butene. One possible explanation is that the bond compressions have no effect on the resonance stabilization of the molecule. The second possibility is that the resonance stabilization of benzocyclobutene is decreased by the bond compressions, but that the stabilization of the transition state by the cycloalkane ring is less for benzoycyclobutene than for tetralin and indane.

It is of interest to note that indane and tetralin are both more reactive than o-xylene. There is probably very little difference in the steric hindrance to attack in the ortho- positions of these molecules. Nor can, the effect be attributed to the substitution of hydrogen by an alkyl group, since ethylbenzene is less reactive than toluene in the benzoylation reaction.[3] The increased reactivity may be due to the presence of more favorable configurations for hyperconjugation[4] with the alkyl groups in the transition states for substitution of indane and tetralin than for o-xylene.

<center>EXPERIMENTAL</center>

The benzocyclobutene was prepared by the catalytic hydrogenolysis of 1,2-dibromobenzocyclobutene using the method given by Cava and Napier for the hydrogenolysis of 1,2-diiodobenzocyclobutene.[5] Whereas yields of 20–55% were reported using the diiodo- compound, yields of 80–85% were obtained using the dibromo- compound. The hydrocarbon sample by mass spectral analysis[6] contained 99.6% of material with mass number 104, and the infrared spectrum corresponded to that reported for benzocyclobutene.[4] The benzocyclobutane had b.p. 150.5°/754 mm. (lit.,[4] b.p. 150°/748 mm.). The other hydrocarbons had purities of at least 99.5% as shown by cooling curve determinations. The other reactants and the solvent were purified as described previously.[1] The reactions were followed by determining the rate of disappearance of benzoyl chloride.[3]

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(3) H. C. Brown, B. A. Bolto, and F. R. Jensen, J. Org. Chem., 23, 414 (1958).

(4) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, J. Am. Chem. Soc., 80, 2326 (1958).

(5) M. P. Cava and D. R. Napier, J. Am. Chem. Soc., 80, 2255 (1958).

(6) We are indebted to Mr. Seymour Meyerson of the Standard Oil Company (Ind.) for the mass spectra analysis.

Dimer of 10-Methylene-9-phenanthrone

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Although several highly substituted homologs of quinone methide (I) are known only one has been reported which contains its double bond terminally II.[1] In an attempt to obtain a com-

(1) E. Clar, Ber., 69, 1686 (1936) and references cited therein.
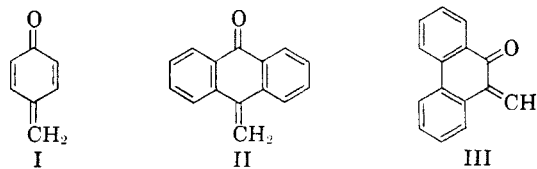
pound having the ortho-functionality of I for purposes of studying its chemistry, we have directed our efforts toward the synthesis of 10-methylene-9-phenanthrone (III). It might be expected to be stable both by analogy with II and by consideration of the relatively small energy difference between it and the fully aromatic phenanthrene system (10-methyl-9-phenanthrol). Naively, perhaps, one might expect it to have properties similar to those of a hyper-reactive aryl vinyl ketone. Molecular orbital calculations are not helpful in making predictions in cases of this sort because of the oxygen atom; a new parameter is required, the uncertainty in which would permit one to have but little faith in the result. At any rate, one would expect the molecule to have a large delocalization energy and a large free valence value at the terminal carbon atom.[2]

The condensation of 9-phenanthrol with formaldehyde and dimethylamine under very mild conditions afforded the expected Mannich base IV which proved to be very unstable. Loss of nitrogen occurred during attempts to purify it and the majority of such experiments gave, directly, a high-melting, nitrogen-free substance V. Treatment of a crude sample of IV with methyl iodide gave the methiodide which was also unstable and afforded, as before, the yellow compound. The reaction of 9-phenanthrol with formaldehyde afforded V directly indicating similar instability of the 10-methylol compound.
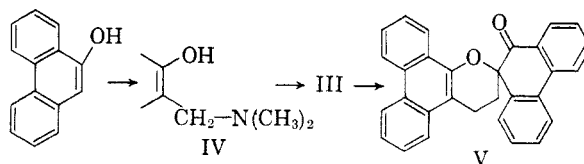
The dimeric quinone methide V absorbs at 5.94 μ in the infrared. Its ultraviolet spectrum exhibits high intensity maxima at 250, 275, 295, and 306 mμ with ε values ($\times 10^4$) 5.65, 2.74, 1.07, and 0.950, respectively. Low intensity absorption is at 340 and 360 mμ with ε ($\times 10^3$) 3.82 and 2.65, respectively. Reduction of V with lithium aluminum hydride afforded the corresponding carbinol. The latter substance absorbs in the infrared at 2.90 μ but the 5.94 band found in the spectrum of V is not present. The ultraviolet spectrum exhibits high intensity absorption at 256, 276, and 297

(2) Compare, for example, with p-quinodimethane, predicted by calculations[3] to be nearly as stable as benzene (stable as reflected by delocalization energy) but highly reactive. Experimental evidence bearing only on its reactivity is available.

mμ with ϵ ($\times$ 10^4) 6.35, 3.32, and 1.44 respectively. Low intensity absorption at 343 and 362 mμ has ϵ 1.92 $\times$ 10^3. This spectrum is almost identical with that of the dihydro dimer of 9,10-phenanthraquinodimethane (VI).[4] Extinction coefficients of low intensity absorption make it clear that only one of the phenanthrene nuclei retains the 9,10-double bond. On the basis of these data, and in consistency with characterized quinone methide dimers in other series,[5] the substance is formulated as V.

VI
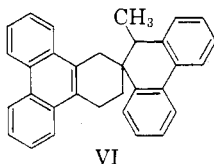
EXPERIMENTAL[6]

9-Phenanthrol. This substance was prepared by the procedure of Bachman[7] (22–40% yields) and also by application of the method developed by Hawthorne[8] for another phenol (26% yield).

10-Dimethylaminomethyl-9-phenanthrol (IV) *and its methiodide.* A solution of 5.9 g. of 9-phenanthrol in 20 ml. of ethanol was treated with 6.0 ml. of 25% aqueous dimethylamine and 2.3 ml. of 36% aqueous formaldehyde. After standing for 8 hr. at room temperature, the mixture was freed of solvent, without heating, at an aspirator. The solid residue (crude IV) could not be purified without decomposition and so was dissolved in ether and converted to the methiodide using 5.0 g. of methyl iodide. After 12 hr. at room temperature the salt was collected by filtration and washed with ether. The methiodide in this crude state (4.0 g. 35%) melted with decomposition at 225°. Attempts to purify it resulted in the formation of V.

Anal. Calcd. for $C_{18}H_{20}NI$: N, 3.55. Found: N, 3.92.

Dimer of 10-methylene-9-phenanthrone (V). A solution of 7.0 g. of 9-phenanthrol, 3.2 ml. of 38% aqueous formaldehyde and 6.2 ml. of 25% aqueous dimethylamine in 60 ml. of ethanol was heated under reflux for 2 hr. The mixture, containing suspended yellow solid, was filtered and the filtrate was concentrated to a small volume whereupon additional solid crystallized. The combined solids were recrystallized from benzene to give 3.2 g. (43%) of well formed yellow prisms of V, m.p. 251–252°.

Anal. Calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89. Found: C, 87.13; H, 4.82.

Spectral data are described in the discussion section.

A similar experiment in which the dimethylamine was replaced by a catalytic quantity of pyridine gave the same substance in 40% yield. Reactions conducted in the absence of base of any kind afforded the dimer in 36% yield.

Lithium aluminum hydride reduction of V. One gram of the dimer (V) was heated for 10 hr. under reflux in a suspension of a very large excess of lithium aluminum hydride in 50 ml. of tetrahydrofuran. Excess hydride was destroyed by

(3) C. A. Coulson, D. P. Craig, A. Maccoll, and A. Pullman, *Discussions Faraday Soc.*, **2**, 46 (1947).

(4) P. D. Gardner and H. Sarrafizadeh R., *J. Am. Chem. Soc.*, in press.

(5) See for example K. Hultzsch, *J. prakt. Chem.*, **159**, 180 (1941).

(6) Melting points are corrected. Infrared spectra were obtained in potassium bromide wafers. Ultraviolet spectra were of 95% ethanol solutions.

(7) W. E. Bachman, *J. Am. Chem. Soc.*, **56**, 1363 (1934).

(8) M. F. Hawthorne, *J. Org. Chem.*, **22**, 1001 (1957).

the cautious addition of water followed by dilute hydrochloric acid. Isolation of the product by ether extraction and the usual processing of the extract afforded 0.90 g. (90%) of the expected carbinol, m.p. 249–250°. This substance appeared as colorless prisms after several recrystallizations from ethyl acetate and had the same melting point. The carbonyl absorption found at 5.94 μ in V was lacking in the spectrum of the carbinol. Hydroxyl absorption appeared at 2.9 μ. The ultraviolet spectrum is described in the discussion.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35; mol. wt. 414. Found: C, 86.64; H, 5.15; mol. wt. 480 (cryoscopic in benzil).

Condensation of *o*-Benzoylbenzoyl Chloride with Ethyl Malonate

C. F. KOELSCH

The compound formed by action of *o*-benzoylbenzoyl chloride on ethoxymagnesiomalonic ester, formerly represented as ethyl 3-phenylphthalidylmalonate (II),[1] is actually the enol form of ethyl *o*-benzoylbenzoylmalonate (I).
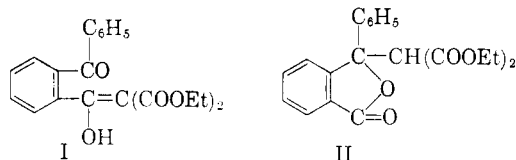
Structure I allows simple formulation of the conversion of the substance into ethyl 3-phenylindone-2-carboxylate (III) by aqueous base, whereas with structure II this change requires assumption of a strained intermediate (IV).
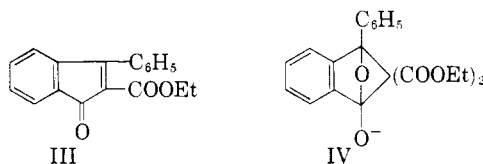
Spectral and chemical properties of the compound are in agreement with I. In chloroform the compound has a sharp absorption band at 3500 cm.$^{-1}$ (enolic OH), a broad band with maxima at 1600, 1650, 1725 and 1770 cm.$^{-1}$ (C=O and C=C—O), and a broad band at 1260–1300 cm.$^{-1}$ (ester). It gives a deep red-brown color with ferric chloride, and it is soluble in cold 1% sodium hydroxide. Acidification of this solution, if it has not been

(1) W. L. Yost and A. Burger, *J. Org. Chem.*, **15**, 1113 (1950).