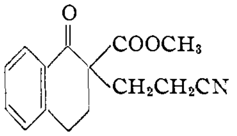
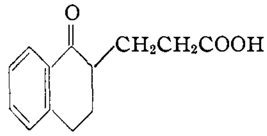
[Contribution from the Chemistry Laboratory of the University of Michigan]

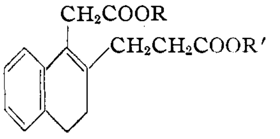
3-Ketohydrophenanthrenes and 2'-Ketohydro-1,2-cyclopentenonaphthalenes

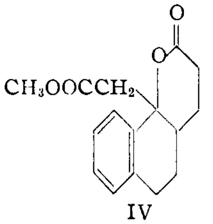
By W. E. Bachmann and G. Dana Johnson[1]

1-Tetralone-2-β-propionic acid (II) was prepared from 2-carbomethoxy-1-tetralone by reaction of its sodio derivative with methyl β-bromopropionate and by cyanoethylation to I followed by hydrolysis and decarboxylation. Reaction of the methyl ester of the acid with zinc and methyl bromoacetate gave the unsaturated acid ester IIIa and not the normal hydroxy ester. The acid ester may have resulted through the intermediate formation of the δ-lactone IV followed by hydrolysis in the isolation process. That the product which was isolated was not the lactone was indicated by its acidic nature and its high absorption maximum (log ε = 4.12) at 264 mμ in the absorption spectrum (Fig. 1). This is to be compared with the spectrum of the γ-lactone VIII (which is similar in structure but more resistant to hydrolysis than the δ-lactone) which absorbs much less strongly (log ε = 2.72) in this region. The double bond appears to be in the ring and not in the exocyclic position in the acetic acid side chain judging from the failure of the corresponding diacid IIIc (which shows the same absorption as the acid ester) to be reduced by sodium amalgam and water. This conclusion is supported by the correspondence of the absorption maximum with the peak of 1,2-dihydronaphthalene at 262 mμ (log ε = 4.01) in hexane.[2]


I


II


IIIa, R = CH_3; R' = H
IIIb, R = R' = CH_3
IIIc, R = R' = H


IV

A Dieckmann cyclization of the dimethyl ester (IIIb) of the unsaturated acid followed by acid hydrolysis and decarboxylation of the resulting β-keto ester yielded 3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (V), which had the same melting point as the ketone prepared from 2-dimethylaminomethyl-1-tetralone and acetoacetic ester in the presence of sodium methoxide.[3] The position of a maximum with log ε = 4.28 at 298 mμ in the absorption spectrum indicated conjugation of the double bond with the aromatic ring and with the carbonyl group.[4] Apparently a shift of the double bond occurs at some stage of the cyclization process.

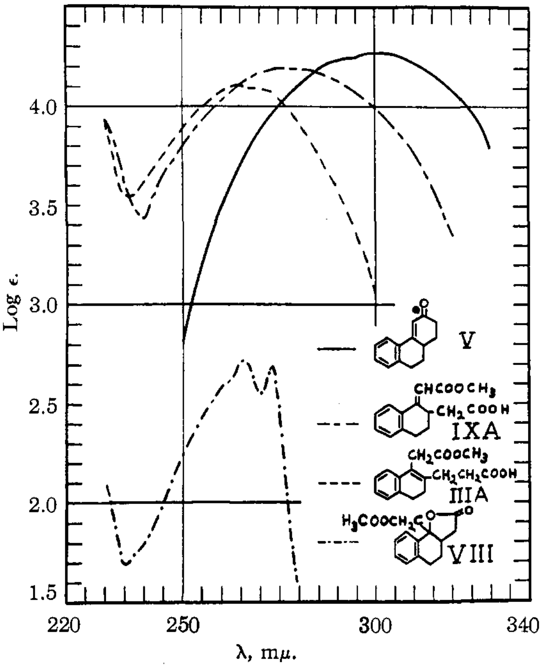
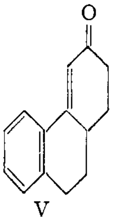
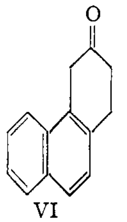


Fig. 1.—Ultraviolet absorption spectra.

The dimethyl ester IIIb was dehydrogenated smoothly by sulfur to the dimethyl ester of 1-carboxymethylnaphthalene-2-β-propionic acid, which was cyclized to 3-keto-1,2,3,4-tetrahydrophenanthrene (VI), a rather unstable ketone. The position of the keto group was proved by conversion of the ketone into 3-methylphenanthrene by reaction with methylmagnesium iodide, followed by dehydration and dehydrogenation of the carbinol.


V


VI

The saturated diester prepared by hydrogenation of IIIb in the presence of Adams catalyst was cyclized to 3-keto-1,2,3,4,4a,9,10,10a-octahydro-

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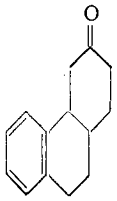
[1] From the Ph.D. dissertation of G. Dana Johnson, 1946. Present address: Department of Chemistry, Indiana University.

[2] Morton and de Gouveia, *J. Chem. Soc.*, 916 (1934).

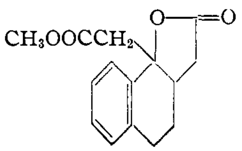
[3] Mannich, Koch and Borkowsky, *Ber.*, 70, 355 (1937).

[4] Compare (a) Wilds, *et al.*, This Journal, 69, 1985 (1947); (b) Bachmann and Dreiding, *J. Org. Chem.*, 13, 317 (1948).

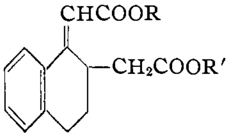
phenanthrene (VII). Only one of the two possible forms (*cis* and *trans*) was obtained; its configuration has not been established. All three 3-ketohydrophenanthrenes, the tetrahydro-, hexahydro- and the octahydro-compound, were converted into phenanthrene by a Wolff–Kishner reduction followed by dehydrogenation of the product.



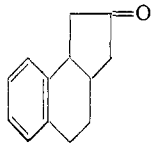
VII



VIII



IXa, R = CH_3; R′ = H
IXb, R = R′ = CH_3
IXc, R = R′ = H



X

A similar series of ketones in which the carbonyl group was part of a five-membered ring was prepared in a similar manner from diesters which contained one less methylene group in the side chain in the 2-position of the naphthalene ring. The starting material was 1-tetralone-2-acetic acid which was prepared from 2-carbomethoxy-1-tetralone and methyl bromoacetate and also from 2-bromo-1-tetralone and malonic ester in the manner of Bergs.[5] The methyl ester of 1-tetralone-2-acetic acid in a Reformatsky reaction with methyl bromoacetate gave the lactone VIII. Hydrolysis of the lactone with one equivalent of alkali yielded the isomeric acid ester IXa. The position of the double bond in the diacid IXc appears to be different from that in the homolog IIIc, since reduction of IXc by sodium amalgam proceeded readily. This indicated the existence of the triple conjugation shown in the formula. Moreover, the maximum in the ultraviolet absorption spectrum of IXa and of IXc is located about 11 mμ higher than in IIIc as would be expected of a completely conjugated system.

The dimethyl ester IXb was cyclized to $\Delta^{1-1'}$-2′-keto-3,4-dihydro-1,2-cyclopentenonaphthalene (like X but with a double bond). The intense absorption (log ϵ = 4.38) at 287 mμ indicated that the double bond was conjugated with the carbonyl group and the benzene ring; the peak is located at a lower wave length than the corresponding maximum in the homologous hexahydrophenanthrene ketone V. As this work was being completed, Wilds and Johnson[6] reported the synthesis of this ketone by a different method. The absorption curve for our compound is identical with that obtained by them.[4a]

Although it was possible to cyclize the dimethyl ester of naphthalene-1,2-diacetic acid (prepared by sulfur dehydrogenation of IXb) to a crystalline cyclic β-keto ester, satisfactory hydrolysis and decarboxylation of the β-keto ester to 2′-keto-1,2-cyclopentenonaphthalene has not yet been accomplished.

Sodium amalgam reduction of the unsaturated acid IXc gave a mixture of the *cis* and *trans* forms of 1,2,3,4-tetrahydronaphthlane-1,2-diacetic acid in about equal amounts, from which the *cis* and *trans* forms of 2′-keto-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene (X) were synthesized. Both forms of the cyclic ketone yielded the known 1,2-cyclopentenonaphthalene when subjected to a Wolff–Kishner reduction followed by dehydrogenation of the resulting hydrocarbons.

Experimental[7]

1-Tetralone-2-β-propionic Acid (II). (a) By Cyanoethylation of 2-Carbomethoxy-1-tetralone.—To a stirred solution of 100 g. of 2-carbomethoxy-1-tetralone[8] in 800 ml. of dry, peroxide-free dioxane 4 ml. of Triton B (38% aqueous trimethylbenzylammonium hydroxide) was added in five minutes, followed by a solution of 36 ml. of acrylonitrile[9] in 50 ml. of dioxane in the course of twenty minutes. The reaction failed completely with dioxane which contained peroxide. The temperature rose from room temperature to about 40°. Stirring was continued for an additional two hours; sufficient 10% hydrochloric acid was added to the dark solution to give a clear brownish-yellow solution; and the dioxane was removed in a current of air. Addition of methanol induced crystallization of the product, which was collected by filtration and washed thoroughly with a saturated, ice-cold solution of 60–70° petroleum ether in methanol; yield, 110 g. of nearly colorless needles; m. p. 75–76°. From the filtrates an additional 6 g. of the product was obtained; total yield, 92%. In this manner 293 g. of 2-carbomethoxy-1-tetralone was converted to 338 g. of **2-carbomethoxy-2-(β-cyanoethyl)-1-tetralone** (I). The compound crystallized from a mixture of methanol and 60–70° petroleum ether in colorless needles; yield 331 g. (90%); m. p. 76–77°. Two more recrystallizations of a sample from methanol resulted in no change in the melting point.

Anal. Calcd. for $C_{15}H_{15}O_3N$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.98; H, 5.62; N, 5.46.

A solution of 51.5 g. of the nitrile in 150 ml. of glacial acetic acid, 300 ml. of concentrated hydrochloric acid, and 20 ml. of water was heated on a steam-bath for four hours, cooled somewhat, and poured with stirring on a mixture of 1000 g. each of ice and water; yield, 42.3 g. (97%); m. p. 105–107°. In this manner 327 g. of the cyanoethyl product gave 270 g. of **1-tetralone-2-β-propionic acid** (II). Recrystallization from acetone gave 264 g. (95%) of colorless rhombs; m. p. 108–110°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.54; H, 6.52.

(b) From 2-Carbomethoxy-1-tetralone and Methyl β-Bromopropionate.—To the solution of sodium methoxide from 1.6 g. of sodium and 80 ml. of absolute methanol was added a solution of 7.1 g. of 2-carbomethoxy-1-tetralone in 80 ml. of dry benzene. The mixture was refluxed on a steam-bath for one hour, cooled, and treated with 11.7 g. of methyl β-bromopropionate. The reaction mixture was allowed to stand for one and one-half hours with oc-

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[5] Bergs, *Ber.*, **63**, 1285 (1930).

[6] Wilds and Johnson, This Journal, **68**, 86 (1946).

[7] Most of the analyses were performed by the Micro-Tech Laboratories, Skokie, Illinois, and the rest by Mrs. Lea Gafney of the Chemistry Department, Indiana University, Bloomington, Indiana.

[8] Bachmann and Thomas, This Journal, **63**, 598 (1941).

[9] Bruson, *ibid.*, **64**, 2457 (1942).

casional shaking; during this time nearly all solid material disappeared. The mixture was then refluxed for one-half hour in a water-bath, cooled, treated with ice-water and extracted with benzene. The product, which was obtained as a liquid by evaporation of the benzene, was heated with 50 ml. of concentrated hydrochloric acid, 50 ml. of glacial acetic acid, and 5 ml. of water for two hours on a steam-bath. The cooled mixture was diluted with 300 ml. of water and extracted with benzene. The benzene solution was extracted with 5% sodium hydroxide and the solution of the sodium salt was treated with Norit, filtered, and acidified; yield 5.4 g. (71%) of crude 1-tetralone-2-β-propionic acid (II); m. p. 99–103°. Upon crystallization of a sample from a mixture of acetone and water, fine colorless needles were obtained exactly as in (a); m. p. 108–110°.

1-Carboxymethyl-3,4-dihydronaphthalene-2-β-propionic Acid (IIIc).—To a solution of 100 g. of 1-tetralone-2-β-propionic acid in 320 ml. of absolute methanol was slowly added with swirling 32 ml. of concentrated sulfuric acid. The solution was refluxed on a steam-bath for one hour, about one-half of the solvent was removed by distillation under reduced pressure on a steam-bath, the residue was diluted with 800 ml. of water, and the mixture was extracted with ether. The ether extracts were washed with saturated sodium bicarbonate solution, dried, and treated with Norit. The liquid dimethyl ester isolated by evaporation of the solution was dried thoroughly in a vacuum desiccator.

To a solution of 20 g. of the methyl ester in 200 ml. of dry benzene was added 20 g. of clean, dry 20-mesh zinc, 14 ml. of methyl bromoacetate, and a small crystal of iodine. The mixture was refluxed on a steam-bath with frequent shaking until the reaction started. At forty-five-minute intervals thereafter 10 g. of zinc was added until a total of three hours reaction time had elapsed. After one hour an additional 6 ml. of methyl bromoacetate was added. After three hours the cooled mixture was treated with 150 ml. of cold 10% hydrochloric acid and shaken vigorously. The solutions were decanted into a separatory funnel and the zinc was washed thoroughly with ether by decantation. The combined extracts were separated and the aqueous layer was extracted with ether. The combined ether-benzene extracts were washed with water and extracted with concentrated aqueous ammonia which had been diluted with an equal volume of water. The ammoniacal extracts were acidified with hydrochloric acid, extracted with ether, and the dried ether solution was treated with Norit. Removal of the ether left **1-carbomethoxymethyl-3,4-dihydronaphthalene-2-β-propionic acid** (IIIa); yield, 16.8 g.; m. p. 84–88°. A sample after three recrystallizations from methanol formed fine colorless needles; m. p. 94–95°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.22; H, 6.59.

The ultraviolet absorption spectrum (Fig. 1) was obtained on a 0.0011% solution of the acid ester IIIa in methanol by means of a Beckman quartz spectrophotometer.

A solution of 20 g. of the acid ester in 100 ml. of methanol and 300 ml. of 0.5 *N* sodium hydroxide was refluxed for one hour on a steam-bath. After removal of one-half of the solvent in a current of air, the residual solution was acidified with concentrated hydrochloric acid and chilled; yield, 18.2 g. (96%); m. p. 145–148°. A sample of **1-carboxymethyl-3,4-dihydronaphthalene-2-β-propionic acid** after three recrystallizations from benzene formed fine colorless needles; m. p. 147–149°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.33; H, 6.31.

The acid reacted immediately with a solution of bromine in carbon tetrachloride and with potassium permanganate solution.

3-Keto-1,2,3,9,10,10a-hexahydrophenanthrene (V).—The dimethyl ester of 3,4-dihydronaphthalene-1-acetic acid-2-β-propionic acid was obtained readily by esterification of the diacid IIIc and the acid ester IIIa by means of anhydrous methanol and concentrated sulfuric acid. A Dieckmann cyclization was run as for the production of VI with sodium methoxide from 0.5 g. of sodium and 0.93 g. of the dimethyl ester in 10 ml. of dry benzene; yield, 0.65 g.; m. p. 110–121°. After three recrystallizations from methanol-water, a sample of **2(or 4-)-carbomethoxy-3-ketohexahydrophenanthrene** formed fine colorless needles; m. p. 126–128°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.96; H, 6.24.

The compound gave no color with ferric chloride, even on heating. It reacted immediately with bromine in carbon tetrachloride, and with potassium permanganate solution.

Hydrolysis and decarboxylation of 0.95 g. of the β-keto ester was accomplished as for the production of VI; yield, 0.7 g.; m. p. 68–75°. After three recrystallizations from methanol-water the cyclic ketone formed needles with a very pale yellow color; m. p. 79–80° (reported,[2] 80°).

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.40; H, 7.24.

The ketone instantly decolorized bromine–carbon tetrachloride solution. The ultraviolet absorption was measured on a 0.0005% solution of the ketone in methanol; a maximum ($\log \epsilon = 4.28$) appears at 298 mμ (Fig. 1).

The 2,4-dinitrophenylhydrazone crystallized from methanol in clusters of crimson prisms; m. p. 204–206° dec.

Anal. Calcd. for $C_{20}H_{18}O_4N_4$: N, 14.81. Found: N, 14.75.

The semicarbazone crystallized from acetic acid in fine colorless needles; m. p. 244–245° dec. It turned yellow in a few hours even when kept in an evacuated desiccator in the dark. This phenomenon has been noted with the semicarbazones of other β-aryl-substituted α,β-unsaturated ketones. A satisfactory analysis was not obtained. A suspension of 0.25 g. of the semicarbazone in ethanolic sodium ethoxide, prepared from 0.5 g. of sodium and 15 ml. of absolute ethanol, was heated in a bomb tube at 170° for twenty hours. Dehydrogenation of the product gave phenanthrene.

3-Keto-1,2,3,4-tetrahydrophenanthrene (VI).—A test-tube containing a mixture of 2 g. of the crude diester IIIb and 0.225 g. of sulfur and fitted with a one-hole stopper bearing a short length of capillary tubing was lowered to the level of the mixture in a metal-bath at 220°. The temperature of the bath was raised to 280° in the course of ten minutes. The cooled mixture was refluxed with 50 ml. of methanol and 20 ml. of 0.5 *N* sodium hydroxide for one hour on a steam-bath. After the solvent had been removed, a solution of the product in 50 ml. of water was heated with Norit; acidification gave 1.56 g. (87%) of the acid; m. p. 178–181°. A sample of **1-carboxymethylnaphthalene-2-β-propionic acid** after three recrystallizations from a mixture of acetone and water formed fine colorless needles; m. p. 183–184°.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 69.56; H, 5.62.

Dehydrogenation with 10% palladium-on-charcoal gave a poor yield of the acid.

The crude dimethyl ester formed by esterification of the acid with methanol and sulfuric acid was dried thoroughly. A solution of 2 g. of the diester in 25 ml. of dry thiophene-free benzene was added to dry sodium methoxide (made by the reaction of 0.32 g. of sodium with 5 ml. of absolute methanol followed by evaporation under reduced pressure on a steam-bath). The mixture was refluxed in an atmosphere of nitrogen in a water-bath for two hours, the cooled mixture was treated with cold 5% hydrochloric acid and extracted with ether, and the combined ether-benzene extracts were washed with water, dried and treated with Norit. Removal of the solvent under reduced pressure yielded 1.54 g. of **2(or 4-)-carbomethoxy-3-keto-1,2,3,4-tetrahydrophenanthrene**; m. p. 113–120°. A sample crystallized three times from methanol formed colorless leaflets; m. p. 124–125°. It gave a light blue-green color with alcoholic ferric chloride upon heating.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.38; H, 5.66.

A solution of 0.25 g. of the β-keto ester in 20 ml. of glacial acetic acid, 10 ml. of concentrated hydrochloric acid, and 1.8 ml. of water was heated on a steam-bath for four hours in an atmosphere of nitrogen, cooled, diluted with 100 ml. of cold water, and extracted with ether. The ether extracts were washed with water and with cold 2% aqueous sodium hydroxide, dried, treated with Norit, and filtered. The solvent was removed under reduced pressure in an atmosphere of carbon dioxide; yield, 0.12 g. (62%); m. p. 54–58°. After evaporative distillation at 0.01 mm., and three recrystallizations from 60–70° petroleum ether, the **3-keto-1,2,3,4-tetrahydrophenanthrene** formed fine colorless needles; m. p. 64–65°. The ketone was unstable in air, being converted to a dark gummy mass in the course of a few hours. A satisfactory analysis was not obtained. The **2,4-dinitrophenylhydrazone**, which was stable, crystallized from a mixture of benzene and methanol in extremely fine red needles; m. p. 246–248° dec.

Anal. Calcd. for $C_{20}H_{16}O_4N_4$: C, 63.82; H, 4.29; N, 14.89. Found: C, 63.66; H, 4.58; N, 14.74.

The **oxime** crystallized from a mixture of acetic acid and water in clusters of fine colorless needles; m. p. 139–141°.

Anal. Calcd. for $C_{14}H_{13}ON$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.00; H, 5.84; N, 6.96.

The **semicarbazone** crystallized in very fine colorless needles upon diluting an acetic acid solution of the substance with water; m. p. 205–207°.

Anal. Calcd. for $C_{15}H_{15}ON_3$: C, 71.12; H, 5.97. Found: C, 71.38; H, 5.95.

A suspension of 0.3 g. of the semicarbazone in ethanolic sodium ethoxide from 0.5 g. of sodium in 15 ml. of absolute ethanol was heated in a bomb tube at 170° for twenty hours, and the product was dehydrogenated with 0.1 g. of 10% palladium-charcoal catalyst at 310–320° for forty-five minutes. The phenanthrene (m. p. 99–100°) and its picrate (m. p. 141–142.5°) were identified through their melting points and by mixed melting points with authentic specimens.

The carbinol formed from 0.5 g. of the ketone and methylmagnesium iodide was heated with 1.7 g. of potassium acid sulfate for one and one-half hours in a bath maintained at 160–165°. The product was heated with 0.2 g. of 10% palladium-charcoal catalyst for forty-five minutes in a bath maintained at 300–320°. The resulting 3-methylphenanthrene after distillation at 0.02 mm. crystallized from alcohol in colorless needles; m. p. 61.5–63° (reported, 61–62°,[10] 62–63°[11]); m. p. picrate, 136–138° (reported,[11] 137–138°).

3-Keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VII).—Numerous attempts to effect a sodium amalgam reduction of 3,4-dihydronaphthalene-1-acetic acid-2-β-propionic acid (IIIc) failed. Catalytic hydrogenation of the diester IIIb was successful. A solution of 5 g. of the diester in 50 ml. of absolute methanol in the presence of 0.2 g. of platinum oxide catalyst was hydrogenated at 30 pounds pressure in four hours. The end of the reaction was indicated by the failure of the solution to decolorize bromine in carbon tetrachloride. Hydrolysis of 2 g. of the crude dimethyl ester in 20 ml. of methanol with 30 ml. of 0.5 *N* sodium hydroxide by one hour of refluxing on a steam-bath gave 1.8 g. (99%) of **1-carboxymethyl-1,2,3,4-tetrahydronaphthalene-2-β-propionic acid**; m. p. 125–129°. A sample after two recrystallizations from acetone-water formed fine colorless needles; m. p. 130–131°. The acid does not decolorize dilute solutions of bromine in carbon tetrachloride or aqueous potassium permanganate.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; neut. equiv., 131. Found: C, 68.34; H, 6.95; neut. equiv., 132.

A Dieckmann cyclization of 2 g. of the crude dimethyl ester of 1,2,3,4-tetrahydronaphthalene-1-acetic acid-2-β-propionic acid carried out as described for VI gave 1.58 g. of **2(or 4-)-carbomethoxy-3-keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene**; m. p. 76–83°. The compound crystallized from methanol in colorless, broad, flat needles; m. p. 93–95°. No crystalline isomer was found; only a small amount of dark-colored oil which resisted crystallization was found in the filtrate.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.37; H, 7.14.

The β-keto ester gave a purple-gray color with alcoholic ferric chloride. It rapidly decolorized bromine in carbon tetrachloride and aqueous potassium permanganate.

Hydrolysis and decarboxylation of 0.3 g. of the β-keto ester by the procedure used for VI gave 0.21 g. of crude **3-keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene** (VII); m. p. 53–56°. Three recrystallizations of the material from 60–70° petroleum ether formed colorless prisms; m. p. 73–74°.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.64; H, 8.11.

The **2,4-dinitrophenylhydrazone** crystallized from a mixture of chloroform and methanol in globular clusters of fine orange needles; m. p. 175–177°.

Anal. Calcd. for $C_{20}H_{20}O_4N_4$: N, 14.73. Found: N, 15.00.

The **semicarbazone** crystallized from aqueous acetic acid in clusters of fine colorless needles; m. p. 229–231° dec.

Anal. Calcd. for $C_{15}H_{19}ON_3$: C, 70.01; H, 7.44; N, 16.33. Found: C, 70.49; H, 7.21; N, 16.05.

A Wolff–Kishner reduction of 0.35 g. of the semicarbazone gave 0.15 g. of hydrocarbon which was dehydrogenated with palladium-on-charcoal to phenanthrene.

1-Tetralone-2-acetic Acid. (a) **From 2-Bromo-1-tetralone.**—A solution of the 2-bromo-1-tetralone[5] from 10 g. of 1-tetralone[12] in 50 ml. of benzene was added to a cooled suspension of sodiomalonic ester which had been prepared by refluxing on a steam-bath 21 ml. of diethyl malonate, 2.4 g. of sodium powder and 100 ml. of dry benzene for four to five hours. The mixture was heated on a steam-bath for one and one-half hours. The crude substituted malonic ester was heated with a solution of 17 g. of potassium hydroxide, 50 ml. of ester and 20 ml. of 95% alcohol on a steam-bath for four hours. The cooled solution was extracted with benzene to remove non-acidic materials, treated with Norit, filtered, cooled, and acidified with 50 ml. of cold concentrated hydrochloric acid; yield, 10.4 g. of tan-colored 1-tetralone-2-malonic acid; m. p. 164° with evolution of gas. Extraction of the aqueous filtrates with ether afforded an additional 3.5 g. of somewhat oily material (presumably partially decarboxylated) which on decarboxylation gave the required acid; total yield, 81%. Bergs[5] employed dry ether in the malonic ester condensation and was unable to obtain a satisfactory yield of the malonic acid (m. p. 168° after recrystallization from alcohol). The dried acid was decarboxylated at 160–180° and the solution of the sodium salt was treated with Norit; yield of 1-tetralone-2-acetic acid, 10.9 g. (95%); m. p. 98–102°. A sample recrystallized from a mixture of ether and petroleum ether melted at 105–108° (reported,[5] 109–110°).

(b) **From 2-Carbomethoxy-1-tetralone.**—By the same procedure used to prepare 1-tetralone-2-β-propionic acid (II), the sodio derivative of 6 g. of 2-carbomethoxy-1-tetralone was condensed with 5.9 g. of methyl bromoacetate. The resulting **methyl ester of 2-carbomethoxy-1-tetralone-2-acetic acid** crystallized from methanol in fine colorless needles; m. p. 81.8–82.1°.

Anal. Calcd. for $C_{15}H_{16}O_5$: C, 65.20; H, 5.84. Found: C, 65.06; H, 5.84.

Hydrolysis and decarboxylation of the product gave 5 g. (83%) of 1-tetralone-2-acetic acid; m. p. 100–105°. After two recrystallizations from a mixture of ether and

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[10] Bachmann and Cortes, THIS JOURNAL, **65**, 1329 (1943).

[11] Haworth, *J. Chem. Soc.*, 1125 (1932).

[12] Thompson, *Organic Syntheses*, **20**, 94 (1940).

petroleum ether, a sample had a m. p. 106–108°, alone and when mixed with the product in (a).

Preparation of the Lactone VIII.—The **methyl ester of 1-tetralone-2-acetic acid**, prepared with diazomethane, crystallized in small colorless plates from methanol containing a little water; m. p. 55–56.5°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.35; H, 6.36.

A Reformatsky reaction was carried out with 2.18 g. of the methyl ester, 10 ml. of dry ether, 10 ml. of dry benzene, 10 g. of 20-mesh zinc, 1.5 ml. of methyl bromoacetate and a small crystal of iodine. The mixture was stirred with a wire Hershberg stirrer[13] while it refluxed on a water-bath. The reaction began after fifteen to thirty minutes; it was continued in the manner described for IIIa. The cooled mixture was treated with cold, dilute acetic acid, and extracted with benzene. The benzene extracts were washed with water, dried, treated with Norit, filtered, and the benzene removed under reduced pressure. When the residual oil was treated with a little methanol, the **lactone of 1-hydroxy-1-carbomethoxymethyl-1,2,3,4-tetrahydronaphthalene-2-acetic acid** (VIII) crystallized in colorless prisms; yield, 1.53 g. (59%); m. p. 97–98°. A sample recrystallized from methanol melted at 100–100.5°. The lactone is insoluble in aqueous ammonia and only slowly soluble in aqueous sodium hydroxide.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.46; H, 6.49.

The ultraviolet absorption (Fig. 1) was measured on a 0.01% solution of the lactone in methanol.

Hydrolysis of the Lactone to the Unsaturated Acid Ester (IXa).—In one experiment in which 7.5 g. of the lactone (VIII) was refluxed for one hour with only one equivalent of sodium hydroxide (60 ml. of 0.5 *N*) and 100 ml. of methanol, 5.5 g. (74%) of the **methyl ester of 2-carboxymethyl-1-tetrahydronaphthylideneacetic acid** (IXa) was obtained; m. p. 113–116°. A sample crystallized from benzene in fine colorless needles; m. p. 116–117°. A mixture of this compound and the lactone (VIII) melted at 85–88°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.35; H, 6.48.

The ultraviolet absorption spectrum was measured on a 0.001% solution of the acid ester in methanol; log ϵ = 4.19 at 275 mμ (Fig. 1).

Hydrolysis of the Lactone to the Unsaturated Diacid (IXc).—A solution of 1.53 g. of the lactone (VIII) and 8.03 ml. of 0.977 *N* sodium hydroxide in 20 ml. of methanol was refluxed on a steam-bath for one hour. From this solution 1.33 g. (91%) of the unsaturated acid was isolated; m. p. 197–198°. A sample of **1-tetrahydronaphthylidene-1,2-diacetic acid** (IXc) crystallized from a mixture of benzene and acetone in fine, colorless needles; m. p. 204–206°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.28; H, 5.81.

Naphthalene-1,2-diacetic Acid.—The action of ethereal diazomethane on the unsaturated dicarboxylic acid IXc or the monomethyl ester IXa gave a liquid dimethyl ester IXb. Dehydrogenation of 2 g. of the diester by sulfur followed by hydrolysis as described for IIIb gave 1.2 g. of crude naphthalene-1,2-diacetic acid; m. p. 180–190°. A sample after four recrystallizations from a mixture of benzene and acetone formed colorless prisms; m. p. 216–218°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.89; H, 5.11.

1'-(or 3')-Carbomethoxy-2'-keto-1,2-cyclopentenonaphthalene.—Esterification of 2.9 g. of the diacid with methanol and sulfuric acid gave 3 g. (92%) of the **dimethyl ester of naphthalene-1,2-diacetic acid**; m. p. 89–91°. A sample after three recrystallizations from methanol formed colorless leaflets; m. p. 91–92°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.66; H, 5.96.

A Dieckmann cyclization of 1 g. of the dimethyl ester carried out as described for VI gave 0.8 g. of 1'-(or 3')-carbomethoxy-2'-keto-1,2-cyclopentenonaphthalene; m. p. 130–135°. Crystallization of a sample from a mixture of acetone and methanol formed fine colorless needles; m. p. 145–146.5°. The compound gave a deep blue-green color with alcoholic ferric chloride.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.04. Found: C, 75.03; H, 5.38.

Heating a solution of 0.4 g. of the β-keto ester in 40 ml. of glacial acetic acid, 20 ml. of concentrated hydrochloric acid and 2 ml. of water for four hours resulted in a nearly black solution from which was isolated only 0.04 g. of an unstable ketone (colorless needles from petroleum ether; m. p. 98–100°) which gave a 2,4-dinitrophenylhydrazone (orange-yellow prisms from chloroform–alcohol; m. p. 214–216° dec.) for which satisfactory analyses were not obtained. Varying the concentrations of acetic acid and water and the time of heating gave the same results or unreacted material.

$\Delta^{1-1'}$-2'-Keto-3,4-dihydro-1,2-cyclopentenonaphthalene.—The Dieckmann cyclization of the dimethyl ester IXb gave a 82% yield of β-keto ester (m. p. 100–108°). Hydrolysis and decarboxylation of 0.88 g. of the keto ester with a mixture of hydrochloric acid and acetic acid gave 0.46 g. of $\Delta^{1-1'}$-2'-keto-3,4-dihydro-1,2-cyclopentenonaphthalene; m. p. 57–68°. After four recrystallizations from 60–75° petroleum ether the ketone formed colorless prisms; m. p. 72–73.5° (reported,[6] 74–75°).

The 2,4-dinitrophenylhydrazone was treated with hot acetic acid. The material soluble in acetic acid precipitated in fine dark red needles on addition of water; m. p. 251–253° dec. The material insoluble in acetic acid formed lighter red prisms; m. p. 252–254° dec. (reported,[6] dark red needles; m. p. 250.5–251° dec., and lighter red plates; m. p. 247.5–248° dec. from a mixture of benzene and toluene). The ultraviolet absorption was measured on a 0.0005% solution of the ketone in methanol; log ϵ = 4.38 at 287 mμ (reported,[4a] log ϵ = 4.38).

1,2,3,4-Tetrahydronaphthalene-1,2-diacetic Acid.—A mixture of 60 g. of 2% sodium amalgam and a solution of 4.47 g. of the unsaturated acid IXc in 40 ml. of *M* sodium hydroxide was shaken vigorously for thirty minutes; excess alkali was neutralized with hydrochloric acid and the mixture was shaken with another 60 g. of amalgam for thirty minutes. The isolated acid (3.61 g., m. p. 134–136°) consisted of a mixture of the *cis* and *trans* forms. By repeated recrystallizations from benzene and from aqueous acetone it was possible to obtain one of the forms (m. p. 145–146°; called the α-form since its configuration is not known) in a pure state in 20% yield. Both forms were isolated by the method used by Drake and McVey[14] on a mixture of different acids. A mixture of the crude isomeric acids (2.44 g.) was shaken with 32.8 ml. of 0.1 *N* sodium hydroxide for twenty-four hours. After the removal of the insoluble acid by filtration, the filtrate was acidified and the acid which precipitated was recrystallized five times from acetone–water and five times from benzene–petroleum ether (60–75°). The **β-1,2,3,4-tetrahydronaphthalene-1,2-diacetic acid** formed colorless needles; m. p. 142–143°.

The insoluble portion from the previous operation was again shaken with 32.8 ml. of the alkali for twenty-four hours and the acid which remained undissolved was recrystallized as above, yielding the **α-1,2,3,4-tetrahydronaphthalene-1,2-diacetic acid** as colorless rods; m. p. 146–147°. A mixture of the pure α- and β-forms of the acid melted at 137–140°.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: (α-acid) C, 67.78; H, 6.86, 6.66; (β-acid) C, 68.20; H, 6.75.

Cyclization of the Stereoisomeric Acids.—A Dieckmann cyclization of the dimethyl ester from 1.53 g. of the α-form

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[13] Hershberg, *Ind. Eng. Chem.*, **8**, 313 (1936).

[14] Drake and McVey, *J. Org. Chem.*, **4**, 464 (1939).

of 1,2,3,4-tetrahydronaphthalene-1,2-diacetic acid, carried out as described for VI, yielded 1.24 g. of α-1′-(or 3′)-**carbomethoxy-2′-keto-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene**, which after three recrystallizations from methanol formed colorless prisms; m. p. 108–109°.

Similarly from the ester of 1.29 g. of the β-acid 0.98 g. of the **β-form** of the keto ester was obtained, which after three recrystallizations from methanol formed fine colorless needles; m. p. 113–115°. A mixture of the two pure forms melted at 90–95°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: (α-form) C, 73.94; H, 6.74; (β-form) C, 73.70; H, 6.82.

The cyclic keto esters can be separated from each other more readily and in better yield than can the original acids. Cyclization of the dimethyl esters prepared from 1.66 g. of the mixture of acids yielded 1.48 g. of a mixture of the two forms of the keto esters; m. p. 70–91°. The mixture was dissolved in the minimum of hot methanol and a one-third excess of the solvent was added. On chilling, the β-form of the keto ester precipitated in nearly pure state. When the filtrate was concentrated to one-half its volume and chilled, a small amount of the mixed isomers separated; from the concentrated filtrate the nearly pure α-form of the keto ester separated. Two recrystallizations from methanol yielded the pure compounds. About equal amounts of the two forms were obtained.

Hydrolysis and decarboxylation of 0.7 g. of the α-form of the cyclic keto ester by a mixture of acetic acid and hydrochloric acid gave a quantitative yield of the α-form **of 2′-keto-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene** (X); m. p. 83–85°. It crystallized from methanol in colorless rectangular plates; m. p. 85–86°.

Similarly, the **β-form of X** was obtained in 94% yield (m. p. 48–49°) from the isomeric keto ester; it crystallized from methanol in colorless needles; m. p. 51–52°.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: (α-form) C, 83.74; H, 6.64; (β-form) C, 83.94; H, 7.71.

The 2,4-dinitrophenylhydrazones were recrystallized from methanol-chloroform; α-form, yellow needles with m. p. 260–261°; β-form, orange-yellow needles with m. p. 240–241° dec.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: N, 15.29. Found: (α-form) N, 15.11; (β-form) N, 15.12.

The semicarbazones of both forms crystallized in very fine colorless plates; α-form, m. p. 254–256° dec.; β-form, m. p. 220–222° dec.

Anal. Calcd. for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: (α-form) C, 69.43; H, 6.94; N, 17.34; (β-form) C, 69.09; H, 7.34; N, 16.81.

A suspension of 0.25 g. of the semicarbazone (α- or β-form) in ethanolic sodium ethoxide from 0.46 g. of sodium and 13 ml. of absolute alcohol was heated at 170° for twenty hours in a bomb tube. The isolated yellow liquid was heated with 0.2 g. of 10% palladium-charcoal catalyst at 300–320° for forty-five minutes. The product formed a picrate, which after two recrystallizations from ethanol melted at 106–107°, alone and when mixed with an authentic specimen of the picrate of 1,2-cyclopentenonaphthalene.

Summary

Three 3-ketohydrophenanthrenes and two 2′-ketohydro-1,2-cyclopentenonaphthalenes were synthesized by methods involving the Reformatsky and Dieckmann reactions.[15]

[15] A similar series of ketones has been prepared from **2-carbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene** by L. E. Miller in this Laboratory. These results will be published soon.

ANN ARBOR, MICHIGAN RECEIVED JUNE 20, 1949

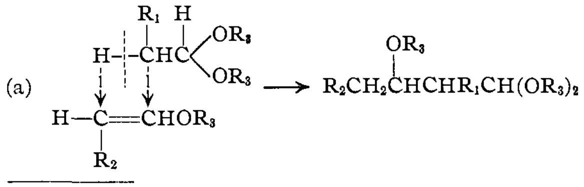
[CONTRIBUTION FROM THE PROCESS DEVELOPMENT LABORATORY, CARBIDE AND CARBON CHEMICALS CORPORATION]

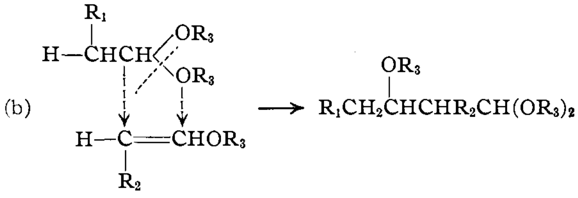
Reaction of Acetals and α,β-Unsaturated Ethers

BY R. I. HOAGLIN AND D. H. HIRSH

During the course of an investigation of the chemistry of vinyl ethers the reaction of acetals and α,β-unsaturated ethers was studied. Examples of this reaction were reported by Mueller-Cunradi and Pieroh in a U. S. patent[1] which describes the condensation of acetaldehyde acetals and vinyl ethers in the presence of catalysts capable of effecting the polymerization of vinyl ethers.

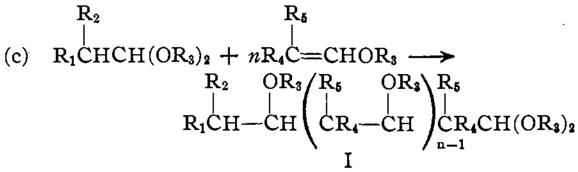
A priori the reaction of an acetal with an α,β-unsaturated ether could involve a splitting of either an alpha hydrogen, as suggested by Mueller-Cunradi and Pieroh, or an alkoxy group from the acetal with addition of the corresponding resulting fragments to the double bond of the unsaturated ether as shown in reactions (a) and (b).





R_1 and R_2 may be hydrogen atoms or alkyl radicals; R_3 is an alkyl radical.

The present study showed that an alkoxy group is split from the acetal molecule and that the course of reaction indicated in (b) is correct. The investigation also showed that the reaction could be extended to include acetals of aldehydes other than acetaldehyde and also α,β-unsaturated ethers other than those derived from vinyl alcohol. The results may be generalized by the following equation, where R_1, R_2, R_4 and R_5 may



$$\text{(c)}\quad R_1\overset{R_2}{\overset{|}{C}}HCH(OR_3)_2 + nR_4\overset{R_5}{\overset{|}{C}}{=}CHOR_3 \longrightarrow R_1\underset{}{\overset{R_2}{\overset{|}{C}}}H{-}\overset{OR_3}{\overset{|}{C}}H\left(\overset{R_5}{\overset{|}{C}}R_4{-}\overset{OR_3}{\overset{|}{C}}H\right)_{n-1}\overset{R_5}{\overset{|}{C}}R_4CH(OR_3)_2$$

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[1] Mueller-Cunradi and Pieroh, U. S. Patent 2,165,962 (1939).