

had prepared these compounds by a laborious seven step synthesis starting from the corresponding xylene isomer. This route was obviously not satisfactory for relatively large scale preparation of these materials.

When the commercially available divinylbenzene mixture<sup>2</sup> (40% *m*- and *p*-divinylbenzenes) is brominated in chloroform solution, 1,4-bis(1,2-dibromoethyl)benzene separates on cooling. Recrystallization from chloroform yields the pure material. The bromination residue now contains 1,3-bis(1,2-dibromoethyl)benzene along with considerable quantities of the dibromodiethylbenzenes from the ethylstyrenes in the starting material. A molecular distillation readily separates the dibromodiethylbenzenes from the tetrabromodiethylbenzene. The latter fraction on crystallization from ethanol yields pure 1,3-bis(1,2-dibromoethyl)benzene. Treatment with four moles of potassium *t*-butoxide in *t*-butanol readily converts the tetrabromodiethylbenzenes to the respective diethynylbenzenes.

#### EXPERIMENTAL

**Bromination of mixed divinylbenzenes.** Bromine (1300 g., 8.13 moles) was added over 2 hr. with stirring to a cooled solution of 750 g. mixed divinylbenzene (40% = 2.3 moles *m*- and *p*-divinylbenzene) in 1200 ml. of chloroform. The reaction mixture was then cooled to 5° and a voluminous precipitate settled out which was separated by filtration. Recrystallization from chloroform yielded 264 g. (0.59 mole) of 1,4-bis(1,2-dibromoethyl)benzene, m.p. 155–157° (lit.<sup>1</sup> m.p. 157°). The two filtrates were combined and the chloroform removed on a rotating evaporator at 100° (3 mm.). The residue was then fractionated in a molecular still. Distillation at 50° (40–70  $\mu$ ) and then at 80° (20–50  $\mu$ ) separated most of the dibromodiethylbenzenes. The residue which was a viscous sirup was distilled at 150° (12–30  $\mu$ ). The distillate crystallized when triturated with cold alcohol and after recrystallization from alcohol yielded 420 g. (0.93 mole, combined yield of 66%), 1,3-bis(1,2-dibromoethyl)benzene, m.p. 65–66.5° (lit.<sup>1</sup> m.p. 64°).

***p*-Diethynylbenzene.** To a solution of 18 g. (0.46 mole) of potassium in 1 l. of *t*-butanol at the temperature of reflux was added 50 g. (0.11 mole) of 1,4-bis(1,2-dibromoethyl)benzene. After 1 hr. the reaction mixture was made up to 4 l. with ice water and the pale yellow solid was removed by filtration. There was isolated 9.8 g. (0.078 mole, 71% yield) of *p*-diethynylbenzene, m.p. 95° (lit.<sup>1</sup> m.p. 95°). Sublimation at 90–100° (2 mm.) gave a colorless solid m.p. 96.5°.

***m*-Diethynylbenzene** was prepared in an identical fashion and in comparable yield from 1,3-bis(1,2-dibromoethyl)benzene. After flooding with water the product was isolated by ether extraction and distillation to yield *m*-diethynylbenzene, b.p. 78° (14 mm.),  $n_D^{20}$  1.5825 (lit.<sup>1</sup> b.p. 78° (15 mm.)  $n_D^{18}$  1.5841).

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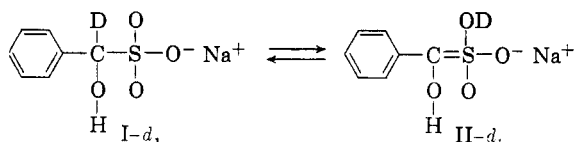
(2) Purchased from Monomer-Polymer Laboratories, 5000 Langdon Street, P.O. Box 9522, Philadelphia 24, Pa.

## Absence of Exchange by the "Aldehydic" Hydrogen of Benzaldehyde Sodium Bisulfite

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In 1939 Thompson and Cromwell reported that in contrast to the lack of hydrogen-deuterium exchange by aldehydes, benzaldehyde-*d*<sub>1</sub> sodium bisulfite (I-*d*<sub>1</sub>) exchanged up to 76% with conductivity water in a period of seventeen days.<sup>1</sup> They suggested that this could be evidence for the enolization of the bisulfite complex. Such an enol form (II-*d*<sub>1</sub>) would be of particular interest since it postulates an expanded valence shell of ten electrons for the sulfur atom in the complex.



We desired to prepare some deuterated benzaldehydes by utilizing the reverse of this reported exchange reaction. We first attempted to prepare benzaldehyde-*d*<sub>1</sub> by placing benzaldehyde sodium bisulfite (I) in excess deuterium oxide for a long period of time, as indicated in experiment 1, Table I. The infrared spectrum of the aldehyde showed that no exchange had occurred.<sup>2</sup> Similar experiments (2, 4, and 5 through 9) were made using different methods of separating the products, and of determining the extent of exchange by infrared analysis. These experiments were conducted under various conditions such as exposure to near ultraviolet light or in the presence of added substances which might somehow have acted as catalysts in the original work. Experiment 3 is essentially a duplication of one experiment of the reported exchange reaction, using benzaldehyde prepared from lithium aluminum deuteride.<sup>2</sup> In every experiment no hydrogen-deuterium exchange was found on the "carbonyl" carbon of I or I-*d*<sub>1</sub>. Thus, there is no evidence for the existence of an enol form, such as II-*d*<sub>1</sub>.

The attempted exchange experiments are summarized in Table I. The infrared spectra of I and I-*d*<sub>1</sub> are shown in Fig. 1. The deuterated complex is readily distinguished from I by the absence of bands at 1411 and 845 cm.<sup>-1</sup> and the presence of bands at 1347, 969, 945, and 766 cm.<sup>-1</sup> 3.

(1) A. F. Thompson, Jr., and N. H. Cromwell, *J. Am. Chem. Soc.*, **61**, 1374 (1939).

(2) K. B. Wiberg, *J. Am. Chem. Soc.*, **76**, 5371 (1954).

(3) Deutero-benzaldehyde is easily distinguished from benzaldehyde by the large shift in the C—H stretching frequency (*cf.* ref. 2), and also shows the absence of bands at approximately 1387, 826, and 714 cm.<sup>-1</sup> and the presence of bands at approximately 1222, 791, and 733 cm.<sup>-1</sup>.

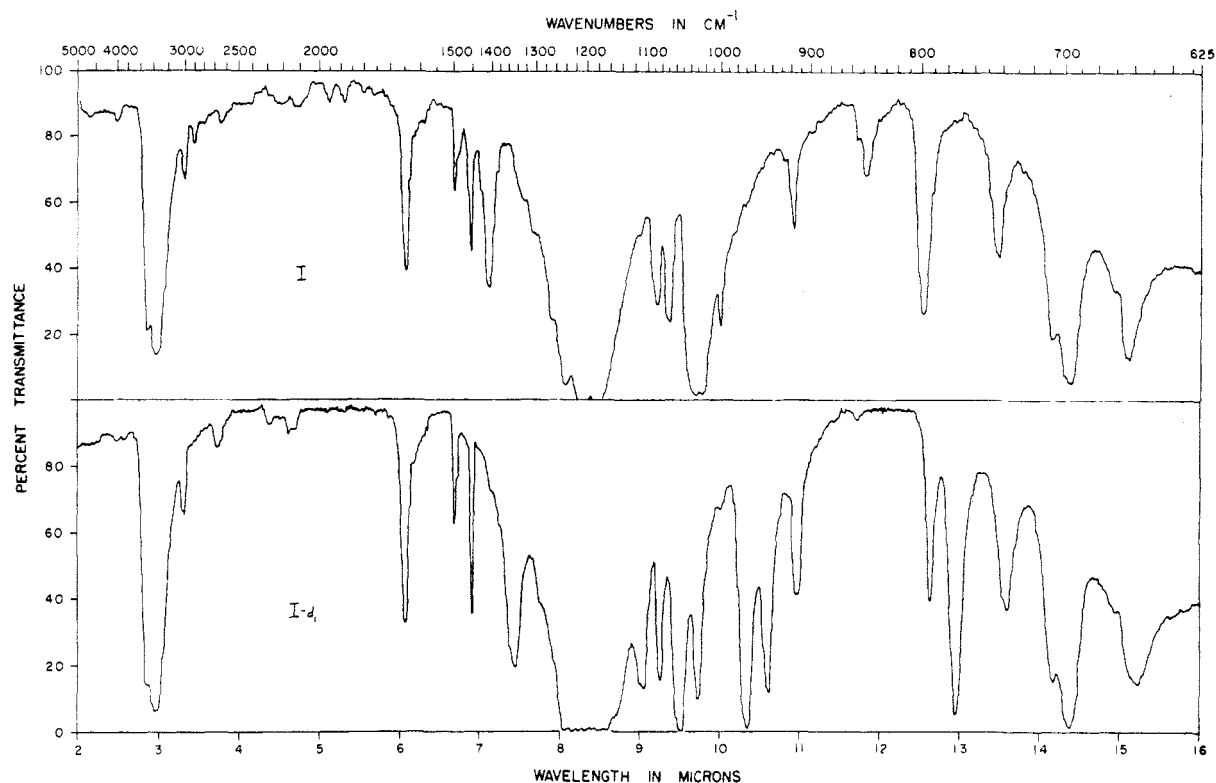


Fig. 1. Infrared spectra of benzaldehyde sodium bisulfite (I) and benzaldehyde- $d_1$  sodium bisulfite (I- $d_1$ ) in potassium bromide disks

TABLE I  
ATTEMPTED PROTIUM EXCHANGE IN BENZALDEHYDE SODIUM BISULFITE ADDITION COMPOUND (I)

Expt.	Reactants	Mole Ratio of Reactants	Period, Days	Light	Method of Separation	Products Analyzed
<sup>a</sup>	I- $d_1$ /H <sub>2</sub> O	1/11.1	17	—	Vac. distln.	H <sub>2</sub> O
1	I/D <sub>2</sub> O	1/31.5	28	Dark	Na <sub>2</sub> CO <sub>3</sub> rxn.	BzH
2	I/D <sub>2</sub> O	1/35	26	Dark	Vac. distln.	BzH
3	I- $d_1$ /H <sub>2</sub> O	1/11.7	34	Dark	Vac. distln.	H <sub>2</sub> O
4	I- $d_1$ /H <sub>2</sub> O	1/11.1	2	Near UV	Evaporation	I
5	I/D <sub>2</sub> O	1/31.5	45	Rm. light	Evaporation	I
6	(Same as 5; 1 drop 6N HCl added to 2 ml. of solution)					
7	(Same as 5; 1 drop 6N NaOH added to 2 ml. of solution)					
8	(Same as 5; ca. 100 mg. 5% Pd-BaSO <sub>4</sub> added to 2 ml. of solution)					
9	(Same as 5; ca. 50 mg. quinoline-sulfur added to 2 ml. of solution)					

<sup>a</sup> Ref. 1.

The increases in the density of water observed in the work of Thompson and Cromwell<sup>1</sup> could not have been due to an exchange reaction. A possible explanation of their results may be found in our observation that benzaldehyde and sulfur dioxide vapors appear to exist in equilibrium with the benzaldehyde sodium bisulfite complex. In the vacuum distillation of water from a water-complex mixture at room temperature, small but significant amounts of benzaldehyde and sulfur dioxide are carried over into the water, which would increase its density.

#### EXPERIMENTAL

Benzaldehyde sodium bisulfite (I) was prepared by mixing 40% aqueous sodium bisulfite with a slight excess of freshly

distilled benzaldehyde, allowing the complex to separate on standing, filtering it, washing it three times with ether and drying over phosphorus pentoxide at 1  $\mu$  for 1.5 hr. Benzaldehyde- $d_1$  sodium bisulfite (I- $d_1$ ) was prepared by Wiberg's method.<sup>2</sup> The 5% palladium-barium sulfate and the quinoline-sulfur were prepared as described in *Organic Reactions*.<sup>4</sup>

*Reaction conditions and separation of products.* All experiments were carried out in evacuated, out-gassed, sealed-off tubes.<sup>1</sup> These were allowed to stand at room temperature, in the dark or in room light as indicated in Table I, except for experiment 5 in which exposure was made with a water cooled AH-6 mercury arc (glass envelope) for 29 hr. using Corning glass filter No. 5840 followed by 20 hr. without a filter. Separation by vacuum distillation was made at 25° for water and between 60° and 115° for benzaldehyde. In experiments 1 and 3 the complex was treated with an excess

(4) E. Mosettig and R. Mazingo, *Org. Reactions*, IV, 386-9 (1948).

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- $d_1$  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- $d_1$  were run using the model 85 microscope attachment to the 112. Spectra of I and I- $d_1$  (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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(5) R. C. Gore, R. B. Barnes, and E. Petersen, *Anal. Chem.*, **21**, 382 (1949).

### 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.