wt., 204.26. Found: C, 94.05; H, 5.95; mol. wt. (Rast), 215.

The product did not depress the melting point of a sample of diphenylsuccindene-10, m. p. 205.4–207.8°, prepared essentially according to Brand and Müller[4]; the final reduction of 9,12-dichlorodiphenylsuccindadiene-9,12 was conducted with zinc dust in refluxing acetic acid solution (37% yield of crystallized product; found: C, 94.02; H, 6.00; absorption spectrum in ethanol: max. 310 mμ, log E 4.56).

From the more soluble fraction there was obtained 60 mg. of **1,2,5,6-dibenzcycloöctatetraene** in the form of colorless crystals, m. p. 106.8–108.1°. A crystallographic examination[20] indicated acicular crystals showing parallel and 45° extinction and probably monoclinic; they are biaxial positive with α near $\beta = 1.678$, $\gamma > 1.76$, moderate 2 v.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.92; mol. wt., 204.26. Found: C, 94.05; H, 5.90; mol. wt. (Rast), 212.

The hydrocarbon gave distinct melting point depressions when mixed with diphenylsuccindane and with dihydroanthracene. The substance readily decolorizes permanganate solution and a solution of bromine in carbon tetrachloride. Solutions in benzene are fluorescent. The hydrocarbon apparently does not form a picrate.

Other Decarboxylation Experiments.—Several further trials were made in an endeavor to improve the yield of the desired product and to determine how the by-product arises. In an experiment conducted as just described but with rigid control of the temperature to 260–265°, dibenzcycloöctatetraene was the sole product but the yield was no better. Decarboxylation of 200 mg. of diacid with freshly reduced copper powder in quinoline solution at 225–245° (forty-five minutes) afforded 26 mg. (19%) of dibenzcycloöctatetraene, m. p. 106–108°; the hydrocarbon was obtained in about the same yield when the reaction was conducted in a sealed tube at 285°, and no diphenylsuccindene was detected in either instance. Decarboxylation in quinaldine at 240–250° gave similar results (16% yield of material melting at 100–103°). Trials in a subliming apparatus with reduced copper or with basic copper carbonate as catalyst resulted in the formation of both isomers in low yields.

The best results were obtained with copper chromite catalyst as follows. A mixture of 1 g. of the diacid with 2 g. of copper chromite catalyst 39KAF, layered with 1 g. of catalyst, was placed in a 25-cc. flask connected by a ground-glass joint and a right-angle tube to a receiving flask cooled in a dry ice-bath. Moderate suction was applied to the system and the temperature of the reaction mixture was raised to 260–300° for one hour. A crystalline product that collected in the receiver was crystallized from alcohol and afforded 150 mg. (22%) of colorless needles of 1,2,5,6-dibenzcycloöctatetraene, m. p. 107.2–108.8°. Decidedly less satisfactory results were obtained with the same catalyst and a solution of the diacid in 2,6-dimethylquinoline or in 1,6-dimethylnaphthalene.

1,2,5,6-Dibenzcycloöctadiene-1,5.—Dibenzcycloöctatetraene (76 mg.) was hydrogenated in absolute alcohol (30 cc.) in the presence of Adams catalyst (100 mg.) at a pressure of 2300 lb. (five hours). When the filtered solution was concentrated and diluted with a few drops of water the product separated in colorless, rectangular crystals, m. p. 106–109°; yield 50 mg. (65%). Recrystallization from ligroin (30–60°) raised the melting point to 108.5–110°. Mixtures with the starting material and with diphenylsuccindane showed definite depressions in melting point. A mixture with a sample of the known *s*-dibenzcycloöctadiene[5] that became available after the completion of this work melted at 108.5–110°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.24; H, 7.75; mol. wt., 208.29. Found: C, 91.88; H, 8.00; mol. wt. (Rast), 197.

Diphenylsuccindane.[18]—This hydrocarbon was prepared for purposes of comparison, both by the hydrogenation of diphenylsuccindene-10, as reported by Brand and Müller,[4] and by the Clemmensen–Martin reduction of diphenylsuccindanedione-9,12; the yield from 3.8 g. of diketone was 2.7 g. (80%); m. p. 102.8–104°.

Summary

1,2,5,6-Dibenzcycloöctatetraene has been synthesized from *o*-phthalaldehyde and *o*-phenylenediacetonitrile and found to be chemically reactive. The spectra of the hydrocarbon and two of its derivatives show evidence of at most only partial conjugation between the benzene rings and the free double bonds, and it is concluded that the eight-membered ring is non-planar and hence incapable of full resonance stabilization.

(18) Roser, *Ann.*, **247**, 153 (1888).

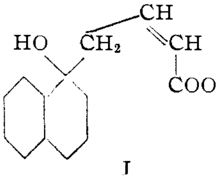
CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 31, 1946

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

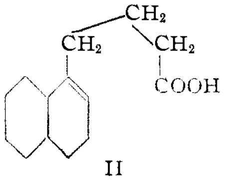
Synthesis of 1-Keto-$\Delta^{4a,10a}$-dodecahydrophenanthrene, *cis*-9-Methyl-1-decalone, and other Cyclic Ketones

BY W. E. BACHMANN AND N. L. WENDLER[1]

The unsaturated hydroxy ester I was prepared from 1-decalone, zinc and methyl γ-bromocrotonate.[2] In order to avoid the formation of a dienic ester,[3] the Reformatsky reaction was carried out in a mixture of equal volumes of ether and benzene at about 60°. The unsaturated hydroxy ester was reduced catalytically over Raney nickel in methanol, and the product was dehydrated and hydrolyzed to what is probably γ-($\Delta^{1,2}$-octahydro-1-naphthyl)-butyric acid (II). A sample of this acid was readily dehydrogenated to the known



I



II

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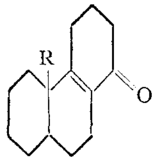
(1) From the Ph.D. dissertation of N. L. Wendler, 1944.

(2) Ziegler, *et al.* [*Ann.*, **551**, 80, 120 (1942)] describe an elegant method of preparing methyl γ-bromocrotonate and its application in the Reformatsky reaction. See also Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

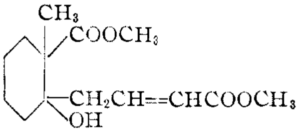
(3) Fuson and his co-workers [Fuson, Arnold and Cooke, THIS JOURNAL, **60**, 2272 (1938); Fuson and Southwick, *ibid.*, **66**, 679 (1944)], who made the important discovery that methyl γ-iodocrotonate can be used in the Reformatsky reaction, prepared the dienic ester rather than the hydroxy ester from the reaction with cyclohexanone in boiling benzene. See also Cook and Schoental, *J. Chem. Soc.*, 289 (1945).



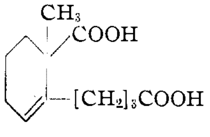
IIIa, R = H
IIIb, R = CH_3

γ-1-naphthylbutyric acid. The acid chloride of the unsaturated acid was cyclized by means of anhydrous stannic chloride, and the product was dehydrohalogenated by means of dimethylaniline to what is undoubtedly 1-keto-$\Delta^{4a,10a}$-dodecahydrophenanthrene (IIIa).[4] Confirmation of this structure is being sought in the reactions of the compound. Application of these reactions to the 9-methyl-1-decalones is in progress in order to obtain IIIb, from which it should be possible to prepare desoxyandrosterone by known methods.

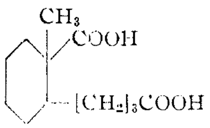
From 2-methyl-2-carbomethoxycyclohexanone, zinc and methyl γ-bromocrotonate, the hydroxy ester IV was prepared. After catalytic reduction, the product was dehydrated and hydrolyzed, and the resulting unsaturated dicarboxylic acid (V, position of double bond not established) was hydrogenated in acetic acid in the presence of Adams catalyst to γ-2-methyl-2-carboxycyclohexanebutyric acid[6] (VI). Through the Dieckmann method this acid was converted into 9-methyl-1-decalone (VII), which proved to be the so-called *cis*-form, previously prepared by Cook and Lawrence[5] and recently by Johnson.[6] Experiments are in progress to determine whether the *trans*-form of the acid VI can be obtained by variations in the conditions of reduction.



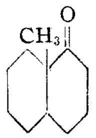
IV



V

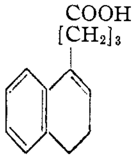


VI

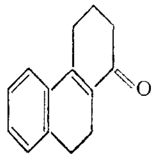


VII

γ-(3,4-Dihydro-1-naphthyl)-butyric acid (VIII) was prepared in 50% yield from 1-tetralone through the Reformatsky reaction. Its acid chloride cyclized to the alicyclic ring when treated with stannic chloride. The product obtained after a dehydrohalogenation treatment is most likely 1-keto-1,2,3,4,9,10-hexahydrophenanthrene (IX).[4] It was dehydrogenated by sulfur to 1-keto-1,2,3,4-tetrahydrophenanthrene. It is planned to apply these procedures to the preparation of the 7-methoxy derivative.

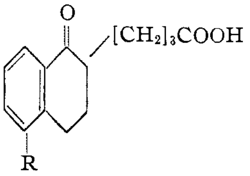


VIII

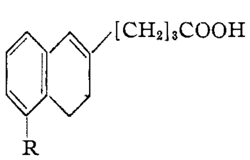


IX

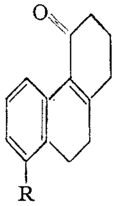
4-Keto-1,2,3,4,9,10-hexahydrophenanthrene (XIIa) was prepared by cyclization of γ-(3,4-dihydro-2-naphthyl)-butyric acid (XIa). This acid was obtained from the keto acid Xa by aluminum isopropoxide reduction, followed by dehydration. The preparation of the keto acid from 1-tetralone followed the procedure employed previously for a substituted tetralone.[7] Dehydrogenation of a sample of the unsaturated ketone XIIa by means of sulfur yielded the known 4-keto-1,2,3,4-tetrahydrophenanthrene. The 8-methoxy-substituted ketone XIIb was prepared in a similar manner from 5-methoxy-1-tetralone. Its structure was established by its conversion into 1-methoxyphenanthrene through catalytic reduction of the carbonyl group, followed by dehydration and catalytic dehydrogenation by means of palladium.



Xa, R = H
Xb, R = OCH_3



XIa, R = H
XIb, R = OCH_3



XIIa, R = H
XIIb, R = OCH_3

Experimental

γ-($\Delta^{1,9}$-Octahydro-1-naphthyl)-butyric Acid. (II).—A mixture of 10 g. of zinc, 7.6 g. of 1-decalone,[6] 9 g. of methyl γ-bromocrotonate,[2] and a crystal of iodine in 25 cc. of anhydrous ether and 25 cc. of benzene was refluxed on a steam-bath. A total of three additions of 5 g. of zinc and 3 g. of methyl γ-bromocrotonate was made at one hour intervals; after the last addition the mixture was refluxed for an additional two hours. The cooled mixture was added to ice and dilute acetic acid, and the product was separated from the aqueous solution by means of ether. The ether solution was washed successively with 1% ammonium hydroxide, water and saturated salt solution and then dried. The oily product containing I, which remained after evaporation of the solvent, was dissolved in

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[4] Recently Andre Dreiding of this Laboratory has prepared this ketone by employing a mixture of acetic anhydride and zinc chloride for the cyclization of the unsaturated acid. He has also obtained confirmation of the structure of the ketone from ultraviolet absorption spectra. These results will be reported in a future communication.

[5] Cook and Lawrence, *J. Chem. Soc.*, 817 (1937).

[6] Johnson, THIS JOURNAL, **65**, 1317 (1943).

[7] Bachmann and R. C. Edgerton, *ibid.*, **62**, 2220 (1940).

50 cc. of ethanol and hydrogenated in the presence of 5 g. of Raney nickel at 30 pounds pressure in the course of fifteen minutes. The product obtained by evaporation of the solvent after separation of the catalyst by centrifugation was heated with 18 g. of potassium acid sulfate at 160° for one hour. The product from this treatment was saponified by refluxing with a solution of 25 g. of potassium hydroxide in 250 cc. of 50% ethanol for three hours. The resulting acid (II) was purified by evaporative distillation at 115–120° (0.05 mm.); yield of colorless oil, 3–3.5 g.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.67; H, 10.00. Found: C, 75.59; H, 10.01.

The unsaturated acid readily decolorizes bromine in carbon tetrachloride and slowly reduces dilute aqueous potassium permanganate. Dehydrogenation of a sample by heating with four equivalents of sulfur afforded the known γ-1-naphthylbutyric acid; m. p. 105–107°.

1-Keto-$\Delta^{4a,10a}$-dodecahydrophenanthrene (IIIa).—The aforementioned unsaturated acid was converted into its sodium salt by means of a solution of sodium methoxide in methanol. The methanol was removed by evaporation, and the sodium salt was added to a solution of 3 g. of oxalyl chloride in 25 cc. of benzene. After two hours of refluxing, the mixture was filtered and the benzene was evaporated under reduced pressure. The resulting acid chloride in 15 cc. of carbon disulfide was chilled to −10° and treated with a solution of 3 cc. of anhydrous stannic chloride in 25 cc. of carbon disulfide according to the procedure of Cook and Lawrence.[8] After one hour at −10°, the mixture was allowed to stand at room temperature for two hours and was then poured onto ice and water. The carbon disulfide was evaporated, the product was extracted with ether, and the ether solution was washed with dilute alkali in order to remove unchanged acid. The oil which remained after the removal of the ether was refluxed with 15 cc. of dimethylaniline for three hours; ether was added to the cooled mixture and the dimethylaniline was removed with aqueous acid. Evaporative distillation of the product at 120–130° (0.05 mm.) yielded the ketone IIIa as a colorless oil. A solution of 0.5 g. of the ketone, 1.5 g. of semicarbazide hydrochloride, and 5 cc. of pyridine in 25 cc. of methanol was refluxed. The **semicarbazone** was obtained crystalline by trituration with methanol; from this solvent it crystallized in colorless needles; m. p. 225° dec.

Anal. Calcd. for $C_{15}H_{23}ON_3$: C, 68.97; H, 8.81. Found: C, 68.95; H, 8.77.

The **2,4-dinitrophenylhydrazone** was prepared in boiling ethanol containing a drop of sulfuric acid; it crystallized from ethanol in brilliant red needles; m. p. 215–216°.

Anal. Calcd. for $C_{20}H_{24}O_4N_4$: C, 62.50; H, 6.25. Found: C, 62.28; H, 6.56.

γ-2-Methyl-2-carboxycyclohexanebutyric Acid (VI).—A mixture of 10 g. of zinc, 8.5 g. of 2-methyl-2-carbomethoxycyclohexanone, 9 g. of methyl γ-bromocrotonate, and a little iodine was refluxed in 50 cc. of a 1:1 mixture of ether and benzene; reaction set in within one-half hour as shown by the separation of a yellow solid. Further additions of zinc and bromoester were made and the reaction was carried out as described for the preparation of II. Hydrogenation of the Reformatsky product (IV) was carried out in 50 cc. of methanol with 5 g. of Raney nickel at 30 pounds pressure. Removal of the catalyst and evaporation of the solvent at 50° afforded the saturated Reformatsky ester as an oil.

Pure thionyl chloride (6.5 cc.) was added dropwise with swirling to a solution of the product in 40 cc. of anhydrous ether and 15 cc. of pyridine which had been chilled to 0–5°. After one hour at room temperature the mixture was poured onto ice water and the product was taken up in ether. The ethereal extract was washed with dilute hydrochloric acid, with sodium bicarbonate solution and with water. The oil which remained after evaporation of the dried solution was refluxed for ten hours with a solution of 10 g. of potassium hydroxide in 100 cc. of methanol; the methanol was removed and the residue was heated for two hours with 100 cc. of 20% potassium hydroxide solution. The cooled solution was diluted with an equal volume of water, extracted with ether, and then acidified. The resulting unsaturated dibasic acid (V or isomer) which was collected as an oil resisted all attempts to induce crystallization. It was hydrogenated in 50 cc. of acetic acid in the presence of 0.2 g. of platinum oxide catalyst. The acetic acid was removed under reduced pressure and water was added to the residual oil; after several weeks in a refrigerator the saturated dibasic acid (VI) solidified; weight, 5.5 g. This crude acid was used in subsequent operations. A sample of the acid after recrystallization from dilute methanol and then from ether–petroleum ether (Norit) formed colorless crystals; m. p. 109–112°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77. Found: C, 63.42; H, 9.05.

***cis*-9-Methyl-1-decalone (VII)**.—Four grams of the crude acid (VI) was converted into the dimethyl ester by means of diazomethane and the ester was evaporatively distilled at 105–110° (0.05 mm.). The colorless liquid diester was dissolved in 75 cc. of dry benzene and added to a flask containing anhydrous sodium methoxide, prepared from 0.8 g. of sodium. The mixture was refluxed in a nitrogen atmosphere for three hours on a steam bath, then cooled and acidified with dilute acetic acid. The organic solution was washed with sodium bicarbonate solution until neutral and then dried. Evaporation of the solvent left the 2-carbomethoxy-9-methyl-1-decalone as a liquid. The compound failed to give a color with ferric chloride. The β-ketoester was refluxed with a mixture of 50 cc. of concentrated hydrochloric acid and 50 cc. of acetic acid for twelve hours in a system provided with a mercury trap. The mixture was diluted with two volumes of water, saturated with salt and extracted several times with ether. The ether extract was washed with sodium bicarbonate solution, dried and evaporated. The residual 9-methyl-1-decalone was evaporatively distilled at 80° (0.05 mm.); yield, 2.5 g. (n_{25} 1.4845). After regeneration from its semicarbazone the ketone had n_{25} 1.4922 (reported, 1.4897[5] and 1.4903[6]). The melting points of the semicarbazone (m. p. 228–229°), oxime (m. p. 108–109°) and 2,4-dinitrophenylhydrazone (m. p. 159–160°) checked the values reported previously for these derivatives of *cis*-9-methyl-1-decalone. Mixed melting points of these derivatives with samples kindly sent us by Dr. W. S. Johnson showed no depression. Our lower melting form of the oxime was transformed to the higher melting form (m. p. 114.5–115.5°) by seeding with a sample of Dr. Johnson's higher melting form.

γ-(3,4-Dihydro-1-naphthyl)-butyric Acid (VIII).—The Reformatsky reaction between 7.3 g. of 1-tetralone and methyl γ-bromocrotonate was carried out as described for I. The hydroxy ester after catalytic hydrogenation was dehydrated with 18 g. of potassium acid sulfate at 160° (one hour). The product was separated from the salt and refluxed for two hours with 10 g. of potassium hydroxide in 100 cc. of 50% ethanol. An equal volume of water was added, the solution was extracted with ether, and the aqueous solution was acidified. The desired acid precipitated as an oil which gradually solidified. After recrystallization from ether–petroleum ether it melted at 85–86°; yield, 5.5 g. (50%). It decolorizes instantly a solution of bromine in carbon tetrachloride and reduces aqueous potassium permanganate.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.77; H, 7.40. Found: C, 77.87; H, 7.48.

Dehydrogenation of a sample of the above unsaturated acid with one equivalent of sulfur gave the known γ-1-naphthylbutyric acid; m. p. 107–109° alone and when mixed with an authentic specimen of the compound.

Cyclization of γ-(3,4-Dihydro-1-naphthyl)-butyric Acid. 1-Keto-1,2,3,4,9,10-hexahydrophenanthrene (IX).—One gram of the acid was converted into its sodium salt by means of sodium methoxide as described previously, and the salt was treated with a solution of 1 g. of oxalyl chloride in 10 cc. of benzene. The acid chloride in 10 cc. of carbon

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(8) Cook and Lawrence, *J. Chem. Soc.*, 1637 (1935).

disulfide was treated with 1 cc. of stannic chloride in 10 cc. of carbon disulfide at −10° for one hour and at room temperature for two hours. The product was isolated and heated with 0.5 cc. of dimethylaniline in the manner described previously. Evaporative distillation under reduced pressure followed by crystallization of the distillate from ether–petroleum ether yielded 0.2–0.3 g. of colorless needles of IX; m. p. 48–49°. Usually it was necessary to purify the ketone through its oxime in order to obtain it crystalline. The unsaturated ketone is readily susceptible to photochemical oxidation.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.42; H, 7.05.

The **oxime** crystallized from aqueous alcohol in stout, colorless needles; m. p. 140.5–141.5° cor.

Anal. Calcd. for $C_{14}H_{15}ON$: C, 78.76; H, 7.09; N, 6.56. Found: C, 78.74; H, 7.09; N, 6.07.

Dehydrogenation of a sample of the unsaturated ketone with one equivalent of sulfur at about 250° yielded 1-keto-1,2,3,4-tetrahydrophenanthrene which had the correct analysis and melting point and melted unchanged when mixed with an authentic specimen of the compound. The oximes of the compounds were also identical.

γ-(1-Keto-1,2,3,4-tetrahydro-2-naphthyl)-butyric Acid (Xa).—Dry sodium ethoxide, prepared from 4.6 g. of sodium and 60 cc. of ethanol followed by removal of the excess alcohol *in vacuo* at 100°, was suspended in 100 cc. of dry benzene in an atmosphere of nitrogen; to the cooled suspension a solution of 14.6 g. of 1-tetralone and 29.2 g. of diethyl oxalate in 35 cc. of benzene was added with swirling. After eight hours at room temperature, the mixture was poured onto ice-water, neutral material was extracted with ether, and the glyoxalate was precipitated from the aqueous solution with hydrochloric acid. The ethyl 1-keto-1,2,3,4-tetrahydronaphthalene-2-glyoxalate was recrystallized from ethanol; yield, 17 g. (70%); m. p. 44–45° (reported,[9] 48°).

A mixture of 17 g. of the glyoxalate and 10 g. of powdered soft glass was heated in an oil-bath with stirring at 155–160°. After the evolution of carbon monoxide was complete (fifteen minutes), the ethyl 1-keto-1,2,3,4-tetrahydro-2-naphthoate was separated from the glass by means of ether and distilled under reduced pressure; b. p. 123–125° (0.05 mm.); yield, 16 g. (90%). The keto ester crystallized on chilling; m. p. 34–35° (reported,[9] 34°).

The addition of 7.5 g. of the keto ester in 50 cc. of anhydrous ethanol to a solution of sodium ethoxide prepared from 0.9 g. of sodium and 25 cc. of ethanol resulted in the deposition of the insoluble sodio derivative. To the suspension was added 7.5 g. of γ-bromobutyronitrile in 30 cc. of ethanol and the mixture was refluxed on a steam-bath for twelve hours. The excess alcohol was removed in a current of air, water was added, and the product was extracted with ether. Distillation of the product at 180° (0.2 mm.) yielded 8 g. of γ-(1-keto-2-carbethoxy-1,2,3,4-tetrahydro-2-naphthyl)-butyronitrile as a colorless oil. Five grams of this ester nitrile was hydrolyzed and decarboxylated by boiling for twenty-four hours with a mixture of 50 cc. of acetic acid and 50 cc. of concentrated hydrochloric acid. The solvents were removed under reduced pressure and the residual acid was purified through carbonate extraction from ether solution. The keto acid (Xa) obtained on acidification crystallized from ether–petroleum ether in colorless needles; m. p. 64–65°; yield, 3–3.5 g. (70–75%).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.90. Found: C, 72.20; H, 7.20.

γ-(3,4-Dihydro-2-naphthyl)-butyric Acid (XIa).—A solution of 3 g. of the aforementioned keto acid was treated with an ether solution of diazomethane, and the methyl ester was purified by evaporative distillation at 140° (0.02 mm.). The methyl ester (3.5 g.) was refluxed with a solution of 12 g. of aluminum isopropoxide in 40 cc. of toluene and 1 cc. of isopropyl alcohol for four hours; then 40 cc. of isopropyl alcohol was added and distilled through a vertical air condenser during the course of one hour. This operation with isopropyl alcohol was repeated. The reaction mixture was treated with cold dilute sulfuric acid, the product was extracted with ether, and the ether solution was washed successively with dilute aqueous ammonia and with water. Evaporation of the ether yielded 3 g. of carbinol ester as an oil. A sample on catalytic dehydration and dehydrogenation with palladium on charcoal at 300° afforded the known γ-2-naphthylbutyric acid; m. p. 95–96° alone and when mixed with an authentic specimen.

A mixture of 2 g. of the carbinol ester and 5 g. of potassium acid sulfate was heated at 160° in an oil-bath for one hour. The product obtained by ether extraction was saponified by refluxing with an excess of 10% aqueous potassium hydroxide in 50% ethanol solution for three hours. The hydrolysate, after addition of water and extraction of neutral material with ether, was acidified, and the precipitated acid was recrystallized from petroleum ether. The colorless needles of γ-(3,4-dihydro-2-naphthyl)-butyric acid melted at 70–71°; yield, 1.3 g.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.77; H, 7.40. Found: C, 77.55; H, 7.27.

4-Keto-1,2,3,4,9,10-hexahydrophenanthrene (XIIa).—The acid chloride from 0.6 g. of the acid XIa was prepared from its sodium salt and oxalyl chloride by the procedure described for IIIa. A solution of the acid chloride in 10 cc. of carbon disulfide was added dropwise with swirling to a solution of 5 cc. of stannic chloride in 10 cc. of carbon disulfide at −10°; a dark complex precipitated gradually during the addition and became green. After one hour at −10° and twelve hours in a refrigerator (or two hours at room temperature), the mixture was poured into a mixture of ice, ether and hydrochloric acid. The ether solution was washed with dilute alkali and with water and then evaporated. The residual oil, which slowly gave off hydrogen chloride when warm, was heated with 10 cc. of dimethylaniline for three hours. After the removal of the dimethylaniline and its salt with dilute acid, the product was evaporatively distilled in a high vacuum. The unsaturated cyclic ketone slowly solidified on standing; it crystallized from ether–petroleum ether in colorless needles; m. p. 45°; yield, 0.2–0.3 g.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.80; H, 7.21.

The **oxime** was recrystallized from ethanol; m. p. 187–188°.

Anal. Calcd. for $C_{14}H_{15}ON$: C, 78.76; H, 7.09. Found: C, 78.69; H, 7.09.

A sample of the 4-ketohexahydrophenanthrene on dehydrogenation with one equivalent of sulfur yielded 4-keto-1,2,3,4-tetrahydrophenanthrene; m. p. 64–66° alone and when mixed with known material.

Methyl 1-Keto-5-methoxy-1,2,3,4-tetrahydronaphthalene-2-glyoxalate.—5-Methoxy-1-tetralone[10] (40 g.) was glyoxalated by the method employed on 1-tetralone in 500 cc. of benzene with 50 g. of dimethyl oxalate and the anhydrous sodium methoxide prepared from 10.8 g. of sodium. The glyoxalate obtained by acidification of the aqueous solution of the sodium salt crystallized from methanol in pale yellow needles; yield, 55.4 g. (93%); m. p. 102–103°.

Anal. Calcd. for $C_{14}H_{14}O_5$: C, 64.11; H, 5.34. Found: C, 64.24; H, 5.57.

Methyl 1-Keto-5-methoxy-1,2,3,4-tetrahydro-2-naphthoate.—Decarbonylation of 60 g. of the glyoxalate in the presence of 55 g. of powdered glass at 160–175° was complete in twenty minutes. The keto ester which was isolated by ether extraction was sufficiently pure for the next step. In a small run the product from 2.36 g. of glyoxalate was evaporatively distilled under reduced pressure and recrystallized from ether–petroleum ether; yield 1.85 g. (90%); m. p. 68–69°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.35; H, 5.94.

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(9) Hückel and Goth, *Ber.*, **57**, 1285 (1924).

(10) Lockett and Short, *J. Chem. Soc.*, 787 (1939).

4-Keto-8-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XIIb).—The introduction of the butyronitrile side chain into the preceding keto ester (40 g.) and the hydrolysis and decarboxylation of the resulting product were carried out exactly as described for the preparation of Xa. From the reaction mixture there were isolated 20 g. (50%) of the keto acid, 2–3 g. of phenolic material and 12 g. of 5-methoxy-1-tetralone. The **γ-(1-keto-5-methoxy-1,2,3,4-tetrahydro-2-naphthyl)-butyric acid (Xb)** after evaporative distillation under reduced pressure and recrystallization from ether–petroleum ether melted at 107°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.70; H, 6.87. Found: C, 68.70; H, 6.95.

Ten grams of the keto acid was converted into its methyl ester, the ketone group was reduced by aluminum isopropoxide, and the product was dehydrated and hydrolyzed as described for XIa. The **γ-(5-methoxy-3,4-dihydro-2-naphthyl)-butyric acid (XIb)** was recrystallized from ether–petroleum ether; yield, 6.5 g. (70%); m. p. 126–127°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 72.17; H, 7.23. Found: C, 72.23; H, 7.17.

Cyclization of 4 g. of the acid XIb was carried out according to the procedure described for XIIa. After sublimation under reduced pressure, the **4-keto-8-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XIIb)** crystallized from methanol in colorless prisms; yield, 1.5 g.; m. p. 124–125°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.00. Found: C, 78.73; H, 6.81.

A sample of the ketone was hydrogenated to the alcohol in the presence of platinum oxide and the product was heated at 300° for fifteen minutes with palladium-on-charcoal. The resulting 1-methoxyphenanthrene after sublimation and recrystallization from methanol melted at 103° alone and when mixed with an authentic specimen of the compound.

γ-(1-Methyl-5-methoxy-3,4-dihydro-2-naphthyl)-butyric Acid.—To a solution of 2.6 g. of the methyl ester of Xb in 50 cc. of anhydrous ether was added a solution of methylmagnesium iodide prepared from 1.3 g. of methyl iodide in 25 cc. of ether. The product of hydrolysis was dehydrated with potassium acid sulfate and hydrolyzed with alcoholic potassium hydroxide. The resulting acid crystallized from ether–petroleum ether in colorless prisms; m. p. 108–109°; yield, 0.65 g.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.85; H, 7.70. Found: C, 74.03; H, 8.09.

Cyclization of the acid chloride with stannic chloride was not successful.

Summary

The Reformatsky reaction involving the use of methyl γ-bromocrotonate has been applied to 1-decalone, 1-tetralone and 2-methyl-2-carbomethoxycyclohexanone. From the products cyclic ketones were synthesized.

Two other cyclic ketones were prepared by the method involving in the first step the introduction of a butyric acid side chain into a cyclic β-keto ester.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 12, 1946

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Allylidene Halides. I. The Dichlorobutene Prepared from Crotonaldehyde

BY LAWRENCE J. ANDREWS

Phosphorus pentachloride reacts with α,β-unsaturated aldehydes and ketones to form allylidene chlorides. Oftentimes, however, the allylic isomer of the expected dichloride is obtained; and in some cases only the allylic isomer has been isolated.[1] The product of the reaction of crotonaldehyde with phosphorus pentachloride was first described as 1,1-dichloro-2-butene.[2] Later[1b] it was reported on the basis of Raman spectra measurements that the product also contained 1,3-dichloro-1-butene (see equation 1). However, the boiling points of the isomers were too close to permit their separation by fractionation.

$$(1)\quad CH_3—CH=CH—CHO \xrightarrow{PCl_5}$$
$$CH_3—CH=CH—CHCl_2 + CH_3—CH(Cl)—CH=CHCl$$

In connection with studies of the relative reactivities of different allylic halides underway in this Laboratory it was desired to obtain further information on the composition of this dichloride mixture. This report presents the results of experiments performed in an attempt to secure such information.

Oxidation of the Dichloride.—In agreement with Kirrmann[1b] it was found that the dichlorobutene prepared from crotonaldehyde distilled over a range of a few degrees but could not be separated into fractions with the apparatus available. A sample of the distillate was subjected to oxidative degradation with potassium permanganate in neutral solution.[3,4] Reasonably pure α-chloropropionic acid was isolated from the reaction product, and no significant quantity of dichloroacetic acid could be isolated. This seemed a good indication that the dichloride was actually largely 1,3-dichloro-1-butene.

1-Chloro-1-buten-3-ol.—Supporting, though less conclusive, evidence that the dichloride was largely 1,3-dichloro-1-butene was obtained by comparison of the differences in physical properties of the dichloride and those of 1-chloro-1-buten-3-ol with those recorded[5] for 1,3-dichloropropene and 3-chloro-2-propen-1-ol. These differences

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(1) (a) Kirrmann, Pacaud and Dosque, *Bull. soc. chim.*, [5] **1**, 860 (1934); (b) Kirrmann, *Compt. rend.*, **199**, 1228 (1934); (c) Churbakov, *J. Gen. Chem. U.S.S.R.*, **10**, 977 (1940); (d) Straus and Berkow, *Ann.*, **401**, 121 (1913).

(2) Kekulé, *Ann.*, **162**, 98 (1872).

(3) The method was similar to that used by Ingold and Smith, *J. Chem. Soc.*, 2752 (1931).

(4) Although ozonization procedures have been used in studying structures of similar compounds,[1] the work of Young, McKinnis, Webb and Roberts, THIS JOURNAL, **68**, 293 (1946), shows that ozonization of allylic compounds may lead to the formation of abnormal products. It is, of course, not entirely out of the question that permanganate oxidation might be similarly misleading.

(5) Hatch and Moore, *ibid.*, **66**, 285 (1944).