phenolic hydroxyl group and a split band (1682 cm.$^{-1}$), attributable to a conjugated aromatic ketone group. Substitution bands appear at 850, 765, 750 and 705 cm.$^{-1}$. This compound differs from the chelated hydroxy ketones in being readily soluble in base and in failing to yield a copper chelate derivative.

*Anal.* Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.61; H, 4.15.

**8-Methoxy-7H-benzo[c]fluoren-7-one** (II) was obtained in a yield of 28.8% (0.19 g.). It crystallized from benzene as yellow needles, m.p. 168.5–169°. The infrared spectrum shows bands at 1710 cm.$^{-1}$ (with a small shoulder at 173 cm.$^{-1}$), corresponding to a conjugated aromatic ketone group in a five-membered ring and at 1265 cm.$^{-1}$, corresponding to a methoxyl group. Substitution bands for the benzene ring appear at 800, 740 and 675 cm.$^{-1}$.

*Anal.* Calcd. for $C_{88}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.00; H, 4.58.

The **oxime** separated from absolute ethanol as fine yellow needles, m.p. 253.5–254.5°. The infrared spectrum corresponds to the structure assigned.

*Anal.* Calcd. for $C_{88}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.29; H, 4.75; N, 5.10.

A solution of 0.13 g. of the 8-methoxyfluorenone II, 1 ml. of 47% hydriodic acid and 2 ml. of glacial acetic acid was heated on a steam-cone for 8 hr. The crude **8-hydroxy-7H-benzo[c]fluorenone** was isolated as the copper chelate derivative from which it was recovered by treatment with dilute hydrochloric acid. The infrared spectrum possesses bands at 3350 and 1245 cm.$^{-1}$, attributable to a hydroxyl group and at 1685 cm.$^{-1}$, corresponding to a conjugated chelated ketone group in a five-membered ring.

*Anal.* Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.67; H, 4.01.

**8-Methoxy-7H-benz[d,e]anthracen-7-one** (III) crystallized from benzene as chartruese needles (0.112 g., 16.9%), m.p. 160.5–161°. The infrared spectrum has bands at 1660° cm.$^{-1}$, attributed to a conjugated aromatic ketone group in a six-membered ring; at 1620 (a small shoulder), attributed to the condensed aromatic ring system; at 1600 cm.$^{-1}$, attributed to the C–H stretching on an aromatic ring; and at 1267 cm.$^{-1}$, attributed to a methoxyl group. Substitution bands appear at 800, 762 and 745 cm.$^{-1}$.

*Anal.* Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.86; H, 4.77.

A solution of 0.1 g. of 8-methoxy-7*H*-benz[d,e]anthracen-7-one (III), 1 ml. of 47% hydriodic acid and 3 ml. of glacial acetic acid was heated on a steam-cone for 18 hr. The solution was poured into cold water, and the orange **8-hydroxy-7H-benz[d,e]anthracen-7-one** was recrystallized from isoamyl alcohol. It formed orange-red needles (0.0812 g., 85.7%), m.p. 190.5–191°. The melting point reported in the literature[9] is 187.5–188°. The infrared spectrum has a broad band (from 3032 to 3030 cm.$^{-1}$), attributable to a hydroxyl group that is internally hydrogen bonded and one at 1630 cm.$^{-1}$, attributable to a conjugated aromatic ketone which is strongly hydrogen bonded. Other bands appear at 1250 cm.$^{-1}$, attributable to a phenolic hydroxyl group and at 800 and 750 cm.$^{-1}$, attributed to two kinds of vicinal trisubstitution.

*Anal.* Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.79; H, 4.33.

When treated with cupric acetate in acetone the phenolic ketone formed a chelate derivative which could be reconverted to the hydroxy ketone with dilute hydrochloric acid.

**10-Methoxy-7H-benz[d,e]anthracen-7-one** (V).—Two grams of duryl 4-methoxy-2-($\alpha$-naphthyl)-phenyl ketone was heated with 25 ml. of polyphosphoric acid for 10.5 hr. at 90–100°. Durene was deposited on the sides of the vessel as the reaction progressed. The 8-methoxyfluorenone II, the 10-methoxyfluorenone IV and the 8-methoxybenzanthrone III were isolated in yields of 10.2, 36.6 and 26.6%, respectively.

A fourth isomer, 10-methoxy-7*H*-benz[d,e]anthracen-7-one (V), was isolated in 7.3% yield. It crystallized from chloroform–ethanol as chartruese needles, m.p. 163–163.5°. The infrared spectrum has bands at 1648 cm.$^{-1}$, attributed to a conjugated aromatic ketone group in a six-membered ring; at 1630 cm.$^{-1}$ (a shoulder), attributed to a condensed aromatic ring system; at 1600 cm.$^{-1}$ (strong), attributed to C–H stretching on a benzene ring; at 1250 cm.$^{-1}$ attributed to a methoxyl group; at 843 cm.$^{-1}$, attributed to 1,2,4-substitution on a benzene ring; and at 770 cm.$^{-1}$, attributed to three adjacent hydrogen atoms on a naphthalene ring.

*Anal.* Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.73; H, 4.64.

The ketone V was made in 60% yield by heating 8-methoxy-7*H*-benzo[c]fluoren-7-one (II) for 24 hr. with polyphosphoric acid at 120–125°. The 10-methoxy-7*H*-benzo[c]-fluoren-7-one (IV) under similar conditions gave the ketone V in a yield of 50%.

A fourth method of synthesis of the 10-methoxybenzanthrone V consisted in heating 1 g. of duryl 4-methoxy-2-($\alpha$-naphthyl)-phenyl ketone with 25 ml. of polyphosphoric acid 0.104 g. (16.1%) of 10-methoxy-7*H*-benz[c]fluoren-7-one and 0.065 g. (10%) of 10-methoxy-7*H*-benz[d, e]anthracen-7-one. The latter crystallized from chloroform–ethanol as chartreuse needles, m.p. 163–163.5°. Hydrolysis of the 10-methoxybenzanthrone V gave a compound which was easily soluble in base and which failed to yield a copper chelate derivative.

Treatment of duryl 6-methoxy-2-($\alpha$-naphthyl)-phenyl ketone (2 g.) with 25 ml. of polyphosphoric acid, with efficient stirring, for 10 hr. at room temperature gave 0.1723 g. (13.3%) of 8-methoxy-7*H*-benzo[c]fluoren-7-one (II) and 0.0999 g. (7.6%) of 8-methoxy-7*H*-benz[d,e]anthracen-7-one (III). A mixture of 1 g. of the ketone I and 25 ml. of polyphosphoric acid was heated at 120–125° for 20 hr. and then at 170–175° for 2 hr. The crude product, subjected to chromatography, gave 0.1072 g. of 10-methoxy-7*H*-benz-[d,e]anthracen-7-one and 0.062 g. of 10-methoxy-7*H*-benz-[d,e]anthracen-7-one.

URBANA, ILL.

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[9] H. Waldmann, *Chem. Ber.*, **83**, 171 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Derivatives of 8-Methylhexahydrofluorenone[1a]

BY HERBERT O. HOUSE, VASKEN PARAGAMIAN AND DAVID J. WLUKA[1b]

RECEIVED SEPTEMBER 30, 1959

8-Methyl-*cis*-hexahydrofluorenone and 8-methyl-2,3,4,4a-tetrahydrofluorenone have been prepared and alkylated with ethyl bromoacetate. Comparable alkylation of *cis*-hexahydrofluorene and 2,3,4,4a-tetrahydrofluorenone are described. The structure and stereochemistry of the various alkylation products have been determined.

Our previous studies of 1,1a,2,3,4,4a-hexahydrofluoren-9-one[2] had indicated a suitable synthetic route to the corresponding 8-methyl derivative I which was of interest as an intermediate for the synthesis of certain degradation products of gibberellic acid.[3] In the present work the desired

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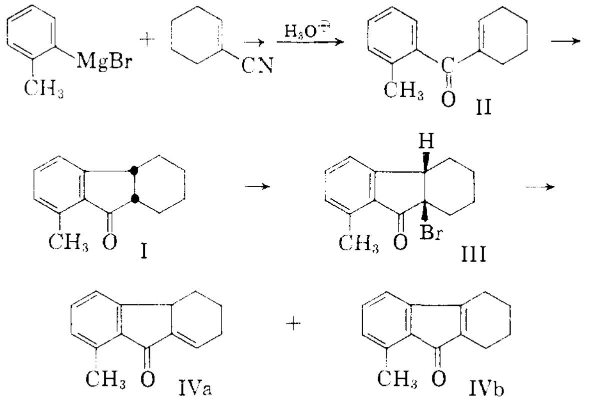
(1) (a) This research has been supported in part by National Science Foundation Grant No. G9486; (b) Alfred P. Sloan Postdoctoral Fellow.

(2) H. O. House, V. Paragamian, R. S. Ro and D. J. Wluka, THIS JOURNAL, **82**, 1457 (1960).

(3) For leading references see B. E. Cross, J. F. Grove, J. MacMillan and T. P. C. Mulholland, *Proc. Chem. Soc.*, **221** (1958).

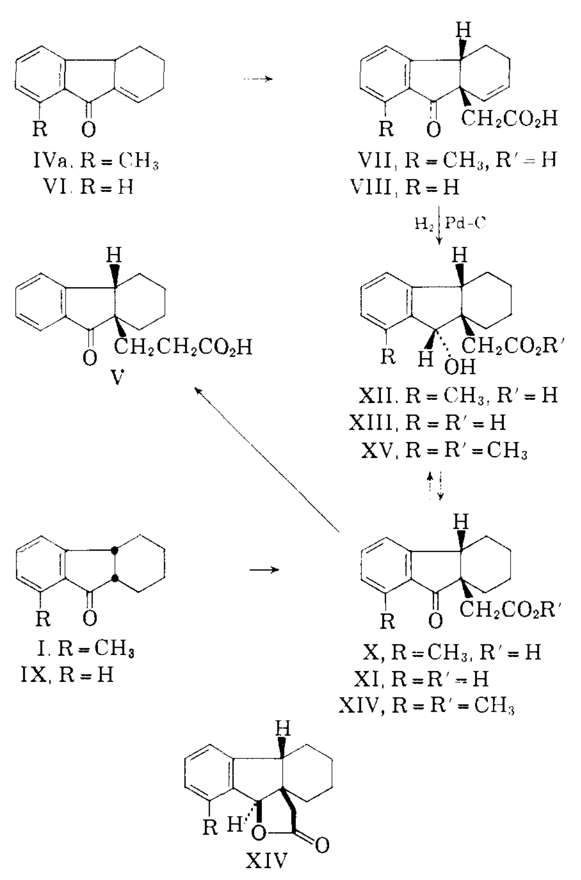
8-methyl ketone I was obtained readily and in good yield by the sulfuric acid-catalyzed cyclization of 1-cyclohexenyl *o*-tolyl ketone (II) which was obtained from the reaction of *o*-tolylmagnesium bromide with 1-cyanocyclohexene. Both the ketone I and the monobromo ketone III obtained by the bromination of I are presumed to have the indicated *cis*-stereochemistry for reasons previously discussed.[2]



In agreement with our previous results[2] in the hexahydrofluorenone series, dehydrobromination of the bromo ketone III in the presence of lithium chloride and dimethylformamide yielded a mixture of 8-methyltetrahydrofluorenones IV in which the isomer IVa with the exocyclic carbon–carbon double bond predominated.

We had established that the Michael adducts obtained from hexahydrofluorenone and either acrylonitrile or methyl acrylate were related stereochemically to the *cis*-keto acid V. It was now of interest to learn whether alkylation of the tetrahydrofluorenones IVa and VI afforded products of the same stereochemical series. Previous examples of the alkylation of $\alpha,\beta$-unsaturated ketones to form $\alpha$-alkyl $\beta,\gamma$-unsaturated ketones[4] led us to expect structures VII and VIII from the alkylation of ketones IVa and VI, respectively. The alkylation of ketones IVa and VI with ethyl $\alpha$-bromoacetate in the presence of potassium *t*-butoxide confirmed the expectation yielding, after saponification, the acids VII and VIII.

The comparable alkylation of the hexahydrofluorenones I and IX afforded the keto acids X and XI. These same keto acids were obtained by the chromic acid oxidation of the hydroxy acids XII and XIII, the products of catalytic reduction of the tetrahydro derivatives VII and VIII. The fact that a *cis* ring fusion was present in the various compounds of the series VIII, XI and XIII was established by converting the keto acid XI to the known[2] *cis*-keto acid V. The analogous stereochemical arrangement can safely be assigned to the series VII, X and XII since inspection of molecular models of the precursors I and IVa of the series indicates that the methyl group does not interfere with approach to position Ia from either side of the molecule.



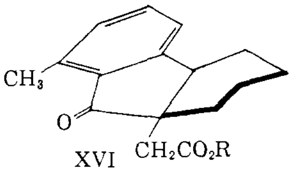
The hydrogenation of the keto acids VII and VIII in the presence of palladium-on-carbon and ethanol was carried to the hydroxy acid stage (XII and XIII) because the rates of hydrogenation of the two unsaturated functions did not differ sufficently to permit the selective reduction of only the carbon–carbon double bond. The major products XII and XIII of these reductions were accompanied by small amounts of neutral components which had infrared bands at 1780 cm.$^{-1}$ compatible with the $\gamma$-lactone structure XIV. We obtained no evidence that either of the hydroxy acids XII or XIII could be readily converted to the lactones XIV.[5] The infrared spectrum of the crude product obtained by heating the acid XIII with acetic anhydride showed no evidence of a band at 1780 cm.$^{-1}$ diagnostic of a $\gamma$-lactone. Therefore the acids XII and XIII may be assigned the indicated stereochemistry in which the carboxymethyl and hydroxy groups are disposed *trans* to each other. Molecular models of these compounds suggest that the $\gamma$-lactones could not be formed from them without introducing excessive

[4] (a) J. M. Conia, *Bull. soc. chim. France*, 690, 943 (1954); (b) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives and R. B. Kelly, THIS JOURNAL, **76**, 2852 (1954); (c) F. Sondheimer and Y. Mazur, *ibid.*, **79**, 2906 (1957); (d) F. Sondheimer and D. Elad, *ibid.*, **79**, 5542 (1957); (e) G. Cooley, B. Ellis and V. Petrow, *J. Chem. Soc.*, 2998 (1955); (f) H. J. Ringold and G. Rosenkranz, *J. Org. Chem.*, **22**, 602 (1957).

(5) In subsequent work, to be published, the pure lactone XIV ($R = CH_3$), a crystalline solid melting at 111–112° with infrared absorption ($CCl_4$) at 1778 cm.$^{-1}$, was obtained as a by-product from the reaction of the hydroxy ester XV with hydrogen bromide. When an aqueous solution of the potassium salt of the *cis*-hydroxy acid, obtained from this lactone XIV ($R = CH_3$), was acidified with cold, dilute hydrochloric acid, the lactone XIV ($R = CH_3$), which reformed immediately, was isolated in 94.5% yield. The salts of the *trans*-hydroxy acids XII and XIII described in the present report have been acidified repeatedly with no indication of lactone formation.

strain. The same hydroxy acid XII was obtained by hydrogenation of the keto acid X.

Hydrogenation of the keto ester XIV under the same conditions used with the acid X afforded the hydroxy ester XV. Since reaction of the hydroxy acid XII with diazomethane afforded the same hydroxy ester XV, the stereochemical course of both catalytic hydrogenations is the same. From a study of molecular models of the acids VII and VIII and the ester XIV in their most probable conformation XVI a distinct preference as to which side of these compounds would be adsorbed on a hydrogenation catalyst would not be predicted on steric grounds. Consequently, we are led to suggest that the steric course of this hydrogenation, and other comparable hydrogenations, is controlled primarily by the preferential absorption of the carboxyl group or the carbomethoxy group on the catalyst surface. Such preferential absorption on the hydrogenation catalyst would necessitate that the hydrogen atoms be transferred to the compound from the side of the molecule on which the carboxyl or carbomethoxyl group is located.



XVI

## Experimental[6]

**1-Cyclohexenyl *o*-Tolyl Ketone** (II).—To an ether solution of *o*-tolylmagnesium bromide, prepared from 300 g. (1.75 moles) of *o*-bromotoluene and 41.6 g. (1.74 g.-atoms) of magnesium, was added 130 g. (1.21 moles) of 1-cyanocyclohexene.[2] After the reaction mixture had been boiled under reflux with stirring for 18 hr., it was poured into excess dilute, aqueous hydrochloric acid and the resulting mixture was heated on a steam-bath overnight. The crude product, isolated by extraction with ether, was washed with aqueous sodium bicarbonate, dried over magnesium sulfate and distilled through a 30-cm. Vigreux column. The pure ketone (212 g. or 85%) was collected as a yellow liquid, b.p. 140–141° (0.55 m.), $n^{28.5}$D 1.5550, which exhibits infrared absorption[7] at 1653 (conj. C=O) and 1630 cm.$^{-1}$ (conj. C=C) and an ultraviolet maximum[8] at 241 mμ (ε 11,900).

*Anal.* Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.17; H, 8.13.

**8-Methyl-*cis*-1, 1a, 2,3,4,4a-hexahydrofluoren-9-one** (I).—To 1.5 l. of concentrated sulfuric acid was added, slowly and with stirring, 145 g. (0.72 mole) of 1-cyclohexenyl *o*-tolyl ketone. The resulting mixture was warmed on a steam-bath for 5 min. and then poured onto ice. The crude product, obtained by extraction with ether, was washed with aqueous sodium bicarbonate and dried over magnesium sulfate. The product separated from petroleum ether as yellow crystals, m.p. 33–35°, yield 119 g. (82%). Recrystallization afforded the pure, white crystalline ketone, m.p. 36–37°, which exhibits infrared absorption[7] at 1710 cm.$^{-1}$ (conj. C=O in a five-membered ring) with ultraviolet maxima[8] at 249 mμ (ε 12,500) and 297 mμ (ε 2,400).

*Anal.* Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.97; H, 8.05.

**1a-Bromo-8-methyl-*cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one** (III).—To a solution of 11.5 g. (0.0575 mole) of 8-methylhexahydrofluoreneone in 60 ml. of anhydrous ether, cooled in an ice bath, was added, dropwise and with stirring, a solution of 9.4 g. (0.058 mole) of bromine in 60 ml. of carbon tetrachloride. The resulting solution was stirred for 10 min. at room temperature and then washed successively with aqueous sodium bisulfite and aqueous sodium bicarbonate and dried over magnesium sulfate. After the solvents had been removed, the residual solid crystallized from petroleum ether as white prisms, m.p. 46.5–48°, yield 12.4 g. (78%). The bromo ketone exhibits infrared absorption[7] at 1722 cm.$^{-1}$ (conj. C=O in a five-membered ring) with ultraviolet maxima[8] at 260 mμ (ε 9,650) and 303 mμ (ε 2,090).

*Anal.* Calcd. for $C_{14}H_{15}BrO$: C, 60.21; H, 5.38; Br, 28.64. Found: C, 60.14; H, 5.39; Br, 28.35.

**8-Methyl-2,3,4,4a-tetrahydrofluoren-9-one** (IVa) **and 8-Methyl-1,2,3,4-tetrahydrofluoren-9-one** (IVb).—A solution of 1a-bromo-8-methyl-*cis*-1,1a,2,3,4,4a-heaxhydrofluoren-9-one (40.0 g., 0.143 mole) and 62 g. (1.43 moles) of lithium chloride in 380 ml. of dimethylformamide was heated to 120° for 6 hr., a slow stream of nitrogen being passed through the mixture throughout the reaction period. The reaction mixture was diluted with water and extracted with ether. After the ethereal extract had been washed with water and dried over magnesium sulfate, the solvent was removed and the residue distilled in a short-path still. The crude product, a bright yellow liquid collected at 135–165° (0.05–0.07 mm.), amounted to 21.9 g. (77%). The ultraviolet spectrum[8] of the crude product indicated the presence of 52% of the 8-methyltetrahydrofluorenenone IVa and 28% of the 8-methyltetrahydrofluorenone IVb. Chromatography of a portion of the crude product on Merck acid-washed alumina separated **8-methyl-1,2,3,4-tetrahydrofluoren-9-one** (IVb), eluted with petroleum ether, which crystallized as yellow needles, m.p. 41–43°. The product exhibits infrared absorption[7] at 1700 cm.$^{-1}$ (conj. C=O in a five-membered ring) with ultraviolet maxima[8] at 239 mμ (ε 34,700), 246 mμ (ε 36,900) and 328 mμ (ε 1,570).

*Anal.* Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.60; H, 7.17.

Subsequent fractions, eluted from the column with 10% ether in petroleum ether, crystallized as pale yellow plates of **8-methyl-2,3,4,4a-tetrahydrofluoren-9-one** (IVa), m.p. 63–64°. The product exhibits infrared absorption[7] at 1700 (conj. C=O in a five-membered ring) and 1655 cm.$^{-1}$ (conj. C=C exocyclic to a five-membered ring) with an ultraviolet maximum[8] at 272 mμ (ε 19,350).

*Anal.* Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.95; H, 6.96.

**1a-Carboxymethyl-8-methyl-*cis*-1a,3,4,4a-tetrahydrofluoren-9-one** (VII).—To a solution of 7.5 g. (0.038 mole) of the crude mixture of 8-methyltetrahydrofluorenones IV in 250 ml. of *t*-butyl alcohol containing the potassium *t*-butoxide prepared from 14.7 g. (0.378 g.-atom) of potassium was added, dropwise and with stirring over a period of 10 min., a solution of ethyl bromoacetate (53 g. or 0.32 mole) in *t*-butyl alcohol. The resulting mixture was refluxed with stirring for 3 min., cooled, acidified with a few drops of concentrated hydrochloric acid, concentrated and diluted with ether. The ethereal solution was washed with water, dried over magnesium sulfate and concentrated under reduced pressure to remove the solvents and the unchanged bromo ester. A solution of the residual material in aqueous methanol containing 7.0 g. (0.11 mole) of 85% potassium hydroxide was refluxed for 11 hr., cooled, diluted with water and extracted with ether. The aqueous phase was acidified with hydrochloric acid and extracted with ether. The ethereal solution was extracted with aqueous sodium bicarbonate and the bicarbonate extract was acidified with hydrochloric acid and extracted with ether. The resulting ethereal extract was dried over magnesium sulfate and concentrated to leave 3.87 g. of a brown oil. A solution of this residue in a petroleum ether–ether mixture deposited 0.84 g. (16.7% based on the 52% 2,3,4,4a-tetrahydrofluororenone present in the starting material) of the desired unsaturated keto acid, m.p. 138–140°. Recrystallization raised the melting point of the product to 139–140°. The product exhibits infrared

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(6) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird, model B, or a Perkin–Elmer, model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, model 11MS. The gas chromatograms were obtained with a 8 mm. × 215 cm. column packed with Dow Silicone Fluid No. 550 suspended on 50–80 mesh ground firebrick. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

(7) Determined as a solution in carbon tetrachloride.

(8) Determined as a solution in ethanol.

absorption[9] at 1700 cm.$^{-1}$ (carboxyl C=O and conj. C=O in a five-membered ring) with broad absorption in the 3$\mu$ region (carboxyl O–H) and ultraviolet maxima[8] at 250 m$\mu$ ($\epsilon$ 10,800) and 298 m$\mu$ ($\epsilon$ 1,910).

*Anal.* Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.73; H, 6.23.

The original ethereal extract from the alkylation reaction, containing the neutral products, was dried over magnesium sulfate and concentrated. A solution of the residue in hexane deposited 3.35 g. of the ester (methyl or ethyl or both) of the unsaturated keto acid, m.p. 95–98°, which exhibits infrared absorption[7] at 1710 (conj. C=O in a five-membered ring) with a shoulder at 1730 cm.$^{-1}$ (ester C=O) and ultraviolet maxima at 250 m$\mu$ ($\epsilon$ 10,300) and 298 m$\mu$ ($\epsilon$ 1,975). A solution of the neutral material in aqueous methanol containing 0.0208 mole of potassium hydroxide was refluxed for 4 hr. and then worked up as previously described to separate an additional 2.61 g. (total yield 3.45 g. or 69% based on the 52% 2,3,4,4a-tetrahydrofluorenone present in the starting material) of the unsaturated keto acid VII, m.p. 141–142.5°, which was identified by a mixed melting point determination.

**1a-Carboxymethyl-8-methyl-*cis*-1,1a-2,3,4,4a-hexahydrofluoren-9-one (X).**—A solution of 20 g. (0.10 mole) of 8-methylhexahydrofluorenone in 50 ml. of *t*-butyl alcohol was added over a period of 15 min. to a solution of potassium *t*-butoxide prepared from 19.5 g. (0.50 g.-atom) of potassium and 200 ml. of *t*-butyl alcohol. After the resulting mixture had been refluxed for 10 min. and cooled in an ice-bath, a solution of 80 g. (0.48 mole) of ethyl bromoacetate in *t*-butyl alcohol was added, dropwise and with stirring. Upon completion of the addition, the reaction mixture was worked up by the same procedure described for the previous alkylation, a 3-hr. reaction period being employed for the saponification. The keto acid separated from its solution in an ethyl acetate–hexane solution as white prisms, m.p. 140.5–141.5°, yield 18.2 g. (70.6%). The keto acid exhibits ultraviolet maxima[8] at 249 m$\mu$ ($\epsilon$ 10,050) and 298 m$\mu$ ($\epsilon$ 2,000) and infrared absorption[9] at 1710 cm.$^{-1}$ (conj. C=O in a five-membered ring) with a shoulder at 1720 cm.$^{-1}$ (carboxyl C=O and broad absorption in the 3$\mu$ region (carboxyl O–H). The infrared spectrum of this product is definitely different from the spectrum of the previously described 1a-carboxymethyl-8-methyl-*cis*-1a,3,4,4a-tetrahydrofluoren-9-one and the melting point of a mixture of the two keto acids is depressed.

*Anal.* Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.22; H, 6.92.

**1a-Carbomethoxymethyl-8-methyl-*cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one (XIV).** A.—A solution of 13.1 g. (0.05 mole) of the saturated keto acid X and several drops of concentrated sulfuric acid in 100 ml. of methanol was refluxed for 3 hr., concentrated, diluted with water and extracted with ether. After the ethereal extract had been washed with aqueous sodium bicarbonate and dried over magnesium sulfate, concentration of the solution afforded the crude ester which solidified on standing. Recrystallization from hexane afforded the pure keto ester as a mixture of crystalline forms, m.p. 76–84°, yield 10.05 g. (73%). Recrystallization of a portion of this material from aqueous ethanol afforded a single crystalline modification of the product as white prisms, m.p. 101–102°. The infrared spectra[7] of both crystalline modifications of the keto ester are identical and exhibit absorption at 1738 (ester C=O) and 1715 cm.$^{-1}$ (conj. C=O in a five-membered ring). The product exhibits ultraviolet maxima[8] at 250 m$\mu$ ($\epsilon$ 12,200) and 299 m$\mu$ ($\epsilon$ 2,300).

*Anal.* Calcd. for $C_{17}H_{20}O_3$: C, 74.95; H, 7.40. Found: C, 74.65; H, 7.27.

B.—Reaction of an ether solution of 2.58 g. (0.01 mole) of the keto acid X with diazomethane[10] followed by the appropriate manipulations yielded 2.24 g. (82.5%) of the previously described keto ester XIV as a mixture of crystalline forms, m.p. 77–82°, from hexane. The infared spectrum of this sample was identical with the spectrum of the sample previously described.

**1a-Carboxymethyl-8-methyl-*cis*-1,1a-2,3,4,4a-hexahydrofluoren-9-ol (XII).** A.—A solution of 1.21 g. (4.73 mmoles) of the unsaturated keto acid VII in ethanol was hydrogenated over 100 mg. of a 10% palladium-on-carbon catalyst at atmospheric pressure and room temperature (26°). The hydrogen uptake ceased after the absorption of 1.72 molar equivalents of hydrogen. After removal of the catalyst by filtration and concentration of the filtrate, a solution of the residue in ether was extracted with aqueous sodium bicarbonate. The aqueous extract was acidified with hydrochloric acid and extracted with ether. Both the acidic and neutral ether extracts were dried over magnesium sulfate and concentrated. The neutral component, 0.04 g. of pale yellow oil which exhibited infrared absorption[7] at 1780 cm.$^{-1}$ (C=O of a $\gamma$-lactone), was not investigated further. Crystallization of the acidic fraction from a hexane–ethyl acetate mixture afforded 0.92 g. (75%) of the hydroxy acid as white crystals, m.p. 143–144°. The product exhibits broad infrared absorption[9] in the 3$\mu$ region (O–H) as well as a band at 1720 cm.$^{-1}$ (carboxyl C=O) and a series of low-intensity ultraviolet maxima[8] in the region 260–280 m$\mu$.

*Anal.* Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.80; H, 7.65.

To a solution of 280 mg. (1.08 mmoles) of the hydroxy acid in 65 ml. of acetone was added, dropwise and with stirring, an 8 *N* solution of chromium trioxide in dilute, aqueous sulfuric acid[11] until the color of the unchanged oxidant persisted. After the addition of a few drops of methanol, the solution was diluted with water and extracted with ether. The ethereal extract was washed with water, dried over magnesium sulfate and concentrated to leave a yellow-orange oil which crystallized from an ethyl acetate–hexane mixture as white prisms, m.p. 139–140°. The oxidation product was shown to be identical with the previously described keto acid X by a mixed melting point determination and by comparison of the infrared spectra of the two samples.

B.—Hydrogenation of an ethanol solution of 3.00 g. (0.0116 mole) of the saturated keto acid X over 350 mg. of a 10% palladium-on-carbon catalyst as previously described resulted in the absorption of 0.96 molar equivalent of hydrogen and yielded, after the aforementioned manipulations, 2.57 g. (85%) of the hydroxy acid XII, m.p. 143–144°, which was identified by a mixed melting point determination. The neutral fraction, an oil amounting to 40 mg., from the hydrogenation was not investigated.

An ether solution of 1.03 g. (3.96 mmoles) of the hydroxy acid XII was treated with diazomethane.[12] After the diazomethane had been consumed the reaction mixture was worked up in the usual way. After separation of 0.62 g. (60% recovery) of the starting hydroxy acid, the neutral fraction amounted to 0.39 g. (36%) of yellow crystals melting at 70–73°. Recrystallizing from aqueous ethanol afforded the pure hydroxy ester as white prisms, m.p. 77–78°. The product was shown to be identical with the hydroxy ester XV, subsequently described, by a mixed melting point determination and by comparison of the infrared spectra of the two samples.

**1a-Carbomethoxymethyl-8-methyl-*cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-ol (XV).**—Hydrogenation of an ethanol solution of 9.7 g. (0.0356 mole) of the keto ester XIV over 1 g. of a 10% palladium-on-carbon catalyst as previously described resulted in the uptake of 0.91 molar equivalent of hydrogen. After removal of the catalyst by filtration and concentration of the solvent, the residual oil (which exhibited no infrared absorption at 1780 cm.$^{-1}$ attributable to a $\gamma$-lactone) crystallized on standing. Recrystallization from aqueous ethanol afforded 7.6 g. (78%) of the pure hydroxy ester as white prisms, m.p. 77–78°. The product exhibits infrared absorption[7] at 3540 (O–H) and 1722 cm.$^{-1}$ (ester C=O) with a series of low-intensity ultraviolet maxima[8] in the region 260–280 m$\mu$.

*Anal.* Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.41; H, 8.03.

**1a-Carboxymethyl-*cis*-1a,3,4,4a-tetrahydrofluoren-9-one (VIII).**—To a solution of potassium *t*-butoxide, prepared from 6.0 g. (0.15 g.-atom) of potassium and 130 ml. of *t*-butyl alcohol, was added a solution of 2.0 g. (0.0109 mole)

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[9] Determined as a suspension in a potassium bromide pellet.

[10] The ether solution of diazomethane, obtained by distillation of a mixture of N,N′-dinitroso-N,N′-dimethylterephthalamide (du Pont EXR-101), ether and 40% aqueous sodium hydroxide, was dried over solid potassium hydroxide prior to use.

[11] A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

[12] Obtained from N-methyl-N-nitrosourea without distillation and dried over solid potassium hydroxide.

of 2,3,4,4a-tetrahydrofluoren-9-one in 20 ml. of *t*-butyl alchol. To the resulting mixture was added, dropwise and with stirring and external cooling, 18.15 g. (0.11 mole) of ethyl bromoacetate. The temperature of the reaction mixture was maintained at 35–40° during the addition of the halide which required 6 min. After the addition was complete, the mixture was stirred for 5 min. and then neutralized by the addition of dilute, aqueous sulfuric acid and concentrated under reduced pressure. The crude ester, isolated by the procedure previously described, was saponified by reaction with a boiling solution of 5 g. of sodium hydroxide in 40 ml. of ethanol under a nitrogen atmosphere for 6 hr. The crude acidic product, isolated in the usual way, was crystallized from an ethyl acetate–petroleum ether mixture as white prisms, m.p. 171–173°, yield 1.76 g. (67%). An additional crystallization afforded the pure keto acid, m.p. 173.5–175°, which exhibits broad infrared absorption[9] in the 3$\mu$ region with bands at 1730 (carboxyl C=O) and 1683 cm.$^{-1}$ (conj. C=O in a five-membered ring lowered by intramolecular hydrogen bonding) and ultraviolet maxima[8] at 244 m$\mu$ ($\epsilon$ 11,200), 288 m$\mu$ ($\epsilon$ 2,140) and 293 m$\mu$ ($\epsilon$ 2,240).

*Anal.* Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.46; H, 5.97.

When this alkylation procedure was applied to 1.23 g. of a mixture of tetrahydrofluorenones containing 55% of 2,3,4,4a-tetrahydrofluoren-9-one and 40% of 1,2,3,4-tetrahydrofluoren-9-one, 0.335 g. (38% yield based on the presence of 55% of the desired isomer in the starting material) of the same unsaturated keto acid, m.p. 171–173.5°, was produced.

**1a-Carboxymethyl-*cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one (XI).**—The previously described alkylation procedure was applied to 1.62 g. (0.0088 mole) of *cis*-hexahydrofluorenone (IX), 7.35 g. (0.044 mole) of ethyl bromoacetate and the potassium *t*-butoxide prepared from 1.76 g. (0.044 g.-atom) of potassium and 45 ml. of *t*-butyl alcohol being employed. After the crude ester had been separated and saponified as previously described, the crude saturated keto acid was crystallized from an ethyl acetate–petroleum ether mixture as white prisms, m.p. 130–131.5°, yield 1.07 g. (50%). Recrystallization raised the melting point of the keto acid to 131–132.5°. The product exhibits broad infrared absorption[13] in the 3$\mu$ region (carboxyl O–H) with a band at 1708 cm.$^{-1}$ (conj. C=O in a five-membered ring) having a shoulder at 1723 cm.$^{-1}$ (carboxyl C=O) and ultraviolet maxima[8] at 245 m$\mu$ ($\epsilon$ 12,400) and 293 m$\mu$ ($\epsilon$ 2,470).

*Anal.* Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.68; H, 6.61.

To a suspension of the dry sodium salt obtained from sodium hydroxide and 0.51 g. (0.0021 mole) of the saturated keto acid XI in 10 ml. of benzene containing 3 drops of pyridine was added 0.27 ml. (0.4 g. or 0.0031 mole) of oxalyl chloride. The reaction mixture was maintained at 10° with stirring for 15 min. and then filtered through glass wool and concentrated. A benzene solution of the residual acid chloride was added, over a 6-min. period with mixing, to a cold ether solution containing excess diazomethane (prepared from nitrosomethylurea, distilled and dried). After the solution had been allowed to stand for 30 min., the excess diazomethane and ether were removed and the residual diazoketone was taken up in 10 ml. of methanol. Nitrogen evolution began after the addition of 10 drops of a solution of 0.5 g. of silver benzoate in 5 ml. of triethylamine.[14] After 1 hr. an additional 5 drops of this solution was added. After 2 hr., at which time 90% of the theoretical volume of nitrogen had been evolved, the methanol solution was heated to boiling, decolorized with Norit and concentrated. A solution of the residue in ether was washed successively with water, dilute aqueous hydrochloric acid, water, aqueous sodium bicarbonate and water and then dried over sodium sulfate and concentrated. The residual crude ester was saponified by reaction for 1.5 hr. with a solution of 1 g. of potassium hydroxide in 12 ml. of methanol. The crude acid, isolated in the usual manner, crystallized from ethyl acetate as white needles, m.p. 109–111°, yield 0.242 g. (45%). The product was shown to be identical with the previously described[2] **1a-(2-carboxyethyl)-*cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-one** (V) by a mixed melting-point determination and by comparison of the infrared spectra of the two samples.

**1a-Carboxymethyl-*cis*-1,1a,2,3,4,4a-hexahydrofluoren-9-ol (XIII).**—A solution of 1.0 g. (0.0041 mole) of the unsaturated keto acid VIII in 30 ml. of ethanol was hydrogenated at room temperature and pressure over 150 mg. of a 10% palladium-on-carbon catalyst. The hydrogen uptake ceased after absorption of 2.0 molar equivalents of hydrogen. The resulting mixture was filtered and the filtrate was concentrated under reduced pressure. An ether solution of the residue was extracted with aqueous sodium bicarbonate and then dried over sodium sulfate and concentrated. The residual, neutral oil exhibited infrared absorption[7] at 1787 (C=O of a $\gamma$-lactone such as XIV) as well as a band at 1710 cm.$^{-1}$ of undetermined origin and low intensity ultraviolet maxima[8] at 267 m$\mu$ ($\epsilon$ 1,080) and 273 m$\mu$ ($\epsilon$ 1,240). The acidic product, separated from the bicarbonate extract by appropriate manipulations, crystallized from a benzene petroleum-ether mixture as white needles, m.p. 136–138°, yield 0.55 g. (55%). Recrystallization afforded the pure hydroxy acid, m.p. 139.5–140.5°, which exhibits broad infrared absorption[13] in the 3 $\mu$ region (O–H) with a band at 1705 cm.$^{-1}$ (carboxy C=O) and ultraviolet maxima at 259 m$\mu$ ($\epsilon$ 920), 266 m$\mu$ ($\epsilon$ 1,050) and 273 m$\mu$ ($\epsilon$ 1,200).

*Anal.* Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.31; H, 7.28.

A solution of 150 mg. of the hydroxy acid XIII in 15 ml. of acetone was oxidized with a 8 *N* solution of chromium trioxide in dilute, aqueous sulfuric acid[11] as previously described. The acid product, isolated in the usual way, crystallized from an ethyl acetate–petroleum ether mixture as white prisms, m.p. 131–132.5°, yield 95 mg. (63%). This product was shown to be identical with the previously described saturated keto acid XI by a mixed melting point determination and by comparison of the infrared spectra of the two samples.

In a subsequent hydrogenation experiment, 1.58 g. (0.0065 mole) of the unsaturated keto acid VIII was reduced over 300 mg. of a 10% palladium-on-carbon catalyst, 1.98 molar equivalents of hydrogen being absorbed. The crude acidic and neutral fractions amounted to 1.425 (90%) and 0.14 g. (9%), respectively. Oxidation of the crude acidic product as previously described afforded 1.135 g. (71% overall yield) of the saturated keto acid XI, m.p. 131–132.5°. Attempts to isolate pure compounds from hydrogenation reactions stopped after the absorption of one molar equivalent of hydrogen were not successful.

A solution of 100 mg. of the hydroxy acid XIII in 2 ml. of acetic anhydride was heated to 100° for 2.5 hr. and then the volatile components were removed under reduced pressure. The infrared spectrum[13] of the residue exhibits absorption at 1805 and 1725 cm.$^{-1}$ (broad), with no discernible absorption peak in the region of 1780 cm.$^{-1}$ (the region of absorption characteristic of the carbonyl group of a $\gamma$-lactone).

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[13] Determined as a solution in chloroform.

[14] This decomposition procedure was developed by M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5163 (1950).