Reduction of (+)-*trans-p*-Menthane-2,5-dione (14) with Lithium Aluminum Hydride.—As above for **13**, 0.160 g (0.95 mmol) of (+)-*trans*-dione **14**, mp 56°, plus 0.150 g (4 mmol) of lithium aluminum hydride, gave a total product which showed three peaks upon gas chromatography, corresponding in retention time to a mixture of diols **2**, **4**, **6**, and **8**. Diols **1**, **3**, **5**, and **7** were not detected. The gas chromatogram is consistent with the following diol composition: **2**, plus **4**, 44%; **6**, 6%; **8**, 50%.

(+)-*p*-Menthane-2,5-diol, mp 144° (8).—Three recrystallizations from hexane–ether of the above mixture of diols **2**, **4**, **6**, and **8**, gave colorless needle-like crystals of diol **8**: 20 mg (12%); mp 144–144.5°; uncontaminated by detectable amounts of diols **1**–**7** (gas chromatography); $[\alpha]^{26}\text{D}$ +20° (*c* 0.876, ethanol); ir (KBr) 1097, 1046, 1030 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.93; H, 11.80.

(+)-*p*-Menthane-2,5-diol, mp 169° (7), from Hydrogenation of Diol 12.—The hydrogenation product[2] of diol **12**, a mixture of diols **7** (59%) and **8** (41%, analysis by gas chromatography), mp 142–153°, 90 mg, was recrystallized five times from benzene–hexane–ether (5:3:2). The crystals, 11 mg, mp 169°, contained 96% diol **7** and 4% diol **8**. The mixture recovered from the combined filtrates was chromatographed on 20 g of alumina (Fisher A-540). Elution with benzene gave white solid. One crystallization from ether–hexane gave diol **8**, 20 mg, mp 142–144°, contaminated with 5% of diol **7**. Further elution with ether–benzene (1:9) gave fractions which after crystallization from hexane–ether yielded 13 mg of diol **7**, contaminated with 5% of diol **8**. The two fractions of impure diol **7**, totaling 24 mg, were combined and rechromatographed on 7 g of alumina. The last fraction obtained by elution with ether–benzene (1:9) was crystallized from hexane–ether to give 5 mg of diol **7**, mp 169°, of 99% purity, $[\alpha]^{26}\text{D}$ +63° (*c* 0.302, ethanol).

(−)-Menthyl Tosylate (20).—(−)-Menthol (Aldrich) gave (−)-menthyl tosylate (**20**), mp 95–96° (reported[24] mp 94°).

Neomenthol from (−)-Menthyl Tosylate (20).—A solution of 1.03 g of (−)-menthyl tosylate (**20**) in 30 ml of dimethylformamide (Fisher reagent grade) was heated for 6 days at 75–80°. The reaction mixture, cooled to 25°, was diluted with 100 ml of water and was extracted with three 150-ml portions of ether. The ether extract was washed with two 50-ml portions of water and then was dried over anhydrous magnesium sulfate. Evaporation of the ether left 0.35 g of yellowish oil which showed a peak at 5.8 μ (presumably neomenthyl formate carbonyl absorption). Thin layer chromatography showed two major spots, one corresponding in R_f value to the starting tosylate **20**. To a stirred suspension of 0.305 g of lithium aluminum hydride in 100 ml of anhydrous ether was added slowly a solution of the above reaction product mixture in 10 ml of ether. After heating under reflux for 5 hr, excess hydride was decomposed by addition of 2 ml of saturated aqueous sodium sulfate solution. The product, isolated by ether extraction, yielded a yellowish oil which gave a gas chromatogram with two major peaks with the same retention times as neomenthol and menthol.[16] Two unidentified minor peaks were also detected.

Registry No.—**1**, 27525-51-5; **2**, 27525-52-6; **3**, 27525-53-7; **4**, 27525-54-8; **5**, 27525-55-9; **6**, 27525-56-0; **7**, 27525-57-1; **8**, 27525-58-2; **9**, 4031-55-4; **10**, 4031-54-3; **11**, 4031-53-2; **12**, 27570-89-4; **13**, 27525-61-7; **14**, 27525-62-8; **16**, 27570-90-7; **17**, 27570-91-8; **19**, 27525-63-9.

(24) W. Hückel and C.-M. Jennewein, *Justus Liebigs Ann. Chem.*, **683**, 100 (1965).

A New Synthesis of 7,12-Dimethylbenz[*a*]anthracene[1]

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Received August 7, 1970

A new synthesis, which may prove general for the synthesis of 7,12-dimethylbenz[*a*]anthracenes from the corresponding benz[*a*]anthracenes, is described. Benz[*a*]anthracene (II) was condensed with vinylene carbonate to yield 7,12-dihydro-7,12-ethanobenz[*a*]anthracene-13,14-diol cyclic carbonate (III). Hydrolysis yielded 7,12-dihydro-7,12-ethanobenz[*a*]anthracene-13,14-diol (IV) which on treatment with lead tetraacetate afforded 7,12-dialdehydo-7,12-dihydrobenz[*a*]anthracene (V). Reduction of V with lithium aluminum hydride yielded 7,12-bis(hydroxymethyl)-7,12-dihydrobenz[*a*]anthracene (VI), the bismethanesulfonyl derivative of which was reduced to 7,12-dihydro-7,12-dimethylbenz[*a*]anthracene (VIII) by lithium aluminum hydride. Aromatization of VIII by heating with sulfur afforded 7,12-dimethylbenz[*a*]anthracene (I). The yields in each step were high. Similarly, 5-fluoro-7,12-dimethylbenz[*a*]anthracene (I_F) was synthesized from 5-fluorobenz[*a*]anthracene (II_F) in high yield.

Three general syntheses of 7,12-dimethylbenz[*a*]anthracene (I) are known. One involves addition of methylmagnesium iodide to benz[*a*]anthraquinone followed by conversion of the resulting diol with acidic methanol to the corresponding dimethoxy derivative which is reduced with metallic sodium (or potassium) to I[3] or to 7,12-dihydro-7,12-dimethylbenz[*a*]anthracene. The latter is converted to I by heating with sulfur.[3] A second method involves treating the abovementioned dimethyldiol with hydrogen iodide to yield 12-methyl-7-iodomethylbenz[*a*]anthracene which is reduced to I with stannous chloride.[4] The third method involves treatment of 12-methylbenz[*a*]anthrone (not isolated) with methylmagnesium bromide, followed by dehydration of the crude carbinol to I.[5]

Each of these methods has potential drawbacks if variously substituted 7,12-dimethylbenz[*a*]anthracenes are desired: the first two, because of possible difficulties in the synthesis of the desired quinones and in finding proper conditions for transforming the dimethyldiols to the desired analogs of I; and the third because benzanthrones are often too sensitive to give high yields on reaction with methylmagnesium halides. For these reasons a new synthesis was deemed desirable. In this paper, such a new route is illustrated in Scheme I.

Since anthracene was known to react with vinylene carbonate to give a Diels–Alder type addition product in good yield,[6] we heated benz[*a*]anthracene in excess vinylene carbonate to produce the adduct III[7] in high

(1) This research was supported by Grant 5 RO 1 CA07394-Ob from the U. S. Public Health Service.

(2) To whom correspondence should be directed.

(3) W. E. Bachmann and J. M. Chermerda, *J. Amer. Chem. Soc.*, **60**, 1023 (1938). Similar reductions were carried out by B. M. Mikhailov and coworkers, *Chem. Abstr.*, 5842 (1939); 6350*i* (1948).

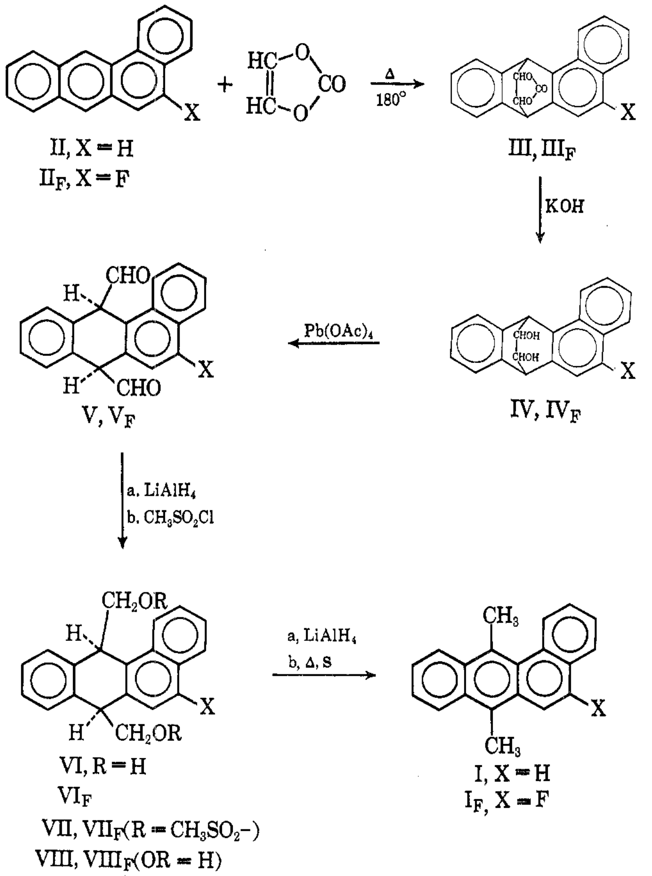
(4) R. B. Sandin and L. F. Fieser, *J. Amer. Chem. Soc.*, **62**, 3098 (1940).

(5) M. S. Newman, *ibid.*, **60**, 1141 (1938).

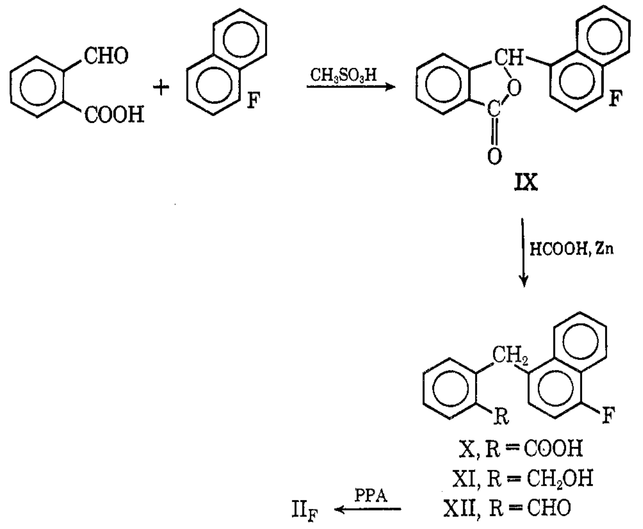
(6) M. S. Newman and R. W. Addor, *ibid.*, **77**, 3789 (1955).

(7) This product was probably a mixture of stereoisomers, but we made no attempts at separation or purification of individual isomers.

SCHEME I



SCHEME II



yield. Alkaline hydrolysis of III yielded the diol IV[7] which was cleaved to the dialdehyde V by lead tetraacetate. Attempts to reduce the aldehyde groups by the Wolff–Kishner method led surprisingly to 7-methylbenz[*a*]anthracene. However, the desired 7,12-dimethylbenz[*a*]anthracene (I) was obtained from V by reduction with lithium aluminum hydride to the diol VI, conversion of the latter to the dimesyl derivative VII, reduction of the latter to VIII with lithium aluminum hydride, and dehydrogenation by heating with sulfur. The yields in each step were very good.

In order to test the above series of reactions with a substituted benz[*a*]anthracene, 5-fluorobenz[*a*]anthracene (II_F) was chosen. All of the above reactions went successfully and the overall yield from II_F to I_F was good. The desired II_F[8] was prepared as shown in Scheme II.

The condensation of 1-fluoronaphthalene with phthalaldehydic acid[9] was best effected at room temperature in concentrated methanesulfonic acid.[10] The conditions necessary to cause condensation of phthalaldehydic acid with fluorobenzene were about the same as those required for condensation of *o*-acetylbenzoic acid with 1,2-dimethoxynaphthalene.[11] That condensation occurred para to the fluorine was established by the fact that X was identical with an authentic sample.[12] Attempts to cyclize XI to 7,12-dihydro-5-fluorobenz[*a*]anthracene by heating with polyphosphoric acid (PPA) followed by heating with sulfur to dehydrogenate afforded only a 10% yield of II_F. However, oxidation of XI to XII, using Sarett's reagent,[13] followed by heating of XII with PPA resulted in high yields of II_F, which was shown to be identical with II_F prepared as described.[12] The above method of converting X to II_F is to be preferred to the earlier synthesis[12] as a higher overall yield of II_F is more reliably obtained. In our experience, routes which involve a benz[*a*]anthrone are liable to give erratic yields, especially on larger scale runs.

Experimental Section[14]

7,12-Dihydro-7,12-ethanobenz[*a*]anthracene-13,14-diol Cyclic Carbonate (III).—A solution of 6.8 g (0.03 mol) of benz[*a*]anthracene[15] in 25.8 g (0.3 mol) of vinylene carbonate[16] was held at reflux (about 175–180°) under nitrogen for 18 hr. On vacuum distillation about 22 g of vinylene carbonate suitable for reuse was recovered. The residue (9.38 g), a brown solid, mp 205–210°, yielded 7.5 g (80%) of yellowish adduct III,[7] mp 219–224°, ir band at 5.55 μ, on crystallization from benzene–petroleum ether (bp 60–110°).

Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.3; H, 4.5. Found: C, 80.5; H, 4.6.

In an experiment essentially the same as the above, the fluorine analog[7] III_F, mp 228–231°, ir band at 5.55 μ, was obtained in 85% yield.

Anal. Calcd for $C_{21}H_{13}FO_3$: C, 75.9; H, 3.9; F, 5.7. Found: C, 76.0; H, 4.0; F, 5.5.

7,12-Bis(hydroxymethyl)-7,12-dihydrobenz[*a*]anthracene (IV).—In a typical experiment a mixture of 3.14 g of III, 2.3 g of potassium hydroxide, 3 ml of water, and 25 ml of ethanol was held at 70–75° for 2 hr. After the usual work-up, the product was crystallized from benzene–petroleum ether to yield 2.60 g (93%) of IV, mp 196–198°, ir broad band at 2.75 μ.

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.3; H, 5.6. Found: C, 83.5; H, 5.4.

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(8) M. S. Newman and K. Naiki, *J. Org. Chem.*, **27**, 863 (1962).

(9) V. W. Floutz, *ibid.*, **25**, 643 (1960), and references therein.

(10) We thank the Pennwalt Manufacturing Co., for a generous gift of 70% methanesulfonic acid. Concentrated acid is easily obtained from this by vacuum distillation.

(11) M. S. Newman and C. C. Davis, *J. Org. Chem.*, **32**, 66 (1967).

(12) M. S. Newman, D. MacDowell, and S. Swaminathan, *ibid.*, **24**, 509 (1959).

(13) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

(14) All melting points are uncorrected. All microanalyses were by Galbraith Laboratories, Knoxville, Tenn. The nmr spectra of all compounds were consistent with the postulated structure. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian Model A-60 instrument at 60 Mc with tetramethylsilane as an internal reference. The term "worked up in the usual way" means that an ether–benzene solution of the reaction products was washed with dilute acid and/or base, with saturated salt solution and was filtered through a cone of anhydrous $MgSO_4$. The solvent was then removed by either distillation or a rotary evaporator.

(15) Used as obtained from Henley and Co., New York, N. Y.

(16) We thank the Union Carbide Plastics Co., Bound Brook, N. J., and the American Cyanamide Corp. for generous gifts of vinylene carbonate.

In a similar way, pure $\mathrm{IV_F}$,[7] mp 230–235°, ir broad band at 2.75 μ, was obtained in 99% yield.

Anal. Calcd for $C_{20}H_{15}FO_2$: C, 78.5; H, 4.9; F, 6.2. Found: C, 78.6; H, 4.8; F, 6.0.

7,12-Dialdehydo-7,12-dihydrobenz[*a*]anthracene (V).—To a stirred solution of 36.5 g of IV in 1.5 l. of benzene and 25 ml of acetic acid at 30–35° was added 92 g of lead tetraacetate in portions during 15 min. After 2 hr the lead oxide was removed by filtration. The filtrate was worked up as usual to yield 32.4 g (89%) of V,[7] mp 175–177°, ir band at 5.75 μ, suitable for the next step. The analytical sample of V, mp 178–180°, was obtained by one recrystallization from benzene–petroleum ether.

Anal. Calcd for $C_{20}H_{14}O_2$: C, 84.0; H, 4.9. Found: C, 84.1; H, 4.8.

7,12-Dialdehydo-7,12-dihydro-5-fluorobenz[*a*]anthracene ($\mathrm{V_F}$).—In a similar way $\mathrm{V_F}$, mp 129–130°, was obtained in 91% yield from $\mathrm{IV_F}$.

Anal. Calcd for $C_{20}H_{13}FO_2$: C, 78.9; , 4.3; F, 6.3. Found: C, 79.0; H, 4.3; F, 6.1.

7,12-Bis(hydroxymethyl)-7,12-dihydrobenz[*a*]anthracene (VI).—To the solution formed by heating a mixture of 2 g of $LiAlH_4$ and 50 ml of dry ether for 4 hr was added a solution of 5.0 g of V in 25 ml of ether and 140 ml of pure tetrahydrofuran during 15 min. After holding at reflux for 6 hr, the usual work-up afforded 4.7 g (94%) of pure VI, mp 172–173°, ir broad band at 3.05 μ, on crystallization from benzene–THF.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.8; H, 6.2. Found: C, 83.1; H, 6.4.

7,12-Dihydroxymethyl-7,12-dihydro-5-fluorobenz[*a*]anthracene ($\mathrm{VI_F}$).—In a similar way $\mathrm{VI_F}$, mp 180–181.5°, ir broad band at 3.05 μ, was obtained in 84% yield.

Anal. Calcd for $C_{20}H_{17}FO_2$: C, 77.8; H, 5.5; F, 6.2. Found: C, 78.0; H, 5.7; F, 5.9.

7,12-Dihydro-7,12-dimethylbenz[*a*]anthracene (VIII).—To a suspension of 5.0 g of VI in 125 ml of methylene chloride was added rapidly a stirred mixture formed by adding 6 g of methanesulfonyl chloride to 5 ml of dry pyridine. The reaction mixture was stirred at room temperature overnight and poured into a mixture of ice and concentrated HCl. The CH_2Cl_2 solution was washed with dilute HCl and worked up as usual. The crude reaction product was heated with 0.05-ml pressure at 60° to remove traces of methanesulfonyl chloride. A solution of this product (8.3 g, yellowish oil) in 50 ml of THF and 60 ml of ether was added during 15 min to the solution formed by refluxing a mixture of 7.5 g of lithium aluminum hydride in 150 ml of ether for 12 hr. After being held at reflux for 18 hr, the reaction mixture was cooled and treated with 7.5 ml of water, 7.5 ml of 15% NaOH, and 23 ml of water. After the usual work-up, the crude product (4.8 g) was chromatographed on 100 g of Woelm grade A neutral alumina using a mixture of petroleum ether and benzene, 1:1, to elute 3.2 g (70%) of pure VIII as colorless crystals suitable for the next step. Recrystallization of a portion from petroleum ether yielded the analytical sample of VIII, mp 103–105°.

Anal. Calcd for $C_{20}H_{18}$: C, 93.1; H, 6.9. Found, C, 93.1; H, 7.0.

When the above reduction with $LiAlH_4$ was conducted in 1:1 ether–THF, the yield of VIII fell to 58%. A mixture of the two possible methyl, hydroxymethyl analogs of VIII was obtained. By mesylation and $LiAlH_4$ reduction, additional VIII could be obtained.

7,12-Dihydro-7,12-dimethyl-5-fluorobenz[*a*]anthracene ($\mathrm{VIII_F}$).—By a procedure similar to that described above, $\mathrm{VIII_F}$ was obtained in 90% yield. The analytical sample, mp 59–62°, was obtained by recrystallization from methanol.

Anal. Calcd for $C_{20}H_{17}F$: C, 87.0; H, 6.2; F, 6.9. Found: C, 87.1; H, 6.6; F, 6.9.

7,12-Dimethylbenz[*a*]anthracene (I).—In a typical experiment a mixture of 1.00 g of VIII and 0.12 g of sulfur was heated to 150° (when H_2S began to be evolved) and then rapidly to 270° for 15 min. The crude hydrocarbon was purified by formation and recrystallization of the picrate to yield 0.90 g (90%) of pure I, mp and mmp (with an authentic sample[17]) 122–123°, prepared by a slight modification of a previous method.[4]

5-Fluoro-7,12-dimethylbenz[*a*]anthracene ($\mathrm{I_F}$).—All solvents used in processing the product of reactions involving $\mathrm{I_F}$ were distilled under nitrogen and a nitrogen atmosphere was maintained throughout because $\mathrm{I_F}$ reacts readily with oxygen to form a peroxide, probably transannular.[18] The melting point of $\mathrm{I_F}$ is not sharp, probably because of traces of peroxide. However, the ir and nmr spectra are consistent with the structure.

In the best of several experiments, a mixture of 1.20 g of $\mathrm{VIII_F}$ and 0.128 g of sulfur was heated slowly to 170° when H_2S was evolved. The mixture was then heated at 195° for 3 hr and at 260° for 5 min. The product was purified by recrystallization of the picrate followed by chromatography over alumina to yield 0.90 g (75%) of VIII, mp 89–91° alone and mixed with a sample previously prepared.[19]

7-Methylbenz[*a*]anthracene.—A solution of 1.2 g of V in 220 ml of alcohol containing 16 g of 85% hydrazine hydrate was refluxed for 30 min. On cooling 1.3 g of crude dihydrazone (no carbonyl absorption in the ir) was obtained as a yellow solid, mp 58–80°. A solution of 1.2 g of this in 40 ml of diethylene glycol containing 1 g of KOH was heated at reflux for 3 hr during which time the theoretical amount of nitrogen was evolved. After the usual work-up 0.5 g of 7-methylbenz[*a*]anthracene, mp and mmp 137.5–139.0°, with authentic hydrocarbon[20] was obtained. The mixture melting point with 12-methylbenz[*a*]anthracene was depressed. In an attempt to effect the reduction with potassium *tert*-butoxide in DMSO,[21] only tar was obtained.

3-(4-Fluoro-1-naphthyl)phthalide (IX).—To a solution of 55 g (0.366 mol) of phthalaldehydic acid in 415 ml of methanesulfonic acid (prepared by adding 13.6 ml of water to 400 ml of concentrated methanesulfonic acid)[10] was added 53 g (0.363 mol) of 1-fluoronaphthalene. After stirring at room temperature overnight the mixture was poured on ice and worked up as usual to yield 91 g (91%) of IX pure enough for the next step. The analytical sample of IX, mp 154.0–154.5°, was obtained by recrystallization from benzene–petroleum ether.

Anal. Calcd for $C_{18}H_{11}FO_2$: C, 77.8; H, 4.0; F, 6.8. Found: C, 77.5; H, 4.0; F, 6.6.

***o*-(4-Fluoro-1-naphthylmethyl)benzoic Acid (X).**—A solution of 6.0 g of IX in 100 ml of 90% formic acid was refluxed over 12 g of zinc dust[22] for 10 hr to yield 5.5 g (91.5%) of pure X, mp and mmp (with an authentic sample[8]) 176–177°.

***o*-(4-Fluoro-1-naphthylmethyl)benzyl Alcohol (XI).**—A solution of 54.5 g of X in 700 ml of ether and 100 ml of THF was added to the mixture formed by refluxing 10 g of $LiAlH_4$ in 200 ml of ether for 2 hr. After refluxing for 3 hr the mixture was decomposed by addition of water. The usual work-up afforded 51.3 g (99%) of XI pure enough for further use. The analytical sample, mp 92.0–93.5°, was obtained by crystallization from benzene-petroleum ether.

Anal. Calcd for $C_{18}H_{15}FO$: C, 81.2; H, 5.6; F, 7.1. Found: C, 81.2; H, 5.6; F, 7.0

5-Fluorobenz[*a*]anthracene (II*).—To a solution ot 20° of 25 g of CrO_3 in 250 ml of pyridine[23] was added a solution of 25 g of XI in 250 ml of pyridine during 15–20 min. The temperature was held near 20° for a further 2 hr and the suspended inorganic matter was removed by filtration. An ether–CH_2Cl_2 solution of the products was well washed with dilute HCl and then K_2CO_3. The crude brownish aldehyde XII (ir band at 5.8 μ) was not purified but dissolved in 75 ml of CH_2Cl_2 and added to 250 ml of PPA with stirring. The CH_2Cl_2 was distilled and the mixture heated on a steam bath for 20 min. After pouring on ice the usual work-up afforded a solid which was purified *via* the picrate to yield 20.4 g (88%) of $\mathrm{II_F}$, mp 129–130°. The melting point was not depressed by an authentic sample.[12]

Registry No.—I, 57-97-6; III, 27525-64-0; $\mathrm{III_F}$, 27525-65-1; IV, 27570-93-0; $\mathrm{IV_F}$, 27525-66-2; V, 27570-94-1; $\mathrm{V_F}$, 27525-67-3; VI, 27525-68-4; $\mathrm{VI_F}$, 27525-69-5; VIII, 24316-23-2; $\mathrm{VIII_F}$, 27525-71-9; IX, 27525-72-0; XI, 27525-73-1.

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[17] M. S. Newman and R. Gaertner, *J. Amer. Chem. Soc.*, **72**, 264 (1950).

[18] J. W. Cook and R. H. Martin, *J. Chem. Soc.*, 1125 (1940).

[19] M. S. Newman and K. Naiki, *J. Org. Chem.*, **27**, 863 (1962). The melting point of the sample prepared in this work had decreased from the reported 92.5–93.0°, undoubtedly due to a small amount of peroxide formation. However, the ir and nmr spectra were identical.

[20] L. F. Fieser and M. S. Newman, *J. Amer. Chem. Soc.*, **58**, 2376 (1936).

[21] D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *ibid.*, **84**, 1734 (1962).

[22] R. L. Letsinger, J. D. Jamison, and A. S. Hussey, *J. Org. Chem.*, **26**, 97 (1961).

[23] Note the precautions described in "Reagents for Organic Synthesis," L. F. Fieser and M. Fieser, Wiley, New York, N. Y., 1967, p 146.