crystals which separated overnight at −5° were washed with water and recrystallized from methanol-water in cubes; yield 0.4 g. (69%), m.p. 216–218°, $\lambda_{max}^{Nujol}$ 2.90 μ.

*Anal.* Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.62; N, 5.66. Found: C, 72.86; H, 8.81; N, 5.92.

The *hydrochloride* crystallized from methanol-ether in cubes of m.p. 236–238°, $\lambda_{max}^{Nujol}$ 2.91, 3.22 μ.

*Anal.* Calcd. for $C_{15}H_{22}ClNO_2$: C, 63.48; H, 7.81; N, 4.94. Found: C, 63.37; H, 8.26; N, 4.95.

*β-9-Ethyl-9-hydroxy-2′-methoxy-2,5-dimethyl-6,7-benzomorphan* (XIV). To 0.5 g. of XIII[5] in 20 ml. of dry ether was added rapidly (stirring) 15 ml. (*ca.* 3 molar equivalents) of 0.4*M* ethereal ethylmagnesium bromide. After refluxing for 2 hr. the solution was poured into ice cold ammonium chloride solution and a little concentrated ammonium hydroxide was added. The dried ethereal layer was evaporated and the 0.5 g. of oil distilled evaporatively at 0.15 mm. (bath temperature 150–160°). It gave $\lambda_{max}^{CHCl_3}$ 2.79 μ (sharp, medium, OH—π bonding).

*Anal.* Calcd. for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15. Found: C, 74.73; H, 9.45.

The *picrate* was prepared in a yield of 0.45 g. (45% based on XIII) by heating together the distillate above, 0.5 g. of picric acid and 12 ml. of ethanol, then cooling gradually, finally to 5°; yellow prisms from alcohol-acetone, m.p. 214–215°.

*Anal.* Calcd. for $C_{23}H_{28}N_4O_9$: C, 54.75; H, 5.60. Found: C, 54.87; H, 5.41.

The *hydrochloride* apparently the monohydrate, crystallized from ethanol-acetone in prisms, m.p. 164–175°.

*Anal.* Calcd. for $C_{17}H_{26}ClNO_2 \cdot H_2O$: C, 61.90; H, 8.56. Found: C, 61.92; H, 8.43.

Neither ethyl- nor propylmagnesium iodide would add to the methobromide of XIII, giving instead a small yield of α-9-carbinol (reduction product).[3]

BETHESDA 14, MD.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

# Syntheses Related to Etiojervane. I. The Synthesis of 1,8-Dimethyl-7-methoxy-1,2,3,4,4a,9a-hexahydrofluorenone-2-carboxylic Acid

RODERICK A. BARNES AND NANCY N. GERBER[1]

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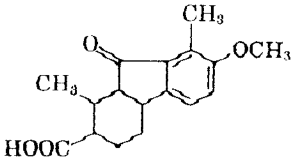
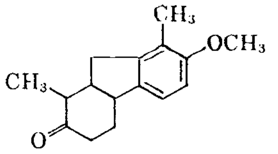
The Diels-Alder reaction of styrylacrylic acid and 4-methoxy-3-methylstyrylacrylic acid (IX) with crotonic acid has been investigated. The product from acid IX could be reduced and after bromination, cyclized to a hexahydrofluorene. This latter substance is potentially an intermediate in the synthesis of a jervine derivative.

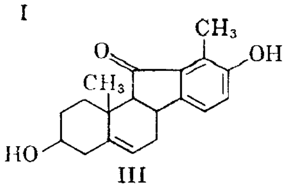
The veratrum alkaloid, jervine, has been found by Fried, Wintersteiner, and co-workers[2,3] to have an abnormal steroid skeleton. The work reported here was part of a program which had as its objective the synthesis of substances with the "etiojervane" ring system. The basic scheme was to prepare ketone II which should be readily transformable to III, a degradation product of jervine.[3]



I



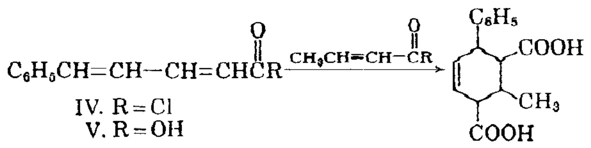
II



III

The Diels-Alder reaction has been used as the key synthetic step and the reaction sequence carried as far as acid I, a substance which can be converted to II.[4]

Alder and co-workers[5] have reported that styrylacrylyl chloride (IV) would react at several temperatures with acrylyl chloride. However, an attempt to replace acrylyl chloride by crotonyl chloride was not successful. Only decomposition of the acid chlorides took place as the reaction temperature was raised. The corresponding acids were more stable and did react in boiling tetralin at 190° to yield the desired adduct VI.



IV. R = Cl
V. R = OH

VI

The diene acid IX necessary for the synthesis of acid I was prepared from 3-methoxy-4-methylbenzaldehyde (VII). Aldehyde VII was conveniently prepared from *o*-methylanisole by reac-

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(1) Abstracted from a portion of the thesis presented by N. N. Gerber to the Graduate School for the Ph.D. degree, May 1957.

(2) J. Fried, O. Wintersteiner, M. Moore, B. M. Islin, and A. Klingsberg, *J. Am. Chem. Soc.*, **73**, 2790 (1951).

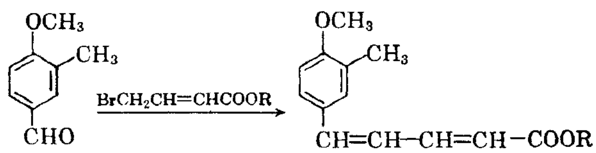
(3) J. Fried and A. Klingsberg, *J. Am. Chem. Soc.*, **75**, 4929 (1953).

(4) To be described in a future communication. An extension of this synthetic plan to the preparation of a hexahydrofluorene related to gibberone has been previously reported; see N. N. Gerber, *J. Am. Chem. Soc.*, **82**, 5216 (1960).

(5) K. Alder, M. Schumacher, and O. Wolff, *Ann.*, **570**, 237 (1950).

tion with *N*,*N*-dimethylformamide and phosphorus oxychloride.[6]

Comparison of VII prepared in this way with a pure sample obtained *via* the Reimer-Tieman reaction showed that it was essentially free of any of the isomer having the aldehyde *ortho* to the methoxyl group.



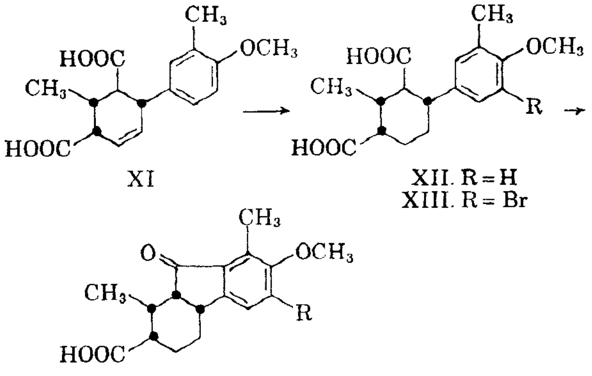
VII

VIII. R = $CH_3$
IX. R = H

$CH_3CH=C(COOC_2H_5)_2$
X

The yields from the Reformatsky reaction with aldehyde VII and γ-bromocrotonate esters were much lower (18–27%) than have been reported for benzaldehyde itself.[7] An alternate synthesis *via* the condensation of VII with ethyl ethylidenemalonate (X) yielded only traces of IX.[8]

The Diels-Alder reaction with acid IX and crotonic acid proceeded under the same conditions as with styrylacrylic acid, although the yields of adduct XI were only 20–26%. Fruitless attempts were made to improve the yields by using trichloroacetic acid as a catalyst[9] and by substituting ethyl ethylidenemalonate (X)[10] for crotonic acid.



XI

XII. R = H
XIII. R = Br

XIV. R = Br
XV. R = H

The double bond of adduct XI did not isomerize during the reaction since its ultraviolet spectrum showed no conjugation with either the carboxyl group or the aromatic ring. Although it seemed very unlikely that crotonic acid could have reacted with IX in the "reverse" manner, the cyclization to XIV was the first definite evidence that the Diels-Alder reaction had proceeded as desired.

The bromination of XII to yield XIII was carried out so that the subsequent cyclization would take place *ortho* to the methyl group of the aromatic ring.[11] The bromine atom was subsequently removed by catalytic hydrogenation. A single attempt to remove the carboxyl group of acid XIV by the Hunsdiecker reaction produced a small amount of neutral material whose strong yellow color and ultraviolet spectrum indicated that it was largely aromatized to a fluorenone.

The stereochemistry of compounds XII–XIV can only be assigned very tentatively. The known course of the Diels-Alder reaction could lead to structure XI or an isomer having *cis* carboxyl groups. Some evidence in favor of XI is provided by the observation that neither this acid nor acid XIII readily formed cyclic anhydrides. Acetyl chloride[12] produced only polymeric anhydrides, but refluxing propionic anhydride generated a small amount of a monomeric anhydride from XI. It is concluded that the carboxyl groups of XI were originally *trans* and at the higher temperature there was isomerization to the *cis* form which then was converted to an anhydride.

By analogy with the cyclization of *cis*- and *trans*-*3*-phenylcyclohexanecarboxylic acids,[13] XIII would be expected to yield a *cis*-hexahydro-9-ketofluorene. However there is at least one example of a 1-ketohydrindane structure in which the *trans* form is the more stable.[13a] If aluminum chloride does actually permit epimerization of a center adjacent to a carboxyl group, it is possible that the carboxyl group of XIV has the reverse orientation from that shown; the cyclohexane ring of only this epimer has a conformation with a single axial substituent.

## EXPERIMENTAL[14]

*4-Methoxy-3-methylbenzaldehyde* (VII). A. A mixture of *o*-methylanisole (430 g.), dimethylformamide (354 g.) and phosphorus oxychloride (663 g.) was allowed to react by the

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[6] N. P. Buu Hoi, N. D. Xuong, M. Sy, G. Lejeune, and N. B. Tien, *Bull. soc. chim. France*, 1594 (1955).

[7] K. Ziegler, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 120 (1942), report a 70% yield of the hydroxyester from benzaldehyde and methyl γ-bromocrotonate.

[8] L. Higginbotham and A. Lapworth, *J. Chem. Soc.*, **121**, 2823 (1922), report a 55% yield of ethyl anisalethylidenemalonate in a similar reaction.

[9] A. Wassermann, *J. Chem. Soc.*, 618, 623 (1942).

[10] K. Alder and H. Rickert, *Ber.*, **72**, 1983 (1939) report ethyl ethylidenemalonate to be a good dieneophile.

[11] It has been previously observed by W. M. Bush, Ph.D. thesis, Rutgers, The State University, 1954, that γ-(3-bromo-4-methoxy-5-methylphenyl)butyric acid cyclizes *ortho* to the methyl group rather than *ortho* to the bromine atom.

[12] W. H. Perkin, *J. Chem. Soc.*, 59, 812 (1891), observed that this reagent readily converted *cis*-hexahydrophthalic acid to its anhydride. See also ref. 5.

[13] C. D. Gutsche, *J. Am. Chem. Soc.*, **73**, 786 (1952), has observed that *trans*-2-phenylcyclohexanecarboxylic acid did not cyclize with anhydrous hydrogen fluoride, but did yield *cis*-1,2,3,4,4a,9a-hexahydro-9-ketofluorene when the corresponding acid chloride was treated with aluminum chloride.

[13a] D. H. R. Barton and G. F. Laws, *J. Chem. Soc.*, 52 (1954).

[14] Analyses were by W. Manser, Zurich, Switzerland. Melting points were determined on a Kofler hot stage. The infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer and the ultraviolet spectra with a Cary recording spectrophotometer.

procedure of Buu-Hoi *et al.*[6] There was obtained 233 g. (44%) of VII which boiled at 128–132° (24 mm.), $n_D^{31}$ 1.5621 and 150 g. (35%) of recovered *o*-methylanisole, b.p. 85–100° (25 mm.), $n_D^{31}$ 1.5115–1.5140.

The 2,4-dinitrophenylhydrazone of VII melted at 235–237° after recrystallization from ethyl acetate.

*Anal.* Calcd. for $C_{15}H_{14}O_5N_4$: C, 54.54; H, 4.27; N, 16.97. Found: C, 54.53; H, 4.28; N, 16.97.

B. The Reimer-Tiemann reaction with *o*-cresol was carried out as described by Brady and Jakobovits.[15] From *o*-cresol (27 g.), potassium hydroxide (147 g.), chloroform (100 g.), and water (200 ml.), there was obtained 13.8 g. (23%) of the bisulfite addition product of the steam-volatile *ortho*-aldehyde and 6.5 g. (19%) of the solid (m.p. 113–118°) *para*-aldehyde. The liquid *ortho*-aldehyde furnished a 2,4-dinitrophenylhydrazone which melted at 260–263° after recrystallization from ethyl acetate.

*Anal.* Calcd. for $C_{14}H_{12}O_5N_4$: C, 53.16; H, 3.83. Found: C, 53.16; H, 3.92.

Methylation of the solid *para* isomer, 4-hydroxy-3-methylbenzaldehyde, (10 g.) in methanol (45 ml.) using dimethyl sulfate (11.3%) and potassium hydroxide (9.4%) in water (9.4 ml.) yielded 5.1 g. (46%) of the pure VII which boiled at 132–139° (25 mm.) $n_D^{24}$ 1.5668. This sample of aldehyde furnished a 2,4-dinitrophenylhydrazone, m.p. 235–237°, identical with that obtained in part A.

The *ortho*-aldehyde was also methylated to yield 2-methoxy-3-methylbenzaldehyde, $n_D^{24}$ 1.5290. The 2,4-dinitrophenylhydrazone of this substance melted at 224–226° after recrystallization from ethanol–ethyl acetate.

*Anal.* Calcd. for $C_{15}H_{14}O_5N_4$: C, 54.55; H, 4.27; N, 16.97. Found: C, 54.97; H, 4.11; N, 17.26.

A mixture of the 2,4-dinitrophenylhydrazones of the *ortho*- and *para*-aldehydes melted at 197–230° after recrystallization from ethanol. This observation together with the large difference in the refractive indices of the two aldehydes indicates that the aldehyde prepared in part A was almost exclusively the *para* isomer.

*Methyl 4-methoxy-3-methylstyrylacrylate* (VIII). Methyl $\gamma$-bromocrotonate (9 g.) and 4-methoxy-3-methylbenzaldehyde (5 g.) were added to zinc strips (3 g.) in dry thiophene-free benzene (25 ml.). When the mixture was heated it refluxed spontaneously for several minutes and then set to a gel after about 15 min. on the steam bath. Dilute acid was added and the benzene layer was separated and concentrated. Distillation of the residue furnished some unchanged aldehyde (1.5 g., b.p. 110–130° (24 mm.), $n_D^{23}$ 1.5522) and VIII which boiled at 160° (0.5 mm.). Some additional VIII was recovered from the residue in the still to yield a total of 3.7 g. of crude solid VIII. A portion of this product was chromatographed on alumina. Elution with benzene furnished a pale yellow solid, m.p. 70–85° which after recrystallization from benzene-iso-octane, melted at 91–93°.

*Anal.* Calcd. for $C_{14}H_{16}O_3$: C, 72.36; H, 6.94. Found: C, 72.11; H, 6.89.

*4-Methoxy-3-methylstyrylacrylic acid* (IX). A. A Reformatsky reaction using ethyl $\gamma$-bromocrotonate (82 g.) was carried out as described for preparation of ester VIII. Processing yielded 15 g. (27%) of ethyl 4-methoxy-3-methylstyrylacrylate which boiled at 140–160° (0.6 mm.) and solidified after standing for several days. This product was saponified by heating at reflux temperature with a solution of water (75 ml.), ethanol (75 ml.), and potassium hydroxide (15 g.). The reaction mixture was diluted with water, extracted with ether and acidified to yield 11.9 g. (90%) of acid IX which melted at 175–195°. The analytical sample obtained by recrystallization from toluene melted at 202–203°, $\lambda_{max}^{C_2H_5OH}$ 245 m$\mu$ (log $\epsilon$ 4.2), 335 m$\mu$ (log $\epsilon$ 4.4).

*Anal.* Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.55; H, 6.47.

The crude sample of VIII (2 g.) obtained in the previous experiment was saponified as described for the ethyl ester. The crude acid was purified by extracting an ether solution with several small portions of 5% bicarbonate solution and acidifying the bicarbonate extracts. The product obtained in this way (0.9 g., 47%), melted at 201–204°.

B. The reaction of ethyl ethylidenemalonate[16] (X, 1.36 g.), aldehyde VII (1.86 g.) and concentrated sulfuric acid (4 drops) was carried out as described by Higginbotham and Lapworth.[8] The major part of the starting materials was recovered unchanged by steam distillation. Alkaline hydrolysis of the nonvolatile residue yielded 0.1 g. of a red gum from which a few crystals of acid IX could be obtained by sublimation.

*p*-Toluenesulfonic acid in refluxing benzene and anhydrous hydrogen chloride in ether also failed to cause the desired condensation.

*Diels-Alder reactions.* A. A solution of styrylacrylyl chloride (IV, 1 g.) and crotonyl chloride (1 g.) in xylene was refluxed for 18 hr. Processing yielded only recovered styrylacrylic acid. With tetralin as the solvent, the product was largely polymeric and only a trace of bicarbonate-soluble material was isolated.

B. Styrylacrylic acid (1 g.), crotonic acid (1 g.) and a trace of hydroquinone were heated in refluxing tetralin (10 g.) for 3 hr. The cold reaction mixture was diluted with ether and extracted with small portions of 5% sodium bicarbonate solution. The first extracts contained the adduct a dibasic acid, and the later extracts unchanged styrylacrylic acid. Acidification of the extracts yielded 0.4 g. (27%) of 2-methyl-4-phenyl-1,2,3,4-tetrahydroisophthalic acid (VI), m.p. 215–220°. Recrystallization from dilute acetic acid raised the melting point to 228–232°. After drying for 8 hr. at 100° the m.p. was 235–240°, but analysis indicated that it still contained water of crystallization,[17] $\lambda_{max}^{C_2H_5OH}$ 258 m$\mu$ (log $\epsilon$ 2.6), 265 m$\mu$ (log $\epsilon$ 2.4), 268 m$\mu$ (log $\epsilon$ 2.3).

*Anal.* Calcd. for $C_{15}H_{16}O_4$: C, 69.23; H, 6.20. Found: C, 68.53; H, 6.96.

C. A solution of crotonic acid (50 g.), 4-methoxy-3-methylstyrylacrylic acid (24.3 g.) and a trace of hydroquinone in tetralin was refluxed for 24 hr. The product was isolated as in part B; there was obtained 16.2 g. (50%) of crude adduct. This material was refluxed with benzene and then allowed to cool. The insoluble material, 4-(4-methoxy-3-methylphenyl)-2-methyl-1,2,3,4-tetrahydroisophthalic acid, XI (8.4 g., 26%), melted at 215–218°. A portion of this product was recrystallized from dilute acetic acid,[17] m.p. 221–224°, $\lambda_{max}^{C_2H_5OH}$ 273 m$\mu$ (log $\epsilon$ 2.6), 276 m$\mu$ (log $\epsilon$ 2.65), 282 m$\mu$ (log $\epsilon$ 2.6).

*Anal.* Calcd. for $C_{17}H_{20}O_5$: C, 67.15; H, 6.63. Calcd. for $C_{17}H_{20}O_5 \cdot 1/2H_2O$: C, 65.16; H, 6.75. Found: C, 65.70; H, 6.85.

The addition of trichloroacetic acid (0.5 g./g. of acid IX) in either tetralin or xylene as solvents resulted in consumption of the diene acid but no adduct could be isolated.

D. Ethyl ethylidenemalonate, X, (2 g.) and acid IX (1 g.) were refluxed in xylene (10 ml.) for 20 hr. The cold reaction mixture deposited 0.5 g. (50%) of recovered acid IX. Saponification of the material remaining after removal of solvents, yielded only polymeric materials.

*Methyl 2-methyl-4-phenyl-1,2,3,4-tetrahydroisophthalate.* Acid VI (0.2 g.) in benzene (5 ml.) was treated with an ether solution of diazomethane prepared from *N*-nitrosomethylurea (0.5 g.). The solvents were removed and the resi-

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(15) O. Brady and J. Jakobovits, *J. Chem. Soc.*, 767 (1950), report that potassium hydroxide yields more of the *para* isomer, but we were unable to confirm this observation with *o*-cresol.

(16) W. S. Fones, *Org. Syntheses*, **32**, 54 (1952).

(17) Nearly all of the dibasic acids obtained in these experiments were very difficult to obtain free from solvents and were best characterized as their ester or amide derivatives. Prolonged heating at higher temperatures had to be avoided because of the possibility of anhydride formation.

due taken up in isooctane. The crystals which separated after prolonged standing (60 mg., m.p. 68–76°) were further purified by chromatography on alumina. Elution with benzene furnished crystalline fractions which after recrystallization from iso-octane melted at 81–83°.

*Anal.* Calcd. for $C_{17}H_{20}O_4$: C, 70.83; H, 6.99. Found: C, 70.57; H, 6.78.

*Phenacyl 4-(4-methoxy-3-methylphenyl)-2-methyl-1,2,3,4-tetrahydroisophthalate.* Acid XI was converted to the phenacyl ester by the usual[18] procedure. The oily product was chromatographed on alumina; elution with 50% benzene-chloroform produced a fraction that crystallized after protracted standing. Recrystallization from benzene-iso-octane and then ethanol-water, finally yielded the pure ester which melted at 138–139.5°.

*Anal.* Calcd. for $C_{33}H_{32}O_7$: C, 73.31; H, 5.97. Found: C, 73.24; H, 6.01.

*Anhydride of 2-methyl-4-phenyl-1,2,3,4-tetrahydroisophthalic acid.* A solution of acid XI (200 mg.) in propionic anhydride (6 ml.) was heated at reflux for 2 hr. The excess propionic anhydride was distilled and the residue heated in a sublimation apparatus at 190° (0.2 mm.). There was obtained 30 mg. (15%) of sublimate which melted at 181–183° after recrystallization from benzene-hexane.

*Anal.* Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.09; H, 6.39.

When a sample of acid XI was heated at reflux with acetyl chloride, a noncrystalline material was obtained which was similar to the nonsublimable material from the propionic anhydride reaction, infrared bands at 5.50, 5.72 $\mu$ (anhydride) and 5.84 $\mu$ (carboxyl). Acid XI was recovered after hydrolysis of this material (polymeric anhydride) with dilute potassium hydroxide.

*4-(4-Methoxy-3-methylphenyl)-2-methylhexahydroisophthalanilide.* A solution of acid XI (0.5 g.) in acetic acid (10 ml.) was hydrogenated using freshly prepared[19] platinum oxide (0.5 g.) at room temperature and atmospheric pressure. Under these conditions there was a fairly sharp break in the rate of hydrogenation after 1 mole had been absorbed (15–60 min.). Extended hydrogenation also reduced the aromatic ring. The product, acid XII, isolated after filtration and evaporation of the solvents was usually oily or only partly crystalline.[17] The anilide was prepared[20] and recrystallized from methyl ethyl ketone, m.p. 345–355°.

*Anal.* Calcd. for $C_{29}H_{32}O_3N_2$: C, 76.29; H, 7.07. Found: C, 76.89, 75.23; H, 7.06, 6.88.

*Methyl 4-(5-bromo-4-methoxy-3-methylphenyl)-2-methylhexahydrophthalate.* A portion (1.2 ml.) of a solution of bromine (1.76 g.) in acetic acid (10 ml.) was added to a solution of acid XII (0.4 g.) in acetic acid (3 ml.). The solution in a glass-stoppered flask was maintained at room temperature for 3 hr. and then at 50° for 21 hr. The reaction mixture was poured into water and filtered. There was obtained 0.37 g. (86%) of acid XIII[17] which melted at 265–270°. A portion of this acid was methylated with diazomethane as in the preparation of the methyl ester of acid VI. This ester was eluted with 50% benzene-isooctane. The crystalline fractions were recrystallized from isooctane, m.p. 95–97°.

*Anal.* Calcd. for $C_{19}H_{25}O_5Br$: C, 55.21; H, 6.10. Found: C, 55.17; H, 6.14.

A sample of acid XIII, when treated with acetyl chloride, yielded only a noncrystalline, glassy material similar to that obtained from acid XI.

*6-Bromo-1,8-dimethyl-7-methoxy-1,2,3,4,4a,9a-hexahydrofluorenone-2-carboxylic acid (XIV).* Acid XIII (2.0 g.) was mixed with phosphorus pentachloride (2.4 g.) and allowed to stand for 1 hr. Phosphorus oxychloride was removed by co-distillation with three 10-ml. portions of benzene and finally by heating at 100° *in vacuo.* The residual acid chloride was dissolved in nitrobenzene (12 ml.) and the solution at 0° was added to an ice-cooled solution of anhydrous aluminum chloride (1.4 g.) in nitrobenzene (20 ml.). The reaction mixture was stored in ice for 4 hr. and then allowed to stand at room temperature for 15 hr. The nitrobenzene was removed by steam distillation and the residue was extracted with ether. Evaporation of the ether and chromatography of the residue on silica gel yielded 1.4 g. (74%) of XIV which melted at 160–185°. A portion was further purified by conversion to the methyl ester with diazomethane followed by chromatography on alumina. Chloroform-benzene (10:90) eluted a yellow oil which after saponification and recrystallization from acetic acid–water and benzene-isooctane produced pure XIV, m.p. 180–185°, $\lambda_{\max}^{C_2H_5OH}$ 262 m$\mu$ (log $\epsilon$ 4.1).

*Anal.* Calcd. for $C_{17}H_{19}O_4Br$: C, 55.61; H, 5.22. Found: C, 55.57; H, 5.29.

*1,8-Dimethyl-7-methoxy-1,2,3,4,4a,9a-hexahydrofluorenone-2-carboxylic acid* (XV). Acid XIV (95 mg.) was added to 3% potassium hydroxide solution (10 ml.) and ethanol (3 ml.) which contained prereduced palladium on barium sulfate catalyst. The suspension was stirred with hydrogen at atmospheric pressure and room temperature. The absorption of hydrogen was complete in 1 hr. The catalyst was filtered, the solution concentrated and acidified to yield 56 mg. (79%) of acid which melted at 155–165°. The analytical sample, prepared by recrystallization from benzene-isooctane, melted at 170–175°.

*Anal.* Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found C, 70.67; H, 6.82.

*Hunsdiecker reaction.* Acid XIV (1.4 g.) was converted to the silver salt (2.06 g., 72%) as previously described.[21] A suspension of the silver salt in carbon tetrachloride (10 ml.) was treated with a solution of bromine (0.5 g.) in carbon tetrachloride (10 ml.) and after the addition, was refluxed for 1 hr. The precipitate was filtered and the solvents removed. The residual oil was chromatographed to yield a neutral substance (0.3 g.) which partly crystallized, m.p. 210–215°, $\lambda_{\max}^{C_2H_5OH}$ 272 m$\mu$ (log $\epsilon$ 4.5).[22]

The major fraction (0.9 g.) was acidic and by methylation and chromatography on alumina was separated into two equal fractions. The more polar fraction was yellow, and became red on saponification, frequently a characteristic of fluorenones. Acidification yielded yellow amorphous material which would not be purified.

New Brunswick, N.J.

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(18) R. Shriner and R. Fuson, *Systematic Identification of Organic Compounds*, Third Edition, John Wiley and Sons, New York, N. Y., p. 157.

(19) R. Adams, V. Vorhees, and R. L. Shriner, *Org. Syntheses*, Coll. Vol. I, 466 (1941).

(20) Ref. 18, p. 158.

(21) R. A. Barnes and R. J. Prochaska, *J. Am. Chem. Soc.*, **72**, 3188 (1950).

(22) A comparison of this maximum and that of acid XIV shows that the difference is similar to that between hexahydrofluorenone ($\lambda_{\max}$ 248 m$\mu$, log $\epsilon$ 4.0) and fluorenone ($\lambda_{\max}$ 252, 256 m$\mu$, log $\epsilon$ 4.7, 5.0).