[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Synthesis of Hydroaromatic Compounds Containing Angular Methyl Groups. V. Equilenin Series

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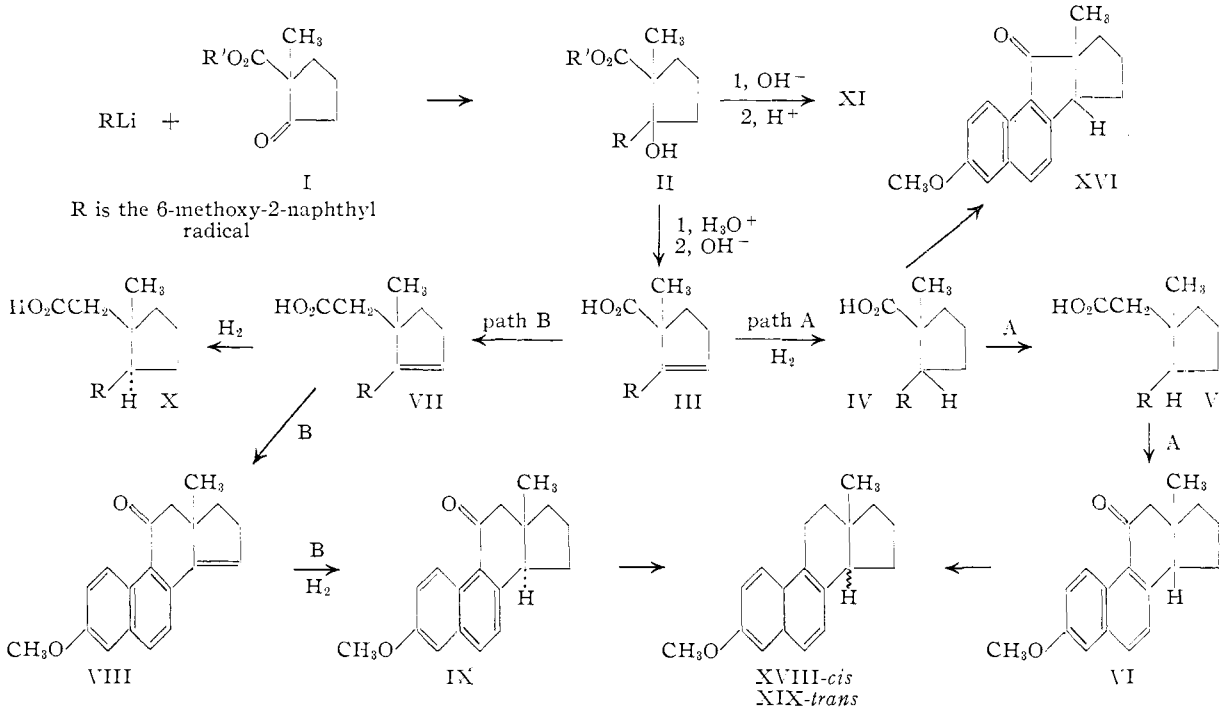
The syntheses of *cis*- (VI) and *trans*-3-methoxy-11-ketoequilenane (IX) and of 3-methoxy-11-keto-14,15-dehydroequilenane (VIII) are described.

In this paper the application of methods previously developed for the synthesis of hydroaromatic compounds containing angular methyl groups and ketonic functions[5] to the synthesis of *cis*- and *trans*-3-methoxy-11-ketoequilenane, VI and IX, is described. The synthetic scheme is illustrated in the chart.



In general the yields were satisfactory although not precisely determined in every case. An interesting feature of these syntheses is the stereospecificity of reduction. Route A (on the right) led mainly to the *cis* isomer, reduction being effected before homologation. Route B led mainly to the *trans* isomer, reduction being effected after homologation and cyclization. This reversal of stereochemical specificity would not have been predicted by any current theory regarding catalytic hydrogenation and the explanation is not apparent from study of molecular models. A noteworthy feature of route B is that the saturated *trans*-acid X did not cyclize to IX under conditions which led to ready ring closure in the *cis* series (V to VI). However, this difficulty was overcome by cyclization of the unsaturated acid VII to VIII, followed by hydrogenation.

The structures of the final products VI and IX were established by reduction to the corresponding *cis*- and *trans*-3-methoxyequilenanes XVIII and XIX and direct comparison of these with authentic samples.[6] The structure of VIII was also confirmed by Huang-Minlon reduction to 3-methoxy-14,15-dehydroequilenane (XVII). The *trans* compound IX was demethylated to the corresponding *trans*-3-hydroxy-11-ketoequilenane, but the corresponding *cis*-3-hydroxy-11-ketoequilenane was not obtained pure.

As in previous cases,[5c] if the hydroxy ester were hydrolyzed with alkali, an open chain keto acid XI (R = H) was obtained. When the isopropyl ester of XI was heated to 200° with boric acid, a compound was obtained which is believed to be the diketone XII on the basis of its analysis, infrared spectrum and chemical behavior. The same diketone XII was obtained in small yield from alkaline hydrolysis of the isopropyl ester of II, presumably by way

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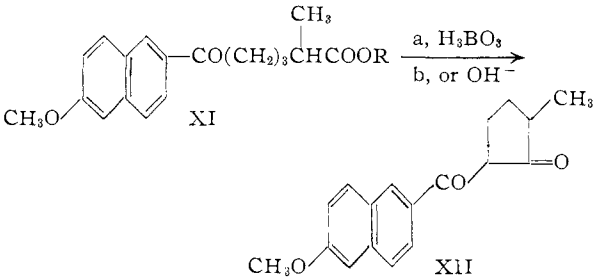
(5) (a) M. S. Newman and M. D. Farbman, THIS JOURNAL, **66**, 1550 (1944); (b) M. S. Newman and R. D. Closson, *ibid.*, **66**, 1553 (1944); (c) M. S. Newman, G. Eglinton and H. Grotta, *ibid.*, **75**, 349 (1953); (d) G. Eglinton, J. C. Nevenzel, M. S. Newman and A. I. Scott, *Chemistry & Industry*, 685 (1953).
(6) A. L. Wilds, J. A. Johnson, Jr., and R. E. Sutton, THIS JOURNAL, **72**, 5524 (1950). We are indebted to Prof. A. L. Wilds for the direct comparisons.

of conversion to keto ester XI (R = i-C_3H_7), followed by base-catalyzed cyclization of XI.



All Arndt–Eistert homologations were carried out by the Newman–Beal modification[7] as conventional procedures[8] gave low yields. When the diazoketone prepared from III was rearranged in t-butyl alcohol[7] a mixture of isomeric t-butyl esters was obtained. The main portion was the expected homologous ester corresponding to VII. Further work on the proof of structure of the isomeric compound is now under way.

VII, *via* the acid chloride, could be readily cyclized to VIII, but the saturated homologated *trans*-acid X did not cyclize under the same or more vigorous conditions. This is interesting in view of the ready cyclization of the *cis*-acid V chloride.[9] However, the *trans*-ketone IX was obtained by hydrogenation of VIII as expected from previous results.[6]

It was noticed that solutions of unsaturated compounds, such as III and VII, in concd. sulfuric acid were deep red whereas solutions of the saturated analogs were yellow. This may be due to amphiquinonoid carbonium ions of the type suggested by Johnson in explaining anomalous cyclization reactions in a similar system.[10]

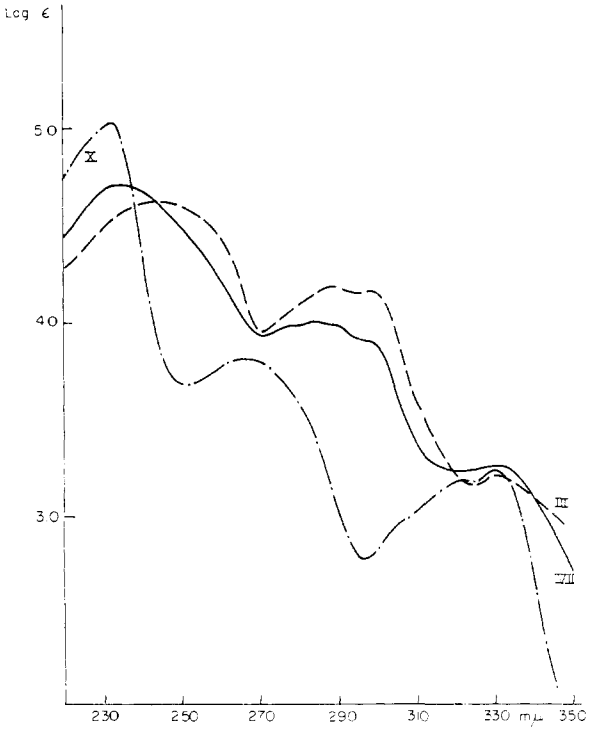
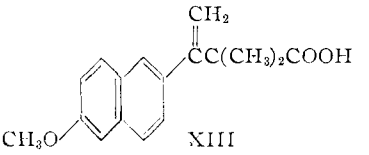


Fig. 1.—Ultraviolet absorption spectra of unsaturated and saturated 2-methoxynaphthyl acids.

Ultraviolet Spectra.—The ultraviolet spectra, see Fig. 1, show clearly the effect of conjugation of the double bond with the methoxynaphthalene nucleus in acids (and also esters) III and VII. The abovementioned isomeric t-butyl ester isolated along with VII also contains a double bond conjugated with the nucleus as shown by its spectrum (not shown—almost identical to VII). The spectra of the unsaturated acids are similar to that of the acid XIII.[11]



The spectra of the saturated acids IV, V and X were all similar to that of the saturated acid corresponding to XIII (see Fig. 1). The spectrum of the unsaturated and saturated ketones VIII and IX are shown in Fig. 2. The *cis* and *trans* isomers VI and IX have almost identical spectra.

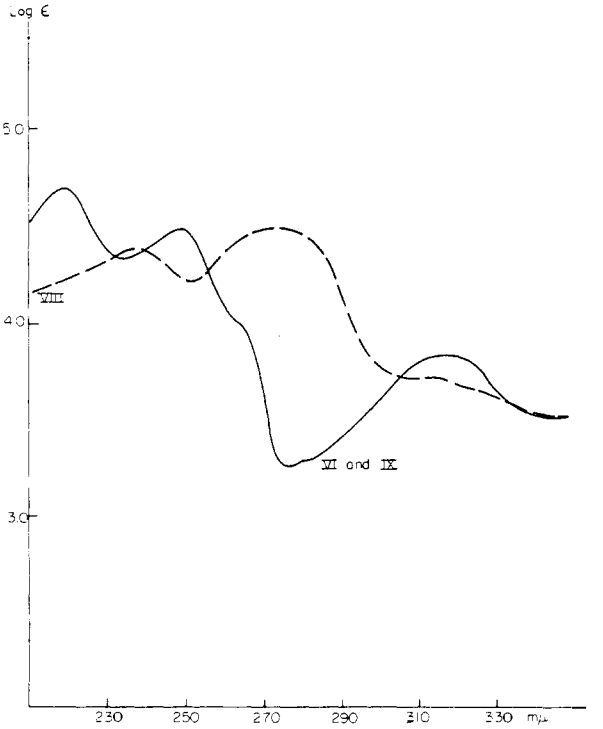


Fig. 2.—Ultraviolet absorption spectra of unsaturated and saturated ketones in the 2-methoxynaphthalene series.

Infrared Spectra.—The cyclopentane ring appears to exert a slight conjugative effect on carboxy and carbalkoxy groups attached to it, as shown by the carbonyl absorption at 5.92 μ (in Nu-

(7) M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5163 (1950).

(8) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 47–53.

(9) These facts suggest that the reduced acid III, previously described in paper III of this series, ref. 5c, is the *cis* isomer since it was readily cyclized.

(10) W. S. Johnson and R. P. Graber, THIS JOURNAL, **72**, 925 (1950).

(11) J. Jacques, M. Legrand and J. Bourdon, *Bull. soc. chim.*, 364 (1954); see also ref. 10, and H. E. Ungnade and N. L. Jennings, THIS JOURNAL, **73**, 873 (1951).

jol) for the acid IV, whereas acids V and X absorbed at 5.81 to 5.85 μ. The esters (methyl, isopropyl and *t*-butyl) of IV absorbed at 5.81 μ compared to 5.75 μ for the esters of V and X.

The isopropyl and *t*-butyl esters were characterized by strong bands at 9.0 and 8.6 μ, respectively. This is presumably a C–O stretching vibration.

In the 3-methoxy compounds the intensity of the naphthalene skeletal bands at 6.0 and 6.2 μ was invariably increased[12] and a medium to strong band at about 9.6 μ[13] and other bands in the 8.0 μ region appeared. Ketonic substitution on the naphthalene nucleus resulted in a single strong skeletal band at 6.1 μ.

We take this opportunity to thank Robert Lieberman and Albert Antoine for taking some of the ultraviolet and infrared spectra and Drs. H. M. Grotta and J. L. McPherson for the preparation of some of the starting materials.

Compounds II (R′ = CH_3), III and IV proved to be almost completely devoid of estrogenic and androgenic activity. We are indebted to Dr. William J. Haines and Mr. Pabst of the Upjohn Company for these assays.

The same compounds were tested for progesterone activity by Dr. Roy Hertz of the National Institutes of Health. The tests are described:

"The test carried out was as follows: each compound was suspended in 0.25 aqueous Tween 80 at a concentration of 1 mg. per cc. Three-week-old New Hampshire Red female chicks were given subcutaneously 0.5 cc. daily of this suspension plus 0.25 mg. of stilbestrol in 0.1 cc. of corn oil. After 8 consecutive days of treatment the animals were autopsied and the oviducts weighed. Control animals received stilbestrol alone.

"There was no significant augmentation of or interference with the expected growth effect of this dose of stilbestrol on the chick oviduct. This is an intermediate dose which is so adjusted as to reveal any antagonistic or supplementary action of the test compound. Progesterone, for instance, will depress the growth effect by about 70%."

Experimental[14]

Isopropyl 1-Methyl-2-oxocyclopentanecarboxylate (I, R′ = C_3H_7-*i*).—This ester, b.p. 104–105° at 10 mm., $n^{28}D$ 1.4378, was prepared in about 68% over-all yield from diisopropyl adipate, b.p. 113–115° at 1.5 mm., $n^{26}D$ 1.4210, with the use of sodium as condensing agent[15] followed by methylation of the initially formed sodium enolate with methyl iodide. It had a single broad absorption at 5.6–5.9 μ.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.2; H, 8.7. Found[c]: 65.4; H, 8.6.

The 2,4-dinitrophenylhydrazone formed orange prisms m.p. 97–98° with sintering at 90°, when crystallized from methanol.

Anal. Calcd. for $C_{16}H_{20}O_6N_4$: C, 52.8; H, 5.5; N, 15.4. Found[c]: C, 53.1; H, 5.6; N, 15.4.

1-Methyl-2-(6-methoxy-2-naphthyl)-2-cyclopentene-1-carboxylic Acid (III).—6-Hydroxy-2-bromonaphthalene (a skin irritant), prepared as described[16] except that stannous chloride was used as reducing agent, was methylated to yield 2-bromo-6-methoxynaphthalene, m.p. 107°. Into a solution of 184 g. of I in 300 ml. of dry ether held at −10 to −5° was forced under nitrogen a solution of 6-methoxy-2-naphthyl lithium, prepared by treating a titrated solution of 1.0 *M* butyllithium[17] in 1 l. of ether with a solution of 240 g. of 6-methoxy-2-bromonaphthalene in 1 l. of benzene, the temperature being held at less than −5° throughout. Exchange was very rapid, as indicated by the fact that carbonation of a part soon after mixing yielded no odor of valeric acid on acidification and a high yield of authentic 6-methoxy-2-naphthoic acid, m.p. 203–204°, not depressed by mixing with an authentic sample.[18] The mixture was stirred for two hours while the temperature rose to 0° and then for 15 hours at 20°. A washed and dried benzene solution (200 ml.) of the neutral reaction products was refluxed for 90 minutes with 4 g. of *p*-toluenesulfonic acid to effect dehydration. After an alkaline wash the product was distilled to yield the crude isopropyl ester of III, a portion of which melted at 65–70° after crystallization from low boiling petroleum ether (Skellysolve F, b.p. 35–40°). The crude ester was hydrolyzed by refluxing for 20 hours with 700 ml. of a 2 *N* solution of potassium hydroxide in 1-propanol. The total crude acid fraction, amounting to a 35–40% yield (a similar yield was obtained with the ethyl ester corresponding to I), was dissolved in a slight excess of warm 1 *N* potassium hydroxide solution and dilute hydrochloric acid was slowly added with constant stirring to a *p*H of 8.0–7.5. This acid fraction was removed and the *p*H then brought to 5.5. The almost colorless acid[19] thus obtained was recrystallized from methanol–water to yield pure III as colorless plates, m.p. 177.8–179.2° with sintering at 160°. The yield of pure acid was usually in the 25–30% region.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.6; H, 6.5. Found[g]: C, 76.8; H, 6.6; λ_{max} 245, 288, 299, 330; log ϵ 4.64, 4.19, 4.16, 3.2.

About 35% of 2-methoxynaphthalene was recovered from the neutral fraction.

In earlier experiments there was isolated isopropyl 2-hydroxy-1-methyl-2-(6-methoxy-2-naphthyl)-cyclopentane carboxylate (II, R′ = C_3H_7), by direct crystallization from the reaction mixture after prior removal of unchanged I by vacuum distillation. Pure II (R = C_3H_7-*i*) melted at 88.5–89.0°. Light absorption (5% solution in carbon tetrachloride, 0.1 mm. thickness) at 2.8 μ(w), 5.81 μ(s) and 6.08, 6.15 μ(m).

Anal. Calcd. for $C_{21}H_{26}O_4$: C, 73.7; H, 7.7. Found[g]: C, 73.4; H, 7.4.

This ester was dehydrated in 10 minutes by refluxing with benzene and a small amount of a sulfonated polystyrene resin (Dowex-G50). However, for crude reaction mixtures, dehydration was better with the *p*-toluenesulfonic acid treatment described. Heating with boric acid was also effective but less convenient.

In one experiment in which the isopropyl ester II was heated with an equal weight of boric acid at 320° for 2 hours a 50% yield of 1-methyl-2-(6-methoxy-2-naphthyl)-1-cyclopentene,[20] m.p. 74°, strong bands at 6.08 and 6.15 μ, was obtained.

2-Methyl-6-oxo-6-(6-methoxy-2-naphthyl)-hexanoic Acid (XI, R = H).—In early experiments the crude reaction mixture from the addition of the 6-methoxy-2-naphthyllithium to I was treated for 3 hours with refluxing 2 *N* propanolic potassium hydroxide. From the acid thus obtained there was isolated XI (R = H), as colorless thin rods, m.p. 123–124°, from methanol in 40% yield. It had strong bands at 5.85, 5.92 and 6.12 μ.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.7. Found[c]: C, 72.2; H, 6.6.

The methyl ester crystallized in lustrous plates, m.p. 45.0–45.5°, from Skellysolve F; strong bands at 5.75, 5.93

(12) Compare L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, and E. E. Vago, E. M. Tanner and K. C. Bryant, *J. Inst. Pet.*, **35**, 293 (1949).

(13) See ref. 12, Bellamy, p. 102.

(14) All m.p.'s are uncorr. unless otherwise noted. Analyses marked c by Clark Microanalytical Laboratories, marked g by Galbraith Microanalytical Laboratories.

(15) P. S. Pinkney, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 119. The method described in Note 5 was followed.

(16) C. F. Koelsch, *Org. Syntheses*, **20**, 18 (1940).

(17) H. Gilman, *et al.*, THIS JOURNAL, **71**, 1499 (1949).

(18) K. Fries and K. Schimmelschmidt, *Ber.*, **58**, 2835 (1925).

(19) Compare M. S. Newman, R. B. Taylor, T. Hodgson and A. B. Garrett, THIS JOURNAL, **69**, 1784 (1947).

(20) W. E. Bachmann and M. C. Kloetzel, *ibid.*, **60**, 2204 (1938). The exact position of the double bond is assumed.

and 6.1 μ. A polymorph, first obtained with diazomethane, melted at 56.0–56.5°.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.6; H, 7.1. Found[c]: C, 73.7; H, 7.1.

The isopropyl ester melted at 48° and crystallized in flat needles from Skellysolve F.

Anal. Calcd. for $C_{21}H_{26}O_4$: C, 73.7; H, 7.7. Found[g]: C, 73.7; H, 7.5.

2-Methyl-6-(6-methoxy-2-naphthyl)-hexanoic Acid (XIV).—Hydrogenation of XI over platinized charcoal in the presence of a trace of palladium chloride under 3 atmospheres pressure afforded XIV, m.p. 79–80°, in 70% yield.

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.6; H, 7.7; OCH_3, 10.6. Found[c]: C, 75.9; H, 7.5; OCH_3, 10.7.

Homologation[7] of XIV afforded 2-methyl-7-(6-methoxy-2-naphthyl)-heptanoic acid (XV), m.p. 81.6–82.8°, in 36% yield (one experiment).

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 76.0; H, 8.0. Found[c]: C, 75.6; H, 7.9.

The crude isopropyl 1-methyl-2-hydroxy-2-(2-naphthyl)-cyclopentanecarboxylate formed by reaction of 2-naphthylmagnesium bromide with I was similarly cleaved with alkali to yield 2-methyl-6-oxo-6-(2-naphthyl)-hexanoic acid, m.p. 124.8–125.2°, in 44% over-all yield.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.6; H, 6.7. Found: C, 75.3; H, 6.5.

The methyl ester, II (R′ = CH_3) melted at 42.0–42.8° cor.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.1; H, 7.1; OCH_3, 10.9. Found[c]: C, 76.1; H, 7.0; OCH_3, 10.9.

Hydrogenation as described above afforded 2-methyl-6-(2-naphthyl)-hexanoic acid, m.p. 61–63° cor.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.7; H, 7.9. Found[c]: C, 80.1; H, 7.9.

5-Methyl-2-(6-methoxy-2-naphthoyl)-cyclopentanone (XII).—(a) A mixture of 13 g. of the isopropyl ester of XI (R = C_3H_7-*i*) and 15 g. of boric acid was heated to 200° over a period of two hours and maintained at that temperature for a further 1.5 hours. The neutral fraction (6 g.) solidified as a pale yellow crystalline mass, m.p. 98–100°. Recrystallized first from Skellysolve B, b.p. 60–70°, and then from methanol, XII was obtained as almost colorless needles, m.p. 101–102°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.7; H, 6.4. Found: C, 76.9; H, 6.7.

(b) The hydroxyester II, 0.9 g., was refluxed in a solution of sodium 2-propoxide prepared from 0.1 g. of sodium in 20 ml. of propanol for 15 hours. The neutral fraction (*ca.* 0.2 g.) was identical with the compound obtained under (a).

XII had no hydroxyl absorption in the infrared but showed intense absorption at 6.24 and 6.35 μ (3% CCl_4), typical of an internally chelated β-diketone. It gave an intense purple-red color with methanolic ferric chloride and a green coloration in chloroform with copper acetate, but failed to give other than a slight oiliness with aqueous or alcoholic 2,4-dinitrophenylhydrazine reagent. XII rapidly dissolved in 5% aqueous potassium hydroxide solution and, after warming the solution for 30 minutes on the steam-bath and then acidifying, the ketoacid XI (R = H) was obtained almost quantitatively.

***cis*-1-Methyl-2-(6-methoxy-2-naphthyl)-cyclopentane-1-carboxylic Acid (IV).**—A solution of 6 g. of III in 125 ml. of glacial acetic acid absorbed the theoretical amount of hydrogen in 45 minutes over 0.1 g. of Adams platinic oxide catalyst. The product, obtained in good yield after recrystallization from methanol, melted at 167–168° after sintering at 135°. After vacuum sublimation the acid IV melted at 168.0–168.4° with sintering at 165°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.1; H, 7.1; OCH_3, 10.9. Found[c]: C, 76.7; H, 7.2; OCH_3, 11.3.

The anilide was crystallized from Skellysolve B to yield clusters of needles, m.p. 108–109°.

Anal. Calcd. for $C_{24}H_{25}O_2N$: C, 80.2; H, 7.0; N, 3.9. Found[c]: C, 80.4; H, 6.9; N, 4.2.

***cis*-1-Methyl-2-(6-methoxy-2-naphthyl)-cyclopentane-1-acetic Acid (V).**—The dried sodium salt (12.2 g.) of IV suspended in 10 ml. of benzene was cooled and treated with 7.6 g. of oxalyl chloride in 40 ml. of benzene. After standing for 3 hours the volatile liquids were removed under vacuum and the residue was dissolved in benzene and added to a solution of excess diazomethane in benzene. The resulting diazoketone was rearranged at 60° for 30 minutes, the *t*-butyl alcohol method[7] being used. After hydrolysis by refluxing in 2 *N* aqueous propanolic potassium hydroxide for 3 hours, 4.3 g. (39%) of crude acid was obtained. The pure acid, m.p. 158–159°, was obtained with little loss by crystallization from methanol; light absorption: λ_{max} at 232, 265, 320/330 mμ; log ϵ 4.98, 3.7, 3.14/3.22.

Anal. Calcd. for $C_{19}H_{22}O_3$: C, 76.5; H, 7.4; OCH_3, 10.6. Found[c]: C, 76.2; H, 7.1; OCH_3, 10.8.

The neutral fraction from the above reaction was found to consist largely of the indanone described below. Cyclization undoubtedly occurred during preparation of the acid chloride from IV.

***cis*-7-Methoxy-10-methyl-2,3-dihydro-1H-cyclopentabenz-[e]indan-10-one (XVI).**—A solution of 2.84 g. of IV in 50 ml. of benzene was added to an ice-cold solution of 1.2 g. of pure thionyl chloride in benzene containing three drops of pyridine. After 30 minutes at 20–25° the mixture was held at 50–60° for 30 minutes. After 1.5 hours at room temperature the solvent was removed and the residue was vacuum distilled to yield 2.21 g. of an oil which on crystallization from Skellysolve B yielded 1.8 g. (68%) of XVI as large colorless prisms, m.p. 88.5–91.0°.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 81.4; H, 6.8.

The picrate, prepared in and crystallized from methanol, formed orange needles, m.p. 129.7–130.0° after sintering at 127°.

Anal. Calcd. for $C_{24}H_{21}O_9N_3$: C, 58.2; H, 4.3; N, 8.5. Found[c]: C, 58.0; H, 4.2; N, 8.6.

The compound would not form a semicarbazone, 2,4-dinitrophenylhydrazone or oxime under the usual conditions. This fact is in agreement with similar findings.[10]

***cis*-3-Methoxy-11-ketoequilenane (VI).**—A solution of 4.8 g. of V in 30 ml. of benzene was treated with 3.7 g. of phosphorus pentachloride. The reaction was completed by warming on a steam-bath. The solution was then cooled in an ice-bath and treated with a solution of 9.1 g. of stannic chloride in 25 ml. of benzene. A deep red color developed immediately. After 8 minutes a second red phase separated whereupon ice was added, followed by concentrated hydrochloric acid and ether. After recovery of 0.7 g. of V, the neutral portion (3.6 g.) formed a pale yellow viscous oil. On treating with picric acid an orange picrate was formed. After two recrystallizations the picrate formed orange needles, m.p. 144.6–145.4° cor., from acetone.

Anal. Calcd. for $C_{25}H_{23}O_9N_3$: C, 59.0; H, 4.6; N, 8.3. Found[c]: C, 58.9; H, 4.7; N, 8.4.

The yield of picrate was good but not exactly determined. A part was decomposed by chromatography to yield pure VI as yellowish blades, m.p. 69–71° cor.: λ_{max}, 246, 313, 345 mμ; log ϵ 4.60, 3.93, 3.64; infrared absorption at 5.99 μ (Nujol mull).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.4; H, 7.2. Found[c]: C, 81.7; H, 7.3.

The semicarbazone[10] melted at 208–216° dec. after crystallization from pyridine–alcohol.

Anal. Calcd. for $C_{20}H_{23}O_2N_3$: N, 12.5. Found[c]: N, 12.5.

1-Methyl-2-(6-methoxy-2-naphthyl)-2-cyclopenten-1-acetic Acid (VII).—The acid chloride of III, prepared from the acid in benzene using oxalyl chloride, was added to an excess of ethereal diazomethane at 0–5°. After standing at 0° for one hour and at 20° for 16 hours the fluffy polymer present was filtered and the filtrate was diluted with Skellysolve F. The diazo ketone separated as bright needles, m.p. 106–108° dec. in 86% yield. Infrared absorption is strong at 4.82 μ (N_2 group[5c]). In the mother liquors evidence for the presence of a small amount of chloroketone was obtained. In the ensuing Wolff rearrangement[7] it was found advantageous to use a solution of diazoketone in *t*-butyl alcohol as dilute as 5% since lower yields were obtained in more concentrated solutions. The additions of 10% silver benzoate in triethylamine catalyst solution were in 0.5-ml. portions at a reaction temperature of 65–70°. About 90–120 minutes was required for completion of reaction. Solvent was then removed under vacuum and the

crude reaction product partly purified by chromatography over activated alumina using benzene as eluent (1.2 l. needed). The passage of desired ester was followed by its deep blue fluorescence in ultraviolet light. The ester was separated into solid and liquid portions which totalled about 72–75% and which consisted of about 2 parts solid *t*-butyl ester of VII, m.p. 73.0–73.5° from Skellysolve F, and 1 part of liquid *t*-butyl ester; light absorption: (solid) $\lambda_{max.}$ 235, 285, 330 mμ; log ε 4.7, 4.0, 3.24; (liquid) $\lambda_{max.}$ 239, 284 330 mμ; log ε 4.7, 4.05, 3.31. The infrared spectra of the two esters were almost identical: carbonyl, 5.8 μ, naphthyl, 6.1, 6.2 μ and *t*-butyl 8.6 μ.

Anal. Calcd. for $C_{23}H_{28}O_3$: C, 78.4; H, 8.0. Found[g]: (solid) C, 78.3; H, 7.8; (liquid) C, 78.4; H, 8.0.

The structure of the liquid ester is under investigation. The solid ester, on 17 hours hydrolysis with aqueous propanolic potassium hydroxide under nitrogen, afforded pure acid VII, m.p. 139–140° cor., only after several recrystallizations from Skellysolve B. The yield of pure acid was never over about 50% and pure acid was needed for subsequent steps; light absorption: $\lambda_{max.}$ 235, 285, 330 mμ; log ε 4.71, 4.0, 3.25.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.0; H, 6.8. Found[g]: C, 77.1; H, 6.9.

3-Methoxy-11-keto-14,15-dehydroequilenane (VIII).—In the best of several experiments 0.69 g. of VII in 3 ml. of benzene was treated at 0° with 0.69 g. of phosphorus pentachloride in 3 ml. of benzene and left for 1.5 hours at 0°. Then 1.2 ml. of stannic chloride in 1 ml. of benzene was added. A deep red complex separated and after 30 min. at 0° and 10 min. at 20° ice and hydrochloric acid were added. By crystallization of the neutral fraction from alcohol after charcoal treatment and chromatography over charcoal (Darco G-60) there was obtained a 35% yield of VIII as pale yellow needles, m.p. 115–122°. Recrystallization from Skellysolve C afforded pure VIII as clusters of colorless needles, m.p. 127.5–128.0°, with moderate loss; light absorption: $\lambda_{max.}$ 235, 275, 315 mμ; log ε 4.4, 4.5, 3.74; infrared bands at 5.95 (C=O), 6.12, 6.21 (naphthyl), 8.1, 9.6 μ (OCH_3).

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found[g]: C, 81.9; H, 6.5.

The 2,4,7-trinitrofluorenone complex formed scarlet needles, m.p. 170–171° cor., from ethanol. *Anal.* Calcd. for $C_{32}H_{23}O_9N_3$: N, 7.1. Found[g]: N, 7.0.

***trans*-3-Methoxy-11-ketoequilenane (IX).**—A solution of 320 mg. of VIII in 30 ml. of 95% alcohol containing 300 mg. of 30% palladized charcoal[21] was stirred in a micro hydrogenation apparatus under a small hydrogen pressure until the theoretical volume had been absorbed (13 min.). There was isolated 300 mg. of stout prisms, m.p. 94–95°, of IX by trituration of the reaction product with Skellysolve F. Recrystallization afforded colorless prisms, m.p. 96.5–97.0°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.4; H, 7.2. Found[g]: C, 81.4; H, 7.6.

(21) Catalyst d, R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940).

***trans*-3-Hydroxy-11-ketoequilenane.**—After heating a solution of 80 mg. of IX in 6 ml. of acetic acid and 6 ml. of 42% hydrobromic acid[22] for 3 hours, the demethylated compound was obtained in 65% yield as buff needles, m.p. 205–210°. Recrystallization (charcoal) from alcohol afforded pale yellow elongated prisms, m.p. 228–230°, with moderate loss.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found[g]: C, 81.3; H, 7.1.

3-Methoxy-14,15-dehydroequilenane (XVII).—A mixture of 112 mg. of VIII (m.p. 127°), 9 ml. of ethylene glycol, 0.9 ml. of 85% hydrazine and 0.8 g. of potassium hydroxide was heated at 100–105° for 2 hr. then held at 195° for 3 hr. under nitrogen, excess water and hydrazine being allowed to distil. The organic matter was taken into ether after acidification of the reaction mixture. Removal of solvents left a yellowish oil which was subjected to methylation with 10% potassium hydroxide and dimethyl sulfate. From this reaction mixture 40 mg. of crystals, m.p. 115–120°, were obtained. Recrystallization (charcoal) from methanol afforded colorless plates, m.p. 123–124° cor. (cloudy melt), of XVII. The m.p. with authentic XVII,[6] m.p. 120.5–124.0° cor. (cloudy melt), was 123–124° after softening at 121°.

A 1,3,5-trinitrobenzene complex, glistening orange-red needles, m.p. 138–139° cor., of XVII was prepared in ethanol. The mixed m.p. with authentic complex,[6] m.p. 139–140.5° cor., was 139–140°.

***trans*-3-Methoxyequilenane (XVIII).**—IX (43 mg.) was reduced by the Huang-Minlon method as described for the reduction of VIII to yield crude XVIII which was difficult to purify as such. However, the addition product with 1,3,5-trinitrobenzene was obtained as orange platelets, m.p. 133–134°, undepressed on admixture with an authentic sample.[6]

***cis*-3-Methoxyequilenane (XIX).**—VI (95 mg.) was reduced as above and the crude product remethylated by treatment with alkali and dimethyl sulfate. After recrystallization from methanol–benzene there was obtained 15 mg. of crude XIX, m.p. 69–71°. The trinitrobenzene complex formed orange needles, m.p. 132.5–135.5°, undepressed on admixture with an authentic sample,[6] m.p. 135.5–137.0°.

***trans*-1-Methyl-2-(6-methoxy-2-naphthyl)-cyclopentyl-1-acetic Acid (X).**—A solution of 175 mg. of VII in 20 ml. of acetic acid containing 20 mg. of platinic oxide absorbed 18 ml. of hydrogen (theory 14 ml.) at 25° during 1 hour. The reduced acid had a m.p. of 145–149° raised to 150.5–151.0° by three recrystallizations from Skellysolve C (b.p. 90–100°).

Anal. Calcd. for $C_{19}H_{22}O_3$: C, 76.5; H, 7.4; OCH_3, 10.4. Found[c]: C, 76.7; H, 7.6; OCH_3, 10.2.

A mixed m.p. with V, m.p. 158–159°, was depressed; light absorption for X: $\lambda_{max.}$ 232, 267, 322, 330 mμ; log ε 5.04, 3.8, 3.19, 3.24.

An attempt to cyclize X under conditions under which V readily cyclized to VI led to almost complete recovery of X.

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(22) A. L. Wilds and W. J. Close, THIS JOURNAL, **69**, 3079 (1947).