

of 3% sodium carbonate followed by ether extraction, drying over magnesium sulfate, and distillation of the benzaldehyde at reduced pressure under nitrogen.

**Analysis.** In all of the experiments infrared absorption spectra were used to analyze for the presence of deuterated and undeuterated products. Most of the spectra were taken with a calcium fluoride prism in a Perkin-Elmer model 112 Spectrometer. The benzaldehyde and benzaldehyde-*d*<sub>1</sub> were run between sodium chloride plates or in carbon tetrachloride solution; water and deuterium oxide were run in thin calcium fluoride cells<sup>3</sup>; crystals of I and I-*d*<sub>1</sub> were run using the model 85 microscope attachment to the 112. Spectra of I and I-*d*<sub>1</sub> (recrystallized from water and dried under vacuum) were also run in potassium bromide disks on a Baird Model A and are shown in Fig. 1.

**Instability of the complex under vacuum.** At 60° large amounts of benzaldehyde, sulfur dioxide, and water were vacuum distilled from I in a period of several days. These were identified by mass spectral analysis with a Consolidated ElectroDynamics model 21-103C mass spectrometer. Similarly, at 25° more than 7% of the benzaldehyde was vacuum distilled from a dry sample of I in 5 days, and was analyzed by its ultraviolet spectrum with a Cary model 11 spectrophotometer. A mixture of 1.86471 g. of I (freshly washed with ether and dried) and 1.48630 g. of water was placed in one arm of a U-tube, which was outgassed and evacuated. The water was vacuum distilled for 2 hr. into the other arm from a maximum temperature of 25°. After dilution to 5.0 ml. the water had a pH of 3.1 compared to an initial pH of 6.0 and the ultraviolet spectrum (measured in a 0.0107 cm. calcium fluoride cell) showed a total of 0.0016 g. of free benzaldehyde. When diluted again by 1/50 (measured in a 1.00 cm. cell) it showed a total of 0.0021 g. of free benzaldehyde. The difference in free aldehyde with concentration can probably be attributed to some benzaldehyde-sulfurous acid complex formation. Thompson and Cromwell, using comparable amounts of water and complex, found that after vacuum distillation the water had increased in total weight between 0.00213 and 0.00756 g. and attributed this to an exchange reaction.

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### Unsaturated Four-Membered Ring Compounds. III. The Reactivity of Benzocyclobutene Toward Electrophilic Substitution

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In view of the possible effects of compression of the bond angles in benzene on the rate of substitution, it was of interest to determine the absolute reactivity of benzocyclobutene towards electrophilic substitution. Although the bond angles and interatomic distances have not been determined for benzocyclobutene, it is to be expected that the bond angles to the cycloalkane ring are appreciably smaller than the normal bond angle of 120°.

The electrophilic reaction selected was the aluminum chloride-catalyzed benzoylation reaction using

ethylene chloride as solvent. Since substitution of a methyl group in benzene increases the rate of reaction by a factor of 132 (Table I), the benzoylation reaction is very sensitive to substitution effects. Any net effect of the fused ring should give a marked change in the rate of benzoylation. The aromatic compounds selected as standards for reference purposes were *o*-xylene, indane, and tetralin.

For this reaction, individual experiments follow second order kinetics according to expression 1.

$$\text{rate} = k_2(\text{C}_6\text{H}_5\text{COCl}\cdot\text{AlCl}_3)(\text{ArH}) \quad (1)$$

However, the value of  $k_2$  depends on the initial concentration of the complex.<sup>1</sup> With benzocyclobutene, the reactions apparently followed second-order kinetics to about 50% reaction and then the rates of reaction fell off rapidly. After ten to fifteen minutes, the reaction mixtures began to darken and turned progressively darker with time. The cause of this behavior was not investigated. The reactions of the other compounds followed second-order kinetics to at least 90% reaction, and the reaction mixtures stayed colorless for at least twenty-four hours.

The results are summarized in Table I.<sup>2</sup> The three compounds with the fused cycloalkane rings react two to three times faster than *o*-xylene. However, benzocyclobutene reacts only slightly faster than indane and tetralin. Since there is no rate acceleration, any decreased stability of benzocyclobutene by the bond compressions must be countered by an equal degree of instability of the transition state.

TABLE I

RATES OF THE ALUMINUM CHLORIDE-CATALYZED BENZOYLATION OF SELECTED BENZENE DERIVATIVES IN ETHYLENE CHLORIDE SOLUTION AT 25°<sup>a</sup>

Aromatic	$k_2 \times 10^3$ (l.m. <sup>-1</sup> sec. <sup>-1</sup> )	Relative Rate <sup>b</sup>
Benzene	0.00855	1/1700
Toluene	1.13	1/13
<i>o</i> -Xylene	15.1	1
Benzocyclobutene	41 <sup>c</sup>	2.8
Indane	28.6	1.9
Tetralin	33.6	2.3

<sup>a</sup> For benzene and toluene, initial concentrations 0.222M; for the other compounds, 0.200M. <sup>b</sup> The small effect of initial concentration on rate is ignored in calculating the relative rates. <sup>c</sup> Less than 50% reaction. The calculated rate constants for benzocyclobutene decrease sharply after 50% reaction.

There are at least two explanations which could account for the "normal" reactivity of benzocyclo-

(1) F. R. Jensen, *J. Am. Chem. Soc.*, **79**, 1226 (1957).

(2) When no unusual reactivities were observed, the decision was made not to determine the manner in which the benzoyl chloride is consumed. The reported rate constants probably represent the upper limit for aromatic substitution.

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 benzocyclobutene 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.<sup>3</sup> The increased reactivity may be due to the presence of more favorable configurations for hyperconjugation<sup>4</sup> with the alkyl groups in the transition states for substitution of indane and tetralin than for *o*-xylene.

#### EXPERIMENTAL

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.<sup>5</sup> 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<sup>6</sup> contained 99.6% of material with mass number 104, and the infrared spectrum corresponded to that reported for benzocyclobutene.<sup>4</sup> The benzocyclobutene had b.p. 150.5°/754 mm. (lit.,<sup>4</sup> 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.<sup>1</sup> The reactions were followed by determining the rate of disappearance of benzoyl chloride.<sup>3</sup>

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

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(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.

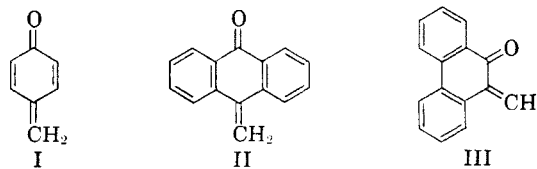
### Dimer of 10-Methylene-9-phenanthrone

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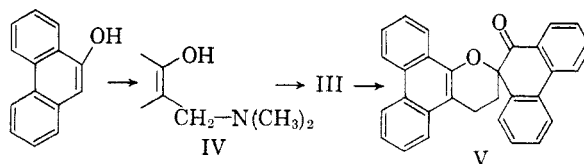
Although several highly substituted homologs of quinone methide (I) are known only one has been reported which contains its double bond terminally II.<sup>1</sup> In an attempt to obtain a com-

(1) F. 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.<sup>2</sup>

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  $\mu$  in the infrared. Its ultraviolet spectrum exhibits high intensity maxima at 250, 275, 295, and 306  $m\mu$  with  $\epsilon$  values ( $\times 10^4$ ) 5.65, 2.74, 1.07, and 0.950, respectively. Low intensity absorption is at 340 and 360  $m\mu$  with  $\epsilon$  ( $\times 10^3$ ) 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  $\mu$  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<sup>3</sup> 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.