°. An analytical sample was prepared by recrystallization as shiny platelets from ethylene chloride, m. p. 166–167.5°; neutral equiv. calcd., 206.2; found, 210.3.

Anal. Calcd. for $C_{11}H_{14}N_2O_2$: N, 13.59. Found: N, 13.44.

γ-Isopropylidenepimelonitrile (VIII) and α-Cyanoethyl-α-isopropenylglutarimide (IX).—Forty-five grams (0.184 mole) of γ-carboxy-γ-isopropenylpimelonitrile was mixed with 4.5 g. of copper-bronze and 4.5 g. of powdered soft glass and heated in a small flask to 200–230° under a stream of nitrogen until evolution of carbon dioxide had ceased. The mixture was cooled and 50 ml. of benzene added, and the solid residue removed by filtration. The filtrate was washed with dilute sulfuric acid, aqueous sodium bicarbonate and water, dried over magnesium sulfate, and some of the benzene removed by distillation. At this point crystals formed in the solution; addition of ether increased this formation. These were removed by filtration and combined with the original solid residue. Fractional distillation of the benzene solution then gave 12.3 g. (41%) of colorless liquid γ-isopropylidenepimelonitrile, b. p. 135–137° (1 mm.); n^{20}_{D} 1.4733.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70. Found: C, 73.81; H, 8.59.

The combined solid residue, containing copper and glass, was warmed with 50 ml. of acetone and filtered. Evaporation of the filtrate gave a greenish-brown solid which after two recrystallizations, from dilute hydro-

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(8) Microanalyses were performed by Misses Emily Davis, Betty Alice Snyder, Theta Spoor, Jane Wood, Mr. Maurice Dare and Mr. Howard Clark.

(9) (a) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, rev. ed., 1940, p. 142; (b) p. 143; (c) p. 53.

(10) Ionescu and Bodea, *Bull. soc. chim.*, **47**, 1408 (1930).

(11) (a) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1941, p. 49; b) p. 179.

(12) Baeyer, *Ann.*, **278**, 91 (1893).

(13) Perkin, *J. Chem. Soc.*, **85**, 654 (1904).

(14) Baeyer, *Ber.*, **27**, 444, 745 (1894).

(15) Perkin and Simonsen, *J. Chem. Soc.*, **91**, 1736 (1907).

chloric acid and from ethanol, yielded 9.8 g. (26%) of white tabular α-cyanoethyl-α-isopropenylglutarimide, m. p. 119–121°: mol. wt. calcd., 206; found (Rast), 221, 198; saponification equiv. calcd. for two saponifiable groups, 103.1; found, 100.2, 99.1. The product was soluble in 5% aqueous sodium hydroxide and insoluble in 5% aqueous sodium bicarbonate.

Anal. Calcd. for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.59. Found: C, 63.84; H, 6.93; N, 13.53.

When mixed with 0.7 g. of copper–bronze, 7.0 g. of product heated to 350° showed no apparent decarboxylation; only a black tar was formed.

Hydrolysis of γ-Isopropylidenepimelonitrile (VIII).—A mixture of 0.7 g. (0.0043 mole) of the dinitrile, 0.4 g. (0.01 mole) of sodium hydroxide and 5 ml. of water was refluxed for six hours. Acidification with concentrated hydrochloric acid and recrystallization of the precipitate from petroleum ether and from water gave 0.1 g. of shiny white platelets, m. p. 104.5–106°; mixed m. p. with γ-isopropylidenepimelic acid (III) 104.5–106°.

Ozonolysis of γ-Isopropylidenepimelonitrile (VIII).—Two grams (0.0123 mole) of the dinitrile dissolved in 25 ml. of purified carbon tetrachloride was cooled in an ice-salt-bath and a stream of *ca.* 200 ml. per minute of 2.6% ozone passed through it for one hour. The ozonide formed a separate layer during this time. The solvent was evaporated (30° at 30 mm.), and 70 ml. of water and 2.85 g. of zinc dust added to the liquid ozonide. The mixture was heated gradually to boiling and 50 ml. distilled into an ice-cooled receiver containing 10 ml. of water. Both the distillate and the residue, tested by means of methone,[10] showed no indication of formaldehyde; nor was formic acid detected.[11b] From the aliquot of the distillate was prepared a 17% yield (based on the dinitrile) of the 2,4-dinitrophenylhydrazone of acetone,[9b] m. p. 125–126°; mixed m. p. with an authentic sample 125–126°.

γ-Formamido-γ-isopropenylpimelic Acid (X).—One gram (0.0048 mole) of α-cyanoethyl-α-isopropenylglutarimide (IX) was heated just below the b. p. for one hour with 1.1 g. (0.019 mole) of potassium hydroxide in 20 ml. of water. The solution was cooled, acidified with concentrated hydrochloric acid, evaporated to dryness at room temperature; the solid was dissolved in acetone, the solution filtered, and the filtrate allowed to evaporate to give 0.9 g. (77%) of colorless tablets, m. p. 154–160°. Two crystallizations from water raised the m. p. to 164.5–166°; neutral equiv. calcd., 121.6; found, 121.1.

Anal. Calcd. for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.05; N, 5.76. Found: C, 54.53; H, 7.15; N, 5.88.

Boiling of γ-formamido-γ-isopropenylpimelic acid with 3% aqueous potassium hydroxide for sixteen hours and with sulfuric–nitrous acid mixture[16] for one hour failed to hydrolyze the amide to a tricarboxylic acid.

Ring Closure of γ-Isopropylidenepimelonitrile (VIII).—A solution of lithium N-ethylaniline was prepared by the procedure of Ziegler and co-workers[17] from 47.6 g. (0.392 mole) of N-ethylaniline in 200 ml. of ether and *n*-butyllithium solution made by the directions of Gilman, Zoellner and Selby[18] from 4.1 g. (0.59 gram-atom) of lithium and 25.3 g. (0.274 mole) of *n*-butyl chloride in 50 ml. of ether. This was stirred and heated to gentle refluxing in a 1-l., three-necked flask, and a solution of 16.3 g. (0.10 mole) of γ-isopropylidenepimelonitrile in 100 ml. of anhydrous ether was added dropwise over a period of five hours. A white precipitate formed as soon as the addition was begun. The reaction mixture was then poured quickly into 360 ml. of 2 *N* hydrochloric acid. The layers were separated; the aqueous layer extracted with three 100-ml. portions of ether, and all the ether solutions combined and washed twice with 20% hydrochloric acid and with water, then dried over magnesium sulfate. Evaporation of the solution gave 13.8 g. of a brown oil, crude 2-cyano-4-isopropylidenecyclohexanone. Attempts to hydrolyze this oil were unsuccessful using 10% aqueous sodium hydroxide and 37 and 50% sulfuric acid solutions. Hydrolysis was accomplished in low yield by means of 10% aqueous sulfuric acid. To 718 ml. of 10% acid was added 8.4 g. of the oil, and the mixture was refluxed for six hours, then steam-distilled. The residue was refluxed for an additional twelve hours and steam distilled. The combined distillates were extracted with ether, the extracts dried over magnesium sulfate, and evaporated to leave 1.0 g. of residual oil from which a 2,4-dinitrophenylhydrazone[9b] and a semicarbazone[9a] were prepared. The 2,4-dinitrophenylhydrazone, orange platelets from ethanol, m. p. 130–132°, showed no depression in mixed m. p. with that of 4-isopropylidenecyclohexanone (VI) prepared by pyrolysis of the triacid (II).

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.39; H, 5.93.

The semicarbazone, colorless crystals from ethanol, m. p. 193–195°, when mixed with that of 4-isopropylidenecyclohexanone (VI), m. p. 196–198°, gave a depressed m. p. 176–185°.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78. Found: C, 61.60; H, 8.91.

Infrared Absorption Spectra.—Determinations were kindly carried out by Mrs. J. L. Johnson, using a Perkin-Elmer Model 12B infrared spectrometer with rock salt optics. The solids were suspended in Nujol for the measurements; the liquid was used pure in a 0.025-mm. cell.

Summary

1. γ-Acetyl-γ-isopropenylpimelonitrile, the cyanoethylation product of mesityl oxide, has been studied as a starting material for substituted cyclohexanones related to monocyclic terpenes.

2. Decarboxylations of γ-carboxy-γ-isopropenylpimelonitrile and γ-carboxy-γ-isopropenylpimelic acid, with and without ring closure of the latter, result in rearrangement of the isopropenyl to isopropylidene groups.

URBANA, ILLINOIS RECEIVED NOVEMBER 5, 1948

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[16] Bouveault, *Bull. soc. chim.*, **9**, 368 (1893); Haller and Bauer, *Compt. rend.*, **152**, 1638 (1911).

[17] Ziegler, Eberle and Ohlinger, *Ann.*, **504**, 116 (1933); Ziegler and Aurnhammer, *ibid.*, **513**, 55 (1934).

[18] Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).