with the constants for III. Its purification was not attempted since the preparation outlined above for III is simpler and leads to a purer product.

3-Vinyl-1,5-hexadiene (XII).—1,4-Pentadiene was prepared by the Boord synthesis.[34] XII was prepared by alkylating the sodium salt, prepared from 23.4 g. of 1,4-pentadiene and the sodamide obtained from 7.94 g. of sodium with 41.8 g. of allyl bromide. The procedure described for III was followed, except that a dry-ice condenser was used to condense the low-boiling hydrocarbons in the preparation of the sodium salt and in the alkylation. Distillation through the column with a 30 × 1.1 cm. packed section gave 7.7 g. (21%) of crude XII, b. p. 101–106°. After repetition of the alkylation, the combined products were redistilled, yielding XII with b. p. 103–103.5°; $n^{25}D$ 1.4301; d^{25}_4 0.7410; MD calcd. 37.75, found 37.73.

Anal. Calcd. for C_8H_{12}: C, 88.80; H, 11.20. Found: C, 88.97; H, 11.23.

We are indebted to Miss Frances Marx, Miss Lois E. May, and Mr. Saul Gottlieb for all the microanalyses reported in this work.

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[34] Shoemaker and Boord, This Journal, **53**, 1505 (1931); Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 146 (1936).

Summary

3-Phenyl-1,5-diolefins (III, V and VII) have been prepared by the alkylation of the sodium salt of allylbenzene with allyl bromide, crotyl chloride and methylvinylcarbinyl chloride in liquid ammonia solution. These hydrocarbons rearrange on heating at 165–185°, yielding 1-phenyl-1,5-diolefins. Inversion of the two butenyl groups occurs during the rearrangement of V and VII. 3-Methyl-1,5-hexadiene has been shown to rearrange partially to 1,5-heptadiene on heating at 300°. The reverse rearrangement occurs to a limited extent at the same temperature.

These observations extend the scope of three-carbon systems in which allyl groups are known to rearrange and establish the reversibility of the rearrangement for a case in which the two isomers have similar stabilities.

New York, N. Y. Received July 1, 1944

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

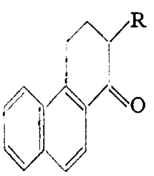
16-Equilenone and 16,17-Substituted Equilenane Derivatives

By A. L Wilds and Lloyd W. Beck

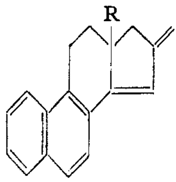
Recently[1] a method was described for the synthesis of partially hydrogenated 1,2-cyclopentenophenanthrene derivatives related to the female sex hormones. The ketone IIIa was prepared by cyclization of the substituted diketo ester (or the related 1,4-diketone) which resulted from the reaction of 2-bromo-1-ketotetrahydrophenanthrene (I) with acetoacetic ester. Since the sex hormones carry a methyl group between the C and D rings, the extension of this method to the homolog of IIIa containing the angular methyl group (III) was of especial interest.

Such an extension of the method would involve the alkylation of acetoacetic ester with a tertiary halide, the 2-methyl-2-bromo ketone corresponding to I, a type of reaction which usually results in dehydrohalogenation rather than the desired alkylation. A test of this step was made, however, using sodiomalonic ester since any alkylation product could be isolated easily, subsequent to hydrolysis and decarboxylation. An improved method was developed for the preparation of 1-keto-2-methyltetrahydrophenanthrene (II) from which the necessary bromo ketone was obtained in excellent yield by bromination.

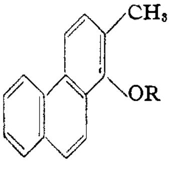
By condensation of the bromo ketone with sodiomalonic ester, it was possible to obtain the acid V in 24% yield. Although the yield was much higher than anticipated, it was still too low to make this a practical synthetic approach. The acid was accompanied by a phenolic fraction from which was isolated 2-methyl-1-phenanthrol (IV) in 18 to 30% yield. This phenanthrol, which has not been described previously, could be prepared in excellent yield by the action of boiling 2,4,6-trimethylpyridine on the bromo ketone to eliminate hydrogen bromide. Upon methylation the phenanthrol gave a methyl ether IVa which agreed in melting point with the compound prepared by Hill and Short[2] in low yield from 3-methyl-2-methoxyphenylacetic acid through the Pschorr synthesis.



I R = Br
II R = CH_3



III R = CH_3
IIIa R = H



IV R = H
IVa R = CH_3

As a more satisfactory method of preparing the desired intermediate compounds for the synthesis of III, we investigated the direct alkylation of the ketone II through reaction of its sodium enolate with an appropriate bromo compound. The enolate, prepared by means of sodium amide, reacted readily with methyl bromoacetate to give

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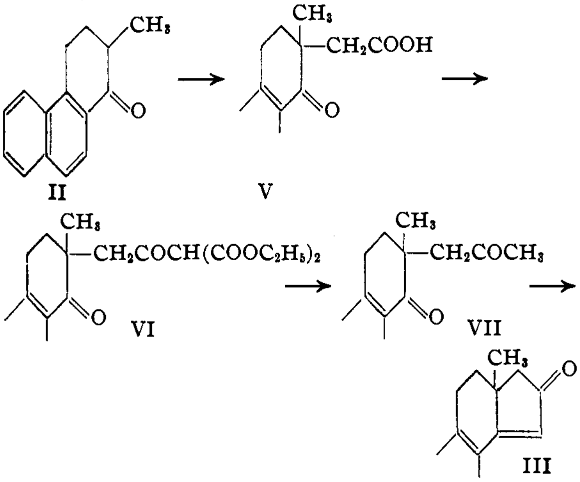
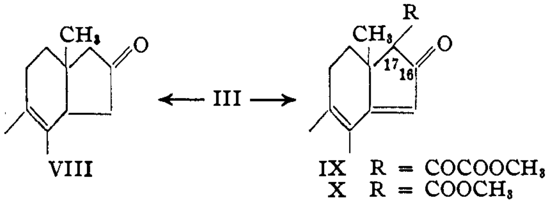
[1] Wilds, This Journal, **64**, 1421 (1942).

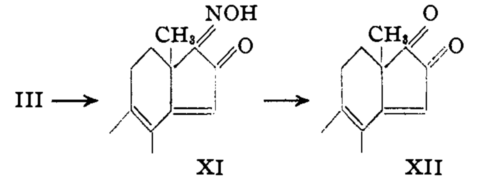
[2] Hill and Short, *J. Chem. Soc.*, 260 (1937).

the acid V in 71% yield after hydrolysis. Unfortunately, attempts to prepare the necessary diketone VII in a similar manner by reaction with bromo- or chloroacetone were unsuccessful. It was possible, however, to use the acid V for this purpose. Condensation of the acid chloride with sodiomalonic ester led to the keto ester VI, which when hydrolyzed with a mixture of acetic and hydrochloric acids gave the diketone VII in 83% over-all yield from V. Cyclization of VII to the ketone III was effected in a nearly quantitative yield by the action of dilute aqueous alkali.



As was reported previously for the unsaturated ketone IIIa, the selective hydrogenation of III proceeded smoothly in the presence of palladium-charcoal to give the reduced ketone VIII. This ketone is a structural isomer of desoxyequilenin (17-equilenone)[3] having the carbonyl group in the 16-position (16-equilenone). Only one of the two possible stereoisomers could be isolated in pure form.[4]

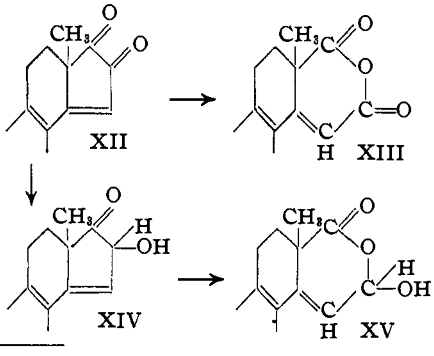




The development of facile synthesis of the unsaturated ketone III from II in three steps, each in good yield, made this a readily accessible intermediate for preparing other cyclopentanophenanthrene derivatives still more closely related in structure to the natural hormones. Furthermore, the introduction of a group in the 17-position of III by condensation reactions was facilitated by the presence of the double bond, since this precluded substitution in the 15-position. Thus, by reaction with dimethyl oxalate the glyoxalate IX was obtained in 92% yield. This compound did not lose carbon monoxide very easily upon heating, but in a preliminary experiment the expected keto ester was isolated in 30% yield. The obvious value of this compound as an intermediate for preparing interesting analogs of a number of the steroids will justify considerable effort in the future to improve this step.

Condensation of III with *n*-butyl nitrite in the presence of potassium *t*-butoxide, by the excellent general procedure of Litvan and Robinson,[5] resulted in the introduction of an oximino group in the 17-position to form XI. This monoöxime could be hydrolyzed with acid in the presence of formaldehyde to the corresponding diketone (XII) in excellent yield. The structure of the diketone was confirmed by oxidation with periodic acid, with the formation of the anhydride XIII. The melting points of this compound and the dibasic acid and dimethyl ester obtained upon reduction of the double bond were in agreement with those reported by Bachmann and Wilds,[3] who prepared the compounds as intermediates in the synthesis of 17-equilenone. The anhydride XIII also was obtained from the oximino ketone XI by a Beckmann type of rearrangement, using *p*-toluenesulfonyl chloride and dilute alkali.[6] The formation of the anhydride rather than the corresponding cyano acid or imide was surprising under these mild conditions, in view of the difficulty encountered by Litvan and Robinson in hydrolyzing their intermediate product (formulated as the imide) resulting from rearrangement of the 16-oximino derivative of estrone methyl ether.[5]

Reduction of the two carbonyl groups and the



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[3] For this nomenclature see Bachmann and Wilds, THIS JOURNAL, **62**, 2084 (1940).

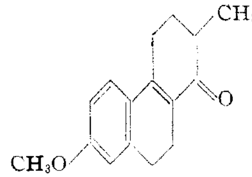
[4] Clemmensen reduction of this ketone has given a crystalline hydrocarbon. By comparison of this compound with the corresponding reduction products of α- and β-17-equilenone we expect to establish the *relative* stereochemical configuration of rings C and D in the two series. This work will be reported later.

[5] Litvan and Robinson, *J. Chem. Soc.*, 1997 (1938).

[6] Chakravarti and Swaminathan, *J. Indian Chem. Soc.*, **11**, 101 (1934), have used this method to open the five-membered ring of the 2-oximino derivative of 5-methoxyhydrindone-1. To the product they assign the structure of the cyano acid (the half nitrile of 4-methoxyhomophthalic acid).

double bond of the diketone XII would lead to the desoxyequilenin analog of estriol. Some experiments have been made in this direction, although the compound has not yet been obtained. Hydrogenation with palladium-charcoal led to the absorption of one mole of hydrogen. Since this dihydro compound did not have the properties of a 1,2-diketone, it was evident that one of the carbonyl groups had been reduced, giving the unsaturated hydroxy ketone XIV, or its isomer with the keto and hydroxyl groups reversed.[7] Oxidation of the dihydro derivative with periodic acid led to a compound, $C_{18}H_{16}O_3$, which is in agreement with the aldehydo acid to be expected by cleavage of the ring of XIV. The masked nature of the acidic group in this compound, which was insoluble in sodium bicarbonate although it dissolved slowly in sodium hydroxide solution, suggests that it exists in the cyclized form as the hydroxy lactone (XV, or its isomer with the carbonyl and hydroxyl groups reversed).[8] Attempts to prepare XIV directly from the oximino ketone XI by reduction with zinc dust and acetic acid were unpromising and led to unidentified mixtures.[9] The further reduction of XIV in the presence of palladium-charcoal went only with difficulty and then gave a mixture, as did reductions with platinum oxide as the catalyst. With a special type of Raney nickel catalyst at atmospheric pressure and room temperature XII was converted into what appears to be the decahydro derivative.

The extension of the reactions now reported to the ketone similar to II but carrying a methoxyl group in the 7-position, and to the corresponding ketone with ring B reduced should lead to interesting compounds in the equilenin and the estrone-estriol series. In this connection use of the ketone XVI[10] may lead to both series of compounds, after hydrogenation or dehydrogenation at the appropriate stages. This work is in progress.



XVI

Experimental[11,12]

α-Methyl-γ-1-naphthylbutyric Acid.—Diethyl β-1-naphthylethylmalonate was prepared from 263 g. of β-1-naphthylethyl bromide[1,13] by a procedure essentially like that of Bachmann, Gregg and Pratt[14]; the yield of ester in the fraction of b.p. 190–215° at 0.6 mm. was 295 g. (84%).

A solution of the sodio derivative, prepared from 82 g. of the substituted malonic ester and 8.3 g. of sodium dissolved in 115 cc. of absolute ethanol, was heated to gentle reflux and methyl bromide gas[15] (dried by passing through calcium chloride and soda lime) was introduced with stirring until the mixture was neutral to litmus (approximately one and one-half hours). A solution of 2.15 g. of sodium in 45 cc. of absolute ethanol was added and methyl bromide again was introduced until the mixture became neutral. Most of the alcohol was then removed under reduced pressure and the cooled residue was treated with 90 cc. of 45% potassium hydroxide solution. The mixture was stirred and heated on the steam-bath with the addition of water as necessary to dissolve the solid salt and heating was continued for two hours after solution was complete. The disubstituted malonic acid was precipitated by the addition of dilute hydrochloric acid, filtered, washed with water and dried. It was decarboxylated without purification by heating in a two-bulb flask in an oil-bath at 185–195° until the evolution of carbon dioxide was complete, then distilled at 0.05 mm. pressure. Recrystallization of the distillate from petroleum ether (b. p. 60–68°) gave 51.0 g. of α-methyl-γ-1-naphthylbutyric acid, m. p. 79–81°. An additional 1.5 g. of the acid (m. p. 75–80°) was obtained in the second crop, bringing the total yield to 88%. Recrystallization from petroleum ether gave the acid as colorless rods with the m. p. 83–84°. Although Haworth[16] reported the m. p. 90° for this acid prepared from naphthalene and methylsuccinic anhydride, we have consistently obtained the lower m. p. even in experiments in which the intermediate disubstituted malonic acid was recrystallized before decarboxylation (m. p. 192–194° with gas) or prepared using diethyl methylmalonate. This last method was used by Cohen, Cook and Hewett,[17] but no m. p. was reported for the acid by them.

1-Keto-2-methyl-1,2,3,4-tetrahydrophenanthrene (II).—A solution of the acid chloride, prepared from 95 g. of α-methyl-γ-1-naphthylbutyric acid, 98 g. of phosphorus pentachloride and 450 cc. of dry, thiophene-free benzene, was cooled to 5° and 120 cc. of stannic chloride in 120 cc. of benzene was added rapidly.[1] The mixture was allowed to stand for thirty minutes at 15° and then the orange complex was hydrolyzed by pouring onto ice and concentrated hydrochloric acid, with the addition of some ether. After washing thoroughly with dilute hydrochloric acid, water and dilute ammonium hydroxide, the solvent was removed and the residue distilled from a two-bulb flask at 0.1 mm. pressure. Recrystallization of the distillate from petroleum ether (60–68°) gave 79 g. (90%) of ketone with the m. p. 69–72° and an additional 3.7 g. (5%) of less pure material, m. p. 55–67°. Further recrystallization of the ketone from petroleum ether gave colorless prisms with

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(7) Experiments on the behavior of this compound at the dropping mercury electrode, kindly carried out by Dr. R. M. Elofson, indicated that it might still be an α,β-unsaturated ketone, rather than the isomer XIV, which would be the expected reduction product in view of the more hindered nature of the 17-keto group. We hope to obtain conclusive evidence on this point from the ultraviolet absorption spectrum of the compound.

(8) The isolation of the cyclic compounds XIII and XV as the products of oxidation of XII and XIV might appear to lead to the attractive hypothesis that this type of intermediate is the direct result of cleavage of the carbon–carbon bond by periodic acid. This conclusion is not necessarily justified, however, since the corresponding dibasic acid and aldehydo acid undergo cyclization readily even in the presence of water.

(9) This type of reaction has been successful with several similar compounds derived from steroidal ketones, in which the five-membered ring was saturated; see, for example: Stodola, Kendall and McKenzie, *J. Org. Chem.*, **6**, 841 (1941); Stodola and Kendall, *ibid.*, **7**, 336 (1942); Huffman and Darby, THIS JOURNAL, **66**, 150 (1944).

(10) Robinson and Walker, *J. Chem. Soc.*, 194 (1936). For an improved synthesis see Bachmann, Kushner and Stevenson, THIS JOURNAL, **64**, 979 (1942).

(11) All m. ps. are corrected unless otherwise noted. Those marked vac. were taken in sealed Pyrex capillary tubes evacuated to approximately 0.5 mm.

(12) We are indebted to the Wisconsin Alumni Research Foundation for a grant to purchase some of the chemicals used in this investigation.

(13) Hoch, *Bull. soc. chim.*, [5] **5**, 268 (1938).

(14) Bachmann, Gregg and Pratt, THIS JOURNAL, **65**, 2315 (1943).

(15) Lucas and Young, *ibid.*, **51**, 2536 (1929).

(16) Haworth, *J. Chem. Soc.*, 1132 (1932).

(17) Cohen, Cook and Hewett, *ibid.*, 1635 (1935).

the m. p. 73–74° (reported by Haworth,[16] 75–76°). We obtained the picrate of the ketone as light yellow needles with the m. p. 79–80°; Haworth reported the m. p. 104° for this derivative. As no analysis was given by him it is possible that his picrate had a ratio of the components different from the 1:1 ratio found for our compound.

Anal. Calcd. for $C_{15}H_{14}O \cdot C_6H_3O_7N_3$: C, 57.4; H, 3.9. Found: C, 57.4; H, 3.9.

2-Bromo-2-methyl-1-keto-1,2,3,4-tetrahydrophenanthrene.—This compound was prepared by bromination of 10.7 g. of the above ketone using the procedure described for the lower homolog.[1] After digestion of the crude bromo ketone with methanol 13.4 g. (91%) of colorless prisms was obtained; m. p. 94–96°. Recrystallization of the compound from acetone–methanol raised the m. p. to 97–98°. The bromo ketone underwent partial decomposition when kept in a soft glass bottle in the dark for several weeks, but was somewhat more stable in a Pyrex glass container.

Anal. Calcd. for $C_{15}H_{13}OBr$: C, 62.3; H, 4.5. Found: C, 62.2; H, 4.5.

Reaction of the Bromo Ketone with Sodiomalonic Ester.—To the clear solution of sodiomalonic ester prepared from 0.25 g. of sodium powder, 2.5 cc. of malonic ester, 15 cc. of dry benzene and 1 cc. of absolute alcohol was added 2 g. of the bromo ketone dissolved in 15 cc. of benzene. The solution was allowed to stand at room temperature for twelve hours and then was refluxed for three hours. The benzene was evaporated and the residue hydrolyzed with 8 cc. of 45% potassium hydroxide and 10 cc. of methanol. From the fraction soluble in sodium bicarbonate was obtained, after heating to 180° and recrystallizing the residue from benzene, 0.45 g. (24%) of 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene-2-acetic acid, m. p. 151–152.5°. No m. p. depression was given when the acid was mixed with a sample (see below) prepared from the ketone using sodium amide and methyl bromoacetate.

From the fraction soluble in sodium hydroxide was obtained 0.26 g. (18%) of 2-methyl-1-phenanthrol (see below) by crystallization from benzene; m. p. 123.5–125°. When alcohol was omitted in the preparation of the sodiomalonic ester, the yield of acid was decreased to 11% and the yield of the phenanthrol raised to 30%.

2-Methyl-1-phenanthrol (IV).—A mixture of 2 g. of the bromo ketone and 10 cc. of 2,4,6-trimethylpyridine (γ-collidine)[18] was heated to reflux in an oil-bath. As the bromo ketone dissolved collidine hydrobromide separated, giving a nearly solid mixture. After heating for one hour the mixture was cooled and water and ether were added. The extract was washed first with dilute hydrochloric acid and water and then with five 50-cc. portions of 10% potassium hydroxide to extract the phenanthrol. Acidification, filtration and drying gave 1.4 g. (97%) of light colored solid with the m. p. 121–123°. Vacuum sublimation of the 2-methyl-1-phenanthrol at 160–170° and 0.3 mm., followed by recrystallization from benzene gave colorless needles with the m. p. 124.5–125°. The compound gave no color with ferric chloride in alcoholic solution.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.2; H, 6.1.

The **benzoate** was prepared in 98% yield by heating a solution of the phenanthrol in dioxane, pyridine and benzoyl chloride for two hours at 100°; m. p. 173–175°, with previous softening. Recrystallization from benzene–ethanol narrowed the m. p. range of the colorless prismatic needles to 174.5–175.5°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.6; H, 5.2. Found: C, 84.6; H, 5.3.

The **methyl ether**, prepared by the action of excess dimethyl sulfate upon a solution of the phenanthrol in 5% potassium hydroxide, was obtained from methanol as thin, colorless leaflets with the m. p. 82–83°. Hill and Short[2] have reported the m. p. 82.5–83° for the compound prepared by another method. It was necessary to fuse the crystals at 100° (0.3 mm.) to free the analytical sample from solvent.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.5; H, 6.3. Found: C, 86.2; H, 6.4.

1-Keto-2-methyl-1,2,3,4-tetrahydrophenanthrene-2-acetic Acid (V).—Sodium amide was prepared from 6.9 g. of sodium, 0.5 g. of ferric nitrate and 150 cc. of liquid ammonia as described in "Organic Reactions"[19] except the initial formation of sodium oxide was omitted. When the reaction was complete, 200 cc. of dry ether was added as the liquid ammonia was allowed to evaporate. The air was displaced by a continuous stream of oxygen-free nitrogen, 20 g. of the ketone II was added and converted into the bright yellow sodium enolate by stirring for at least eight hours at room temperature. The suspension was then cooled in an ice–salt bath and an ice-cold solution of 69 g. of methyl bromoacetate in 50 cc. of dry ether was added through the condenser with stirring. The addition was made as rapidly as possible (ten to fifteen seconds) without allowing the vigorous reaction to become uncontrollable. Finally, the mixture was refluxed for three hours, then poured into water, separated and the aqueous layer re-extracted with ether. The combined extract was washed, filtered, evaporated and the residue was hydrolyzed by refluxing for five hours with a mixture of 120 cc. of 45% potassium hydroxide solution and 120 cc. of methanol. During this period a small amount of solid separated, which after filtration amounted to 0.7 g.; m. p. 235–248°. Recrystallization of this material from dioxane gave colorless clumps of needles with the m. p. 255–256° (uncor.). With sulfuric acid the compound gave a yellow solution turning to bright green. The analytical results were in agreement for a compound containing two molecules of the ketone, less two hydrogen atoms, suggesting the condensation product joined in the 2,2′ position as a possible structure. Attempts to prepare an oxime in pyridine or alcohol–dioxane solution (refluxed twenty hours) gave unchanged material (67–93% recovery). The compound also was unaffected by heating for seventeen hours with acetic anhydride.

Anal. Calcd. for $C_{30}H_{26}O_2$: C, 86.1; H, 6.2. Found: C, 85.8; H, 6.3.

The methanol filtrate from hydrolysis of the ester was diluted and extracted with ether. From the neutral oil (1.6 g.) could be isolated only 0.1 g. of crude starting ketone, m. p. 63–69°. Acidification of the alkaline solution gave a solid acid, which was filtered and recrystallized from benzene. The weight of the substituted acetic acid, dried at 100° to remove benzene of crystallization, was 18.1 g. (71%); m. p. 147–151°. Further recrystallization from benzene gave colorless leaflets with the m. p. 153–153.5°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.2; H, 5.9.

An attempt was made to obtain more of this acid from the dark-colored mother liquors by esterification with methanol and sulfuric acid, followed by evaporative distillation at 0.5 mm. (up to 210°). There was considerable residue in addition to the distillate, and the latter after hydrolysis and recrystallization from benzene gave only a trace of the acid, m. p. 140–146°.

The crystalline **methyl ester** was obtained in 84% yield from the pure acid by means of methanol and sulfuric acid.

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(18) The superiority of γ-collidine over other tertiary bases for the conversion of bromo ketones to the corresponding unsaturated ketones has been demonstrated by Butenandt and others [Butenandt, Mamoli, Dannenberg, Masch and Paland, *Ber.*, **72**, 1617 (1939); Butenandt and Dannenberg, *ibid.*, **73**, 206 (1940); see also Inhoffen, Zühlsdorff and Huang-Minlon, *ibid.*, **73**, 451 (1940)]. Recently Galinovsky, *ibid.*, **76**, 230 (1943) has used collidine to convert the dibromodecalones into the corresponding tetralols in 59–61% yield. Mosettig and Burger, THIS JOURNAL, **57**, 2189 (1935), have prepared 1-phenanthrol from 2-bromo-1-ketotetrahydrophenanthrene and diethylaniline.

(19) Leffler, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1942, Vol. 1, p. 99; Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

After evaporative distillation at 170° (0.04 mm.) and recrystallization from methanol the colorless prisms had the m. p. 73–73.5°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4. Found: C, 76.6; H, 6.3.

Attempts to Alkylate the Ketone II with Other Reagents.—In preliminary experiments, an attempt was made to use potassium *t*-butoxide in *t*-butyl alcohol for the preparation of the enolate of II, following the procedure which Johnson[20] found to be very satisfactory for the methylation of 2-benzal-6-methylcyclohexanone. In the present case reaction with methyl bromoacetate gave after hydrolysis only 16% of the crystalline acid V (m. p. 145–149°) accompanied by twice this amount of an acidic oil which could not be crystallized and 35% of unreacted ketone.

When the sodium enolate of II, prepared with sodium amide as described above, was treated with an excess of chloroacetone at 0°, a vigorous reaction occurred but 60 to 80% of the starting ketone could be recovered and none of the diketone VII was isolated. Similar negative results were obtained at the temperature of dry-ice–ether, or with bromoacetone.

1-Keto-2-methyl-1,2,3,4-tetrahydrophenanthrene-2-acetone (VII).—The acid chloride was prepared from 24 g. of the acid V, 49 cc. of pure thionyl chloride and 250 cc. of dry, thiophene-free benzene containing five drops of pyridine. After forty minutes at room temperature and five minutes at 50°, the solvent and excess thionyl chloride were removed under diminished pressure at room temperature, 100 cc. of dry benzene was added to the residue and again removed under diminished pressure. A solution of the acid chloride in 250 cc. of dry benzene was added to a cooled suspension of sodiomalonic ester, prepared by refluxing for seven hours 4.2 g. of powdered sodium in 43 cc. of diethyl malonate and 500 cc. of dry ether. The mixture was stirred for twelve hours at room temperature and refluxed for two hours, water added and the mixture acidified with acetic acid. The ether extract was concentrated and the residue hydrolyzed and decarboxylated by refluxing for four hours with 250 cc. of concentrated hydrochloric acid, 250 cc. of acetic acid and 100 cc. of water. After dilution to 1500 cc. with water the diketone was separated by filtration and extraction with benzene. The solid was dissolved in the benzene extract and the latter washed with water and sodium bicarbonate solution. The residue, following evaporation of the benzene, was recrystallized from methanol to give 19.45 g. of brown prisms of the diketone VII with the m. p. 106–109°. An additional 0.38 g., m. p. 100–104°, isolated from the filtrate, brought the total yield to 83%. Recrystallization of 4.5 g. of the material in the first crop from methanol (Norit) gave 4.1 g. of pure material as colorless prisms; m. p. 109–109.5°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 81.2; H, 6.6.

From the sodium bicarbonate extracts there was obtained crude starting acid which after one recrystallization from benzene amounted to 1.5 g.; m. p. 140–145°.

$\Delta^{1,1'}$-2'-Keto-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene (III).—Dilute aqueous potassium hydroxide was found to be a better cyclizing medium than methanolic alkali. A suspension of 7.5 g. of the unrecrystallized diketone (m. p. 106–109°) in 750 cc. of 5% potassium hydroxide was refluxed in a nitrogen atmosphere for twenty hours. After cooling, the solid was dissolved in benzene and washed with dilute hydrochloric acid and water. Recrystallization from benzene–methanol gave 6.5 g. of tan ketone, m. p. 146–148°. A second crop with the m. p. 143–148° brought the total yield to 6.73 g. (96%). Evaporative distillation of 6.5 g. at 180° and 0.03 mm., followed by recrystallization from benzene–methanol gave 6.3 g. of colorless leaflets (or sometimes prisms) with the m. p. 147.5–148°. With concentrated sulfuric acid the ketone formed a yellow colored solution.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.1; H, 6.5. Found: C, 87.2; H, 6.5.

The **oxime** was prepared in alcohol–pyridine solution in 86% yield. After recrystallization from alcohol, the m. p. of the colorless clumps of crystals was 197–205° with decomposition, when placed in a bath preheated to 190°. When inserted at 196° it melted completely and partly resolidified, remelting at 197–205° dec. The m. p. was no sharper under vacuum.

Anal.[21] Calcd. for $C_{18}H_{17}ON$: C, 82.1; H, 6.5. Found: C, 82.2, 82.3; H, 6.8, 6.6.

2'-Keto-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentanophenanthrene (VIII).—Selective reduction of the carbon–carbon double bond was found to proceed more smoothly if the unsaturated ketone was first refluxed for three hours in dioxane with Raney nickel catalyst and recrystallized from methanol. A solution of 1 g. of the purified ketone in 25 cc. of pure dioxane was shaken with 0.3 g. of palladium–charcoal catalyst[22] and hydrogen at room temperature and atmospheric pressure. One mole-equivalent of hydrogen was absorbed in eighteen hours. The residue remaining after removing the catalyst and solvent was crystallized from methanol, giving a total of 0.84 g. of crystalline material; m. p. 152–164°. This was predominantly one of the two possible diastereoisomers; one recrystallization from methanol gave 0.56 g. of ketone with the m. p. 166–169°. Another recrystallization gave the pure ketone as colorless leaflets melting at 168.5–169°. No color was formed with sulfuric acid.

Anal.[23] Calcd. for $C_{18}H_{18}O$: C, 86.4; H, 7.2. Found: C, 86.0; H, 7.3.

The **oxime** was prepared in 85% yield in alcohol–pyridine solution. After recrystallization from benzene–methanol, the colorless plates melted at 211–213 (vac.).

Anal.[23] Calcd. for $C_{18}H_{19}ON$: C, 81.5; H, 7.2. Found: C, 81.5; H, 7.2.

Attempts to isolate the other isomer of the ketone by crystallization or by fractional elution of the material adsorbed on a column of alumina led only to mixtures.

The 3'-Monoöxime of $\Delta^{1,1'}$-2',3'-diketo-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene (XI).—A procedure similar to that of Litvan and Robinson[5] was used to introduce an oximino group into the cyclopenteno ring. One gram of the unsaturated ketone III was stirred at 70° with a solution of 0.34 g. of potassium in 30 cc. of dry *t*-butyl alcohol, under a nitrogen atmosphere, until solution was complete (about twenty minutes). The red solution was cooled to room temperature and 1.05 cc. of freshly distilled *n*-butyl nitrite was added dropwise with stirring and external cooling. After stirring for five hours at room temperature, water was added to the thick, chocolate-brown mixture. A longer reaction period or a longer time before adding the butyl nitrite was not advantageous and in some runs resulted in a lowered yield and an impure product. The mixture was acidified and extracted with ether. The ether layer was extracted with several portions of 5% potassium hydroxide solution and the red solution of the potassium salt was again acidified and filtered, giving 1.10 to 1.11 g. (98%) of the yellow oximino ketone; m. p. 223–224° (gas) with sintering at 220°. This material was suitable for hydrolysis without further purification. Recrystallization from methanol gave yellow leaflets sintering at 225°, and melting at 227.5–228° (gas). A brown solution was formed with sulfuric acid.

Anal. Calcd. for $C_{18}H_{15}O_2N$: C, 78.0; H, 5.4. Found: C, 77.7; H, 5.4.

The monooxime was converted to the **dioxime** in 95% yield in alcohol–pyridine solution. After recrystallization from ethanol yellow leaflets were obtained which darkened at 236° and melted at 237–237.5° (gas). The melting point of a mixture with the dioxime prepared below from the diketone showed no depression. The solid gave a reddish-brown solution with sulfuric acid.

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[20] Johnson, THIS JOURNAL, **65**, 1320 (1943).

[21] Microanalysis by Arlington Laboratories, Fairfax, Virginia.

[22] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[23] Microanalysis by Dr. T. S. Ma, Department of Chemistry, University of Chicago.

Beckmann Rearrangement[24] of the Oximino Ketone XI.—To a warm solution of 0.50 g. of the oximino ketone in 25 cc. of 5% potassium hydroxide solution was added 0.70 g. of *p*-toluenesulfonyl chloride in portions with swirling. After ten minutes the color of the solution had changed from red to yellow and nearly all of the reagent had reacted. After warming for one hour on the steam-bath, the solution was filtered and acidified with dilute hydrochloric acid. Recrystallization of the crude solid (0.46 g. or 92% yield, m. p. 173–180°) from benzene–petroleum ether (60–68°) gave the anhydride XIII, m. p. 190–191°. Reduction of the double bond converted the anhydride into the saturated dibasic acid, m. p. 228–229°, which formed a dimethyl ester, m. p. 104–105°, with diazomethane. The melting points of these three compounds were not depressed when mixed with authentic samples[3] or with the compounds prepared below by periodic acid oxidation of the diketone.

$\Delta^{1,1'}$-2',3'-Diketo-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene (XII).—The 3'-monoöxime was hydrolyzed to the diketone using a modification of the method described by Chakravarti and Swaminathan[24] for 2-oximino-4,5-dimethoxyhydrindone-1. The yield in this step was directly dependent upon the purity of the isonitroso ketone. With the purest samples, m. p. 227–228°, the yield of diketone was as high as 91%; with a sample of the monooxime of m. p. 217–222° the yield was only 78%. However, the best over-all yields were obtained using the unpurified monoöxime directly.

A mixture of 1.10 g. of the monoöxime (m. p. 223–224°), 11 cc. of dioxane, 11 cc. of 37% formalin solution, and 5 cc. of concentrated hydrochloric acid was heated to reflux with mechanical stirring. The yellow oxime dissolved within two minutes and after five minutes the unsaturated diketone began to crystallize from the hot solution. After heating for one hour 50 cc. of benzene was added to the hot mixture, giving two clear layers. The benzene layer was washed successively with water, dilute potassium hydroxide solution, dilute acid and finally water. By concentration of the solution and crystallization from benzene–ethanol 0.87 g. of the diketone was obtained, m. p. 201–203°. Additional material from the filtrate (m. p. 197–201°) brought the total yield to 84–90%. By evaporative distillation at 180° (0.03·mm.) and recrystallization from benzene–ethanol the pure diketone was obtained as orange leaflets with the m. p. 203–205°. The compound gave an olive-green solution with concentrated sulfuric acid.

Anal.[23] Calcd. for $C_{18}H_{14}O_2$: C, 82.4; H, 5.4. Found: C, 82.0; H, 5.4.

The **quinoxaline** was prepared in 91% yield by refluxing an ethanol solution of the diketone and *o*-phenylenediamine. The yellow leaflets after recrystallization from methanol melted at 200–200.5°. A purple solution was given with sulfuric acid.

Anal.[21] Calcd. for $C_{24}H_{18}N_2$: C, 86.2; H, 5.4. Found: C, 86.4, 86.4; H, 5.6, 5.7.

The **dioxime**, prepared in ethanol–pyridine solution, was obtained in 88% yield as light yellow leaflets after recrystallization from ethanol; m. p. 237–237.5° (gas) with previous darkening at 235°. It gave a reddish-brown solution with sulfuric acid.

Anal.[23] Calcd. for $C_{18}H_{16}O_2N_2$: C, 74.0; H, 5.5. Found: C, 74.2; H, 5.6.

Periodic Acid Cleavage of the Unsaturated Diketone XII.—To a mixture of 50 mg. of the unsaturated diketone and 5 cc. of pure dioxane was added 130 mg. of periodic acid (H_5IO_6) and 1.5 cc. of water. Upon standing at room temperature all of the diketone dissolved. After forty-two hours, 0.2 cc. of glycerol was added to destroy the excess periodic acid, the solution was diluted and made alkaline with 5% potassium hydroxide solution until the product dissolved. A small amount of neutral material was removed by extraction with ether and the alkaline solution was acidified with dilute hydrochloric acid, giving 45 mg. (83%) of the anhydride of *syn*-2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthrylidene-1-acetic acid (XIII) with the m. p. 185–187°. Recrystallization from acetone gave colorless elongated prisms with the m. p. 186.5–188.5°; when mixed with a sample of the anhydride (m. p. 191–192.5°) prepared by the method of Bachmann and Wilds[3] the crystals melted at 188–192°. Sixty-two milligrams of the anhydride was converted into 34 mg. of α-2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid using 2% sodium amalgam according to the described procedure.[3] The recrystallized acid, m. p. 228.5–229.5°, melted at 228.5–230° when mixed with an authentic specimen of the acid (m. p. 229–231°). The dimethyl esters formed by means of diazomethane from the dibasic acid prepared from the diketone (m. p. 103–105°) and from the acid of Bachmann and Wilds (m. p. 104–104.5°) gave no melting point depression.

Hydrogenation of the Unsaturated Diketone XII.—A solution of 1.26 g. of XII in 50 cc. of purified dioxane was shaken with 0.4 g. of palladium–charcoal catalyst[22] and hydrogen at room temperature and atmospheric pressure. One mole-equivalent of hydrogen was absorbed in four hours. The solution was filtered, evaporated and the product recrystallized from benzene, giving 1.02 g. of material with the m. p. 198–208°. A second crop of 0.10 g., m. p. 160–185°, was obtained from the filtrate. By recrystallization from benzene the m. p. of the light yellow leaflets was raised to 207–208.5°. The product was not analytically pure, but the analysis indicated it to be a dihydro derivative. The compound gave no color with alcoholic ferric chloride, was insoluble in dilute potassium hydroxide and did not form a quinoxaline, indicating that one of the keto groups had been reduced (see XIV) rather than the carbon–carbon double bond. The crystals of the compound gave a bright red color with sulfuric acid and dissolved to an orange solution.

Anal. Calcd. for $C_{18}H_{16}O_2$ (dihydro derivative): C, 81.8; H, 6.1; for $C_{18}H_{18}O_2$ (tetrahydro derivative): C, 81.2; H, 6.8. Found: C, 81.0; H, 6.2.

The reduction product (200 mg.) was cleaved with 525 mg. of periodic acid in the same manner as described for the unsaturated diketone. When the reaction mixture was diluted a white precipitate formed which dissolved only slowly upon adding dilute potassium hydroxide. The alkaline solution was extracted with ether and acidified to give 180 mg. (85%) of a white solid (possible structure XV) with the m. p. 260–264°. Recrystallization from dioxane–water gave light yellow plates melting at 266–275° (vac., uncor.). The crystals gave a brown color with concentrated sulfuric acid and dissolved to a yellow solution. When, in an attempt to determine the neutral equivalent of the material, a solution of the acid in excess 0.05 *N* potassium hydroxide was treated with dilute hydrochloric acid, the solid began reprecipitating from the solution while it was still alkaline to phenolphthalein.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.7. Found: C, 77.2; H, 5.6.

Reduction of XII with Raney Nickel.—A special Raney nickel catalyst was prepared by the procedure of Adkins and Pavlic.[25] One-fourth teaspoon of this catalyst and 15 cc. of purified dioxane were shaken with hydrogen at room temperature and atmospheric pressure until the catalyst ceased to absorb hydrogen. To this suspension 200 mg. of the unsaturated diketone XII and 5 cc. of pure dioxane were added and the shaking with hydrogen continued. After an initial rapid uptake (approximately one-half of the total amount of hydrogen was absorbed in the first twenty minutes), the rate diminished, becoming slow after three to four hours when the uptake corresponded to between three and four mole-equivalents of hydrogen. After removal of the catalyst and solvent, the resulting colorless glass was stirred with a small amount of isopropyl alcohol and cooled in dry-ice-alcohol. Upon filtration 61 mg.

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(24) Chakravarti and Swaminathan, *J. Indian Chem. Soc.*, **11**, 101 (1934).

(25) Full details are contained in the Ph.D. Thesis of A. A. Pavlic, University of Wisconsin, 1942. This catalyst was prepared from the alloy by the addition of sodium hydroxide solution at 50 ± 2°, followed by digestion at 50° and thorough washing.

(29%) was obtained, m. p. 138–142°. After several recrystallizations from isopropyl alcohol the colorless needles melted at 141–142.5° to a cloudy liquid, clear at 147°. On another run in which four moles of hydrogen was absorbed the yield of solid was only 25 mg. (12%).

Anal.[21] Calcd. for $C_{18}H_{22}O_2$ (octahydro derivative): C, 80.0; H, 8.2; for $C_{18}H_{24}O_2$ (decahydro derivative): C, 79.4; H, 8.9. Found: C, 79.7, 79.6; H, 8.6, 8.9.

With the ordinary type of Raney nickel catalyst prepared according to the directions of "Organic Syntheses"[26] reduction did not proceed at room temperature and atmospheric pressure. However, in a bomb at 80° and 2500 pounds pressure for four hours, reduction did occur, giving a mixture from which 19 mg. of solid, m. p. 75–145°, was isolated.

Methyl $\Delta^{1,1'}$-2'-Keto-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene-3'-glyoxalate (IX).—The general method of Bachmann, Cole and Wilds[27] was used. A mixture of 1.16 g. of dimethyl oxalate, 5 cc. of dry, thiophene-free benzene and the methanol-free sodium methoxide prepared from 0.23 g. of sodium was refluxed for one-half hour under nitrogen, cooled and a solution of 0.5 g. of the unsaturated ketone III in 7.5 cc. of benzene was added. The yellow sodio derivative of the product soon started to precipitate and an additional 5 cc. of benzene was added after one-half hour and after four hours. At the end of six hours at room temperature water was added and the benzene layer was extracted thoroughly with 2% sodium hydroxide. By acidification and filtration 0.617 g. (92%) of the yellow glyoxalate was obtained; m. p. 164–168°. After recrystallization from acetone–methanol the yellow prisms had the m. p. 168.5–170° (Pyrex m. p. tube). The compound gave a deep red-brown color with ferric chloride in alcoholic solution, and gave a dark red color with concentrated sulfuric acid.

Anal.[23] Calcd. for $C_{21}H_{18}O_4$: C, 75.4; H, 5.4. Found: C, 75.0; H, 5.5.

Methyl $\Delta^{1,1'}$-2'-Keto-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene-3'-carboxylate (XI).—The glyoxalate did not lose carbon monoxide very quickly even in the presence of soft glass.[27] The following conditions were found to give fair results. Undoubtedly further study will result in improved yields. An intimate mixture of 300 mg. of the pure glyoxalate (m. p. 168–169°) and an equal volume of ground soft glass was heated for one hour in an oil-bath at 190–200° under a nitrogen atmosphere. The cooled residue was dissolved in benzene, decanted from the glass and washed with 2% sodium hydroxide. This treatment removed some unchanged glyoxalate. After washing with dilute acid and water, the benzene solution was evaporated and the dark colored oil treated with Norit in methanol. The latter was then concentrated to 2 cc. and the solution allowed to stand in the refrigerator for a day. Yellow crystals of the keto-ester (82 mg., or 30% yield) were obtained with the m. p. 130–145°. The second crop of 26 mg., m. p. 137–167°, still contained some glyoxalate as shown by the ferric chloride test. Several recrystallizations of the first crop from methanol gave yellow prismatic needles which softened at 145° and melted at 150–157° (uncor.). Despite the wide melting point range the analytical results were satisfactory. The compound gave a green color with alcoholic ferric chloride and an orange colored solution with concentrated sulfuric acid.

Anal.[23] Calcd. for $C_{20}H_{18}O_3$: C, 78.4; H, 5.9. Found: C, 78.8; H, 6.1.

Summary

The method previously employed for the synthesis of $\Delta^{1,1'}$-2'-keto-3,4-dihydro-1,2-cyclopentenophenanthrene has now been extended to the preparation of the related compound carrying an angular methyl group in the 2-position. By reduction this unsaturated ketone was converted into 16-equilenone.

The unsaturated ketone can be used to prepare derivatives of equilenane substituted in the 17-position, of which the 16,17-diketone (through the 17-oximino derivative) is of particular interest. Some attempts to convert this diketone into the desoxyequilenin analog of estriol by reduction are described.

2-Methyl-1-phenanthrol and derivatives have been synthesized.

MADISON, WISCONSIN RECEIVED JULY 7, 1944

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[26] Mozingo, "Organic Syntheses," **21**, 15 (1941). For examples of reduction of the carbonyl group in steroidal ketones by means of Raney nickel at atmospheric pressure see Strassberger and Schwenk, U. S. Patent 2,223,393 (Dec. 3, 1940).

[27] Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 831 (1940).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO.]

Hydrocarbon Reactions in the Presence of Cracking Catalysts. IV. Removal of Side Chains from Aromatics

BY CHARLES L. THOMAS, JAMES HOEKSTRA AND JOHN T. PINKSTON

One of the major differences between the catalytic and the thermal cracking of hydrocarbons lies in the greater selectivity shown by the catalytic method. This fact was clearly demonstrated for aliphatic hydrocarbons by Egloff, Morrell, Thomas and Bloch.[1] It was found that in the presence of synthetic catalysts of the silica–alumina type, the tendency was to split such compounds as octane, cetane, octene, and cetene mostly into C_3 and larger molecules, with but little hydrogen, methane, ethane, and ethylene being formed. In the thermal cracking of such materials substantial proportions of hydrocarbons smaller than C_3 are produced. In view of these results, it became a matter of interest to study the catalytic cracking of phenyl substituted alkanes and to determine whether or not, in this case, similar selectivity obtained.

Experimental

Materials.—The cumene and the ethylbenzene were obtained from the Dow Chemical Company and were purified by fractionation in a Bruun column[2] of twenty-six theoretical plates. The cumene had n^{20}D 1.4911, in excellent agreement with the values n^{20}D 1.4911 of Troyan[3] and

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(1) G. Egloff, J. C. Morrell, C. L. Thomas and H. S. Bloch, THIS JOURNAL, **61**, 3571 (1939).

(2) J. H. Bruun, *Ind. Eng. Chem., Anal. Ed.*, **8**, 224 (1936).

(3) J. E. Troyan, THIS JOURNAL, **64**, 3056 (1942).