yielded a small amount of the keto alcohol IV, m.p. 163–166°. A mixture melting point determination with a known sample showed no depression.

Demethoxylation of duryl o-methoxyphenyl ketone. An ether solution of magnesium bromide was prepared according to the procedure of Wotiz, Hollingsworth, and Dessy.[11] A solution of 1.50 g. of ketone in 10 ml. of ether and 10 ml. of toluene was added dropwise to a cooled mixture of 0.50 g. of ground magnesium, 10 ml. of magnesium bromide solution, and 10 ml. of ether. The mixture was then stirred under nitrogen at ice bath temperature for 8 hr. after which time the solution was decanted from the remaining magnesium into 6*N* hydrochloric acid, ether and chloroform being added for solubility. The organic phase was extracted with 5% sodium bicarbonate, washed with water, and dried over sodium sulfate. Evaporation of the solvent left a red solid, which was chromatographed on alumina. From the fractions arising from elution with 15:1 cyclohexane to ether was obtained, after crystallization from chloroform-ethanol, 0.061 g. (4.7%) of duryl phenyl ketone, m.p. 118–121°, identified by a mixture melting point determination and infrared spectral analysis.

Demethoxylation of 2-methoxy-1-naphthyl mesityl ketone. A solution of 2.00 g. of ketone in 15 ml. of toluene and 10 ml. of ether was added over a 10-min. period to a mixture of 0.80 g. of ground magnesium, 10 ml. of magnesium bromide solution, and 10 ml. of ether. The mixture was stirred under nitrogen for 12 hr. at room temperature. Hydrolysis was effected by adding dropwise 25 ml. of 10% hydrochloric acid to the mixture, cooled in an ice bath. After 12 hr. the solution was poured into an additional 25 ml. of acid, to which 25 ml. of toluene and ether had been added. The organic layer was extracted with 5% sodium bicarbonate, washed with water, and dried over sodium sulfate. Evaporation of the solvent left a red solid, which was subjected to chromatography on alumina. Elution with 15:1 cyclohexane to ether gave, after recrystallization from chloroform-ethanol, 0.211 g. (11.7%) of mesityl 1-naphthyl ketone, identified by reference to its infrared spectrum and a mixture melting point determination.

Attempted carbonation of the mixture arising from reaction of duryl o-methoxyphenyl ketone with the binary mixture, magnesium–magnesium bromide. The mixture from the reaction of duryl *o*-methoxyphenyl ketone and the binary mixture was poured into finely divided Dry Ice with vigorous stirring, ether being added to replace that lost by evaporation. The mixture was allowed to warm to room temperature; ice and dilute hydrochloric acid were then cautiously added. When all the magnesium and other solids had dissolved, the organic layer was washed twice with water and extracted with two 50-ml. portions of 10% sodium hydroxide. A gelatinous inorganic precipitate which formed was removed by filtration. Acidification of the basic extract gave a red solid which was taken up in ether. Removal of solvent left a red oil which was reprecipitated by extraction into a 5% sodium bicarbonate solution and acidification of the solution. A tan solid melting over a wide range above 140° was obtained after dissolving the precipitate in ether and removing the solvent. The tan solid, however, could not be recrystallized from ethanol-water. Its infrared spectrum had a single intense band at 1690 cm.$^{-1}$ and a wide band between 3000 and 3500 cm.$^{-1}$. No band was present at 1665 cm.$^{-1}$; the 1665 cm.$^{-1}$ absorption is attributed to the ketone carbonyl group in *o*-duroylbenzoic acid. The organic layer obtained after extraction with sodium hydroxide was worked up in the usual way. Chromatography of the solid obtained after removal of solvent gave 0.028 g. of duryl phenyl ketone.

Treatment of duryl o-methoxyphenyl ketone with sodium and 4-methyl-2-pentanol. A modification of the procedure of Hansley[6] was used. A mixture of 1.00 g. of sodium cut into small pieces and 20 ml. of toluene was heated under nitrogen until the metal had melted. To the mixture was added dropwise, with stirring, 3.00 g. of ketone in 10 ml. of toluene and 20 ml. of 4-methyl-2-pentanol. Heating under reflux was continued until all the sodium had dissolved. An additional 0.30 g. of sodium was then added, and when the metal had dissolved, heating was stopped. The red solution was poured into an acidified ice water mixture, and the organic phase was extracted with 5% sodium bicarbonate, washed with water, and dried over sodium sulfate. Removal of the solvent left a residue which was chromatographed on alumina as before. Elution with 15:1 cyclohexane to ether gave a solid which was recrystallized from chloroform-ethanol to give 0.256 g. (6.8%) of *o*-duroylphenyl 4-methyl-2-pentyl ether, identified by a mixture melting point determination with a sample synthesized independently. The 20:1 cyclohexane to ether fractions gave clear oils, which were crystallized from methylene chloride–methanol to give 0.363 g. (13.1%) of a compound tentatively identified as *o*-methoxybenzyldurene.

Anal. Calcd. for $C_{18}H_{16}O$: C, 84.99; H, 8.72. Found: C, 85.05; H, 8.82.

The infrared spectrum has bands at 1240 and 750 cm.$^{-1}$. The 1240 cm.$^{-9}$ band is assigned to absorption by an aromatic methoxyl group.[10] The 750 cm.$^{-1}$ band is found in a number of *o*-substituted aromatic hindered ketones studied in this laboratory and has been assigned to an *o*-disubstituted benzene ring.[9] No band was present in the 1650 cm.$^{-1}$ region which is characteristic of a hindered aromatic ketone.

Preparation of o-duroylphenyl 4-methyl-2-pentyl ether. A mixture of 1.45 g. of sodium metal cut into small pieces and 25 ml. of 4-methyl-2-pentanol was heated under reflux until all the metal had dissolved. A solution of 10 g. of *o*-bromophenyl duryl ketone in 40 ml. of benzene was then added, and the mixture was heated under reflux for 34 hr., during which time a finely divided colorless precipitate formed. The reaction mixture was poured into 1*N* hydrochloric acid, which dissolved the solid, leaving two clear phases. The organic phase was washed with 5% sodium bicarbonate and with water, dried over sodium sulfate, and heated on a hot plate to remove solvent. When most of the benzene had distilled, *o*-duroylphenyl 4-methyl-2-pentyl ether crystallized from the hot solution; yield 8.10 g. (75.9%), m.p. 117–118°. The analytical sample, crystallized from chloroform-ethanol, melted at 118–119°.

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.59; H, 8.93.

The infrared spectrum of the material has bands assignable to a hindered conjugated ketone at 1655 cm.$^{-1}$, an aromatic ether at 1245 cm.$^{-1}$, a mesityl group at 865 cm.$^{-1}$, and a 1,2-disubstituted benzene ring at 750 cm.$^{-1}$.

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9,10-*endo*-*o*-Xylylene-9,10-dihydroanthracene

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In view of the remarkable reactivity of anthracene (I) with benzyl radicals as recorded in a previous paper,[1] it appeared of interest to examine

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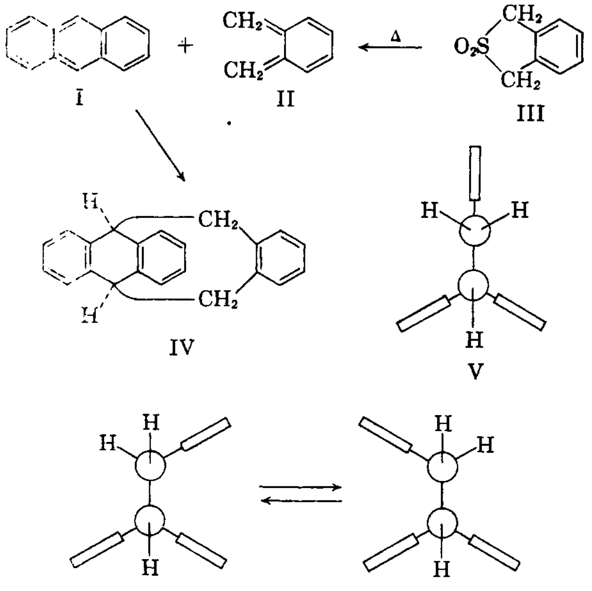
[11] J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956).

(1) K. Sisido, Y. Udô, and H. Nozaki, *J. Am. Chem. Soc.*, **82**, 434 (1960). See also R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 950 (1957); A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1001 (1957).

the reaction of I with *o*-xylylene or *o*-quinodimethane (II). II was obtained easily upon thermal decomposition of 1,3-dihydroisothianaphthene 2,2-dioxide (III) according to the method of Cava and Deana,[2] and was allowed to react *in situ* with I. Thus, heating of an almost equimolar mixture of I and III at 250–300° for thirty minutes, followed by chromatographic separation, furnished a 12% yield of 9,10-*endo*-*o*-xylylene-9,10-dihydroanthracene (IV), m.p. 179°. The constitution of IV was supported by its spectrographic properties.

Inspection of the molecular model of IV revealed that the symmetrical conformation (V)[3] can naturally be constructed only with substantial expansion of bond angles, but the fully eclipsed conformations (VIa and VIb) are devoid of such kind of strain. It is of interest to note signal of the bridgehead methine hydrogens has been observed as a triplet with integrated intensities in the approximate ratio of 1:2:1, while that of methylene hydrogens as a doublet of equal intensity. This fact indicates that each of the methine hydrogens is coupled with adjacent methylene hydrogens which are both completely equivalent. If the actual conformations are to be represented by VIa and VIb, these should be interchangeable with each other with low energy barrier separating them, or the *endo*-*o*-xylylene group must be almost free to flip over from one side to the other under conditions of NMR determination. The ultraviolet spectrum showed no anomaly which might have been expected from the interaction of two benzene rings closely situated in a rigid conformation (VIa or VIb).[4]



I II III IV V VIa VIb

EXPERIMENTAL[5]

9,10-endo-o-Xylylene-9,10-dihydroanthracene (IV). A mixture of 1.0 g. (0.0059 mole) of 1,3-dihydroisothianaphthene 2,2-dioxide (III)[2] and 1.1 g. (0.0062 mole) of anthracene in a small flask was heated at 250–260° for 15 min. in an oil bath. After an additional 15 min. at 300°, the reaction mixture was cooled and taken up in benzene. The benzene solution was chromatographed on a column of alumina. Elution with benzene afforded 0.2 g. (12% yield based on III) of colorless leaflets, m.p. 179° after two recrystallizations from ethanol. Considerable amounts of anthracene and polymeric materials were also isolated, besides a small quantity of anthraquinone (m.p. and mixed m.p. 274°).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.39; H, 6.48.

The NMR spectrum was obtained with a Varian spectrometer operating at 40 mc. on a *ca.* 0.1*M* solution of IV in carbon tetrachloride. Frequencies are given relative to water as an external standard. A doublet at −89 and −78 cps. (aromatic hydrogens), a triplet centering at 20.5 cps. with a separation of ±6.8 cps. (methine hydrogens), and a doublet centering at 62 cps. (methylene hydrogens) were observed, the integrated intensities being in the ratio of 6:1:2 in accordance with the formula given.

Ultraviolet absorption (in iso-octane): λ_{max} 252 (ϵ 1000), 260 (610), 266 (1000), and 274 mμ (1350).

Infrared absorptions (potassium bromide): 3077, 3049, 2933, 2865, 1957 (w.), 1923 (w.), 1852 (w.), 1821 (w.), 1585, 1495 (s.), 1481 (s.), 1458 (s.), 1332, 1299, 1225, 1174, 1120, 1098, 1085, 1054, 1033, 963, 946, 915, 872, 825, 763 (v.s.), and 743 cm.$^{-1}$ (v.s.).

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[2] M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

[3] In formulas V, VIa, and VIb the top view of molecule IV has been shown. A thin square denotes an *o*-phenylene group.

[4] For an interesting example of "homoconjugation" interaction of benzene ring with an α,β-unsaturated carbonyl group see J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **79**, 2569 (1957); **80**, 3667 (1958).

[5] Temperatures are uncorrected. Microanalyses were performed by Miss Kenko Ogawa.

1,1,5-Trichloro-1,3-pentadiene from the Pyrolysis of 5,5,5-Trichloro-4-acetoxy-1-pentene

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In an attempt to prepare 5,5,5-trichloro-1,3-pentadiene (I), 5,5,5-trichloro-4-acetoxy-1-pentene (II) was subjected to the usual pyrolytic conditions for elimination of acetic acid.[2] From the pyrolysis

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[1] National Science Foundation Fellow, 1956–1959.

[2] W. J. Bailey and R. Barclay, *J. Am. Chem. Soc.*, **81**, 5393 (1959).