The mesylate of this carbinol is a solid, m.p. 56–58°, which gives, in an over-all yield from the carbinol of 52%, the nitrile, m.p. 92–94° from methanol.

Anal. Calcd. for $C_{20}H_{23}NO_2$: C, 77.66; H, 7.44; N, 4.53. Found: C, 77.24; H, 7.24; N, 4.48.

The acid, obtained in 72% yield from the nitrile, has m.p. 69–70° recrystallized from petroleum ether (60–80°).

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.17; H, 7.31. Found: C, 73.12; H, 7.49.

Monocyclization of I (R = H) with zinc chloride and acetic anhydride. Five grams of I, 30 ml. of glacial acetic acid, 20 ml. of acetic anhydride, and 0.4 g. of freshly fused zinc chloride were refluxed for 2 hr. and then poured onto ice; the mixture was made strongly alkaline with potassium hydroxide and extracted with ether; the ether extract was worked up in the usual way to give, in 95% yield, 2-phenethyltetralone identified as the semicarbazone, m.p. 166–167° (Leuchs[5] gives 166–167°) and 2,4-dinitrophenylhydrazone, m.p. 158–160°.

Double cyclization of I (R = H) with polyphosphoric acid. Two grams of I and 40 g. of polyphosphoric acid were heated with stirring for 3 hr. in an oil bath kept at 125°, allowed to cool, and poured into ice water. Tetrahydrochrysene (1.5 g.) (IV) was collected which, after recrystallization from methanol, melted at 105°. (Salzer[8] gives m.p. 105°.) No other compound could be isolated. The compound was found identical with an authentic sample of IV prepared according to Salzer[8] from 1-phenethyltetralone-2. It was smoothly dehydrogenated to chrysene on heating to 300° with 10% palladium-on-charcoal.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.10; H, 6.90. Found: C, 93.24; H, 6.84.

Cyclization of I (R = H) with hydrofluoric acid. Three grams of I was treated with approximately 150 ml. of anhydrous hydrofluoric acid. After 48 hr. the semisolid residue was extracted with boiling methanol: the residue, 0.3 g., was chrysene, identified by mixed m.p.; the methanol solution deposited on cooling 0.5 g. of IV. From the methanol solution 2.0 g. of II were isolated, identified as the 2,4-dinitrophenylhydrazone.

Cyclization of I (R = OMe). Three grams of I was treated with approximately 50 ml. of anhydrous hydrofluoric acid. After 24 hr. the acid was evaporated and the remaining oil taken up in benzene and chromatographed through activated alumina. The column was washed with a mixture of benzene and petroleum ether (60–80°); except for a very small fraction of impure high-melting material, a colorless solid (2.4 g.) was obtained which, after recrystallization from methanol, melted at 85–86°, and which was identified as the 7-methoxy-2-(4-methoxyphenethyl)tetralone-1.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.42; H, 7.10. Found: C, 77.86; H, 7.17.

Dinitrophenylhydrazone, m.p. 163°, from benzene and ethanol.

Anal. Calcd. for $C_{26}H_{26}N_4O_6$: N, 11.4. Found: N, 11.5.

Cyclization of I (R = OMe) with polyphosphoric acid. A mixture of 1 g. of I with 60 g. of polyphosphoric acid and 1 g. of phosphorus oxychloride was stirred and heated to 120° (bath temperature) for 90 min., left to cool, poured into cold water, and filtered. The residue was boiled with methanol and filtered hot. The remaining solid (0.79 g.) was recrystallized from a mixture of benzene and methanol, m.p. 235–238°. Its ultraviolet spectrum in dioxane solution showed it to be a chrysene derivative: maxima at 375, 357, 340, 325, 310, 278 mμ (log ϵ 3.52, 3.52, 3.34, 4.14, 4.16, 4.6).

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.33; H, 5.56; methoxyl, 10.4. Found: C, 83.23; H, 5.59; methoxyl, 10.2.

From the hot methanol solution a very small quantity of another material separated which, after recrystallization from petroleum ether (60–80°), melted at 166–167°.

Anal. Calcd. for 3,9-dimethoxy-5,6,11,12,13,14-hexahydrochrysene (?): $C_{20}H_{22}O_2$: C, 81.63; H, 7.48; methoxyl, 10.2. Found: C, 81.62; H, 7.47; methoxyl, 10.3.

3,9-Diacetoxychrysene. One gram of 3,9-dimethoxychrysene was boiled for 4 hr. with 57% hydriodic acid; the cold solution was poured into water and filtered, m.p. of crude dihydroxy compound 320°. The diphenol was boiled with 5 ml. of acetic anhydride in 50 ml. of pyridine for 2.5 hr. A solid separated which, after recrystallization from nitromethane, melted at 242–243°.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.74; H, 4.65. Found: C, 76.72; H, 4.79.

Preparation of 1,6-di(4-methoxyphenyl)hexanone-3-ol-4. The methyl ester of 4-methoxyphenylpropionic acid was prepared from methyl 4-methoxycinnamate by hydrogenation in ethyl acetate with 10% palladium-on-charcoal; b.p. 111–112°/0.6 mm. The acyloin was prepared according to Johnson and coworkers[3]: to a suspension of 9.5 g. of powdered sodium in 170 ml. of xylene kept at 105–110°, was added, over 0.5 hr., a solution of 20 g. of methyl 4-methoxyphenylpropionate in 170 ml. of xylene, the reaction being carried out in an atmosphere of pure nitrogen. Heating was continued for a further 0.75 hr., after which the mixture was allowed to cool and sufficient methanol added to destroy the remaining sodium; water was added and the xylene layer separated. After several washings with water the xylene solution was steam-distilled; the yellow oil was extracted with ether, dried over magnesium sulfate, and the ether removed *in vacuo*. The yield of acyloin was 12 g. (75%).

Cyclization of the acyloin with hydrofluoric acid. Five grams of acyloin were treated with approximately 150 ml. of hydrofluoric acid for 24 hr., when the acid was evaporated and the residue dissolved in ether. From the ethereal solution a yellow oil was obtained which was induced to crystallize by trituration with ethyl acetate. The solid (2.5 g.) after recrystallization from ethyl acetate, melted at 235–237°, and proved to be identical with the dimethoxychrysene of m.p. 235–238°, obtained by the polyphosphoric acid cyclization of I (R = OMe). The ethyl acetate solution was concentrated when it yielded a very small amount of a material, m.p. 168–169° after recrystallization from petroleum ether (60–80°) which showed no depression of m.p. with the second material, m.p. 166–167° obtained by the polyphosphoric acid cyclization of I (R = OMe).

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Mesityl Mesitoate

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Mesityl mesitoate does not appear in the chemical literature. The compound was made for comparison with an unidentified material from a Kolbe electrolysis, by way of the Schotten-Baumann reaction.

EXPERIMENTAL

Mesitoic acid,[1,2] 5 g. (0.030 mole), m.p. 153°, was converted to mesitoyl chloride by adding 4 ml. of thionyl chloride and refluxing over a water bath for 30 min. The sodium salt of mesitol was prepared by mixing 4 g. (0.037 mole) of

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[1] D. M. Bowen, *Org. Syntheses*, **Coll. Vol. III,** 553 (1955).

[2] Prepared by B. T. Shawver, Monmouth College.

mesitol,[3] m.p. 72.5–73°, with 10 ml. of 6*N* sodium hydroxide. The mesitoyl chloride was slowly added to the sodium mesitolate through about 30 min., in a 125-ml. Erlenmeyer flask, with shaking. Release of heat resulted. After heat evolution ceased, the mixture was refluxed on a water bath for 30 min. It was then chilled in an ice bath. The crystals which formed were collected by vacuum filtration, washed with water, and recrystallized from approximately 100 ml. of ethyl alcohol; yield 3.75 g. (40%), m.p. 70.5–71.5°.

Anal. Calcd. for ($C_{19}H_{22}O_2$): C, 80.85 H, 7.80. Found: C, 80.55 and 80.29; H, 7.63 and 7.75.[4]

Hydrolysis. Alkaline hydrolysis: Mesityl mesitoate is a hindered ester and as such should be highly resistant to formation and saponification.[5] The ester, 0.25 g., was refluxed 6 hr. with 5 ml. of 6*N* sodium hydroxide. There remained undissolved 0.23 g. of the mesityl mesitoate which was collected by vacuum filtration. The clear filtrate did produce a slight precipitate when acidified.

Acid hydrolysis: One g. of ester in 5 ml. of cold conc. sulfuric acid was drowned with 40 ml. of cold water. The resulting mixture was extracted with ether. The mesitoic acid was next removed from the ether by three sodium bicarbonate washings, (0.2 g. recovered, m.p. 152°). Mesitol, 0.15 g., was extracted from the ether solution by three washings with 2*N* sodium hydroxide, and precipitated with hydrochloric acid while in an ice bath. The crystals were collected by filtration and vacuum desiccated for 48 hr.; m.p. 70–71°. Mixed with mesitol from Organic Research Chemical Ltd., the m.p. was 70.5–71.5°.

All melting points are corrected.

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[3] Supplied by Organic Research Chemical Ltd., Poyle Estate, Bucks, England.

[4] Clark Microanalytical Laboratory, P. O. Box 17, Urbana, Ill.

[5] H. P. Treffers and L. P. Hammett, *J. Am. Chem. Soc.*, 59, 1708 (1937).

Preparation of Crystalline Diphenyldiazomethane

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Diphenyldiazomethane has been used to analyze mixtures of carboxylic acids[1] and as a convenient "blocking agent" for acids since the resulting benzhydryl esters are easily hydrogenolyzed.[2] Benzhydryl esters should also prove useful as derivatives in view of their ease of preparation and the resulting increase in molecular weight.

Hydrazones have been converted to diazo compounds by treatment of the *N*-tosylates with base[3,4] and by oxidation of hydrazones with mercury acetamide,[5] potassium permanganate,[6] Tollens' reagent[6] mercuric oxide,[7] air,[8,9] silver oxide,[10] and manganese dioxide.[10]

The usual preparative method for diphenyldiazomethane by the mercuric oxide oxidation of benzophenone hydrazone requires six hours and yields an oil.[11] The procedure described here requires 75 minutes and gives a crystalline product in high yield. This procedure is an extrapolation of the method of Nenitzescu and Solomonica for the preparation of benzoylphenyldiazomethane[12] and diazofluorene.[12] Diethyl ether rather than petroleum ether[11] is used as the solvent in spite of the reported lower rate of oxidation in ether[13] because of the greater solubility of the hydrazone in ether. Most important is the use of a basic catalyst.

We suggest the role of the basic catalyst is that shown below.

$$(C_6H_5)_2C{=}N{-}NH_2 + HgO \longrightarrow (C_6H_5)_2C{=}N{-}\overset{+}{N}H_2HgO^- \longrightarrow$$

$$\underset{\text{I}}{(C_6H_5)_2C{=}N{-}NH{-}HgOH} \xrightarrow[-H_2O]{OH^-} (C_6H_5)_2C{=}N{-}\overset{-}{N}{-}HgOH \longrightarrow$$

$$(C_6H_5)_2CN_2 + HgOH^-$$

$$HgOH^- \longrightarrow Hg + OH^-$$

This reaction path is similar to that suggested for the mercuric acetate oxidation of tertiary amines[14] and an analogous mechanism serves to explain the mercuric oxide oxidation of 1,1-disubstituted hydrazines, R_2NNH_2, to tetrazines, $R_2NN{=}NNR_2$.[15] Mercuric acetate oxidation of hydrazones yields, in fact, organomercury compounds which are considered to be formed, however, by further reaction of the diazo compound initially formed.[16]

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