

**Hexabutylbenzene.**—To a stirred catalyst solution, maintained at about 86°, was added 41.4 g. (0.3 mole) of 5-decyne<sup>12</sup> in 60 cc. of dry *n*-heptane over a period of about 2 hours. The stirred solution was refluxed gently overnight. After cooling, the reaction solution was centrifuged and then the *n*-heptane solvent was distilled, leaving a brown liquid which solidified on cooling. No 5-decyne was recovered from the distillation. The brown solid obtained weighed 38.3 g. and appeared to be wet with an oil. After several recrystallizations from 95% alcohol it was possible to concentrate the oil (it was insoluble in the alcohol) by decanting the hot alcohol solution away from it. This oil, as yet unidentified, was distilled at 100–112° (0.7 mm.),  $n_{D}^{21.5}$  1.4670, and amounted to 2.9 g. The recrystallized hexabutylbenzene weighed 21.6 g. (52.2% yield) and had a melting point of 56.5–57.5°.

*Anal.*<sup>27</sup> Calcd. for C<sub>30</sub>H<sub>54</sub>: C, 86.88; H, 13.12. Found: C, 86.90; H, 13.07.

(27) The analysis was performed by Huffman Microanalytical Laboratories, Wheatridge, Colo.

The molecular weight was determined by the Beckmann method and found to be 405 while that calculated for hexabutylbenzene is 414.8. The infrared spectrum (determined in KBr disk) of hexabutylbenzene was compared with that of hexaethylbenzene in the region between 1650 and 1450 cm.<sup>-1</sup>, characteristic of the skeletal stretching modes of carbon-carbon bonds in aromatic compounds,<sup>28</sup> and found to match very closely. Thus, hexabutylbenzene had bands at 1638 (w, broad), 1500(m), 1472(s) and 1455(m) cm.<sup>-1</sup> while hexaethylbenzene had bands at 1640(w, broad), 1503(m), 1475(m-s) and 1461(s) cm.<sup>-1</sup>. The band at about 1638 cm.<sup>-1</sup> (w, broad) was also present in the spectrum of hexamethylbenzene.

The recovered catalyst weighed 7.5 g. after being dried in a vacuum desiccator. The difference between this weight and that of the expected weight of spent catalyst<sup>16</sup> was 1.9 g. This difference could be due either to high polymer formation or else to incomplete washing of the recovered catalyst.

(28) L. J. Bellamy, ref. 21, p. 69.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY, AMES, IOWA]

## The Addition of Deuterium Bromide to 1,3-Cyclohexadiene

BY GEORGE S. HAMMOND<sup>1</sup> AND JOHN WARKENTIN

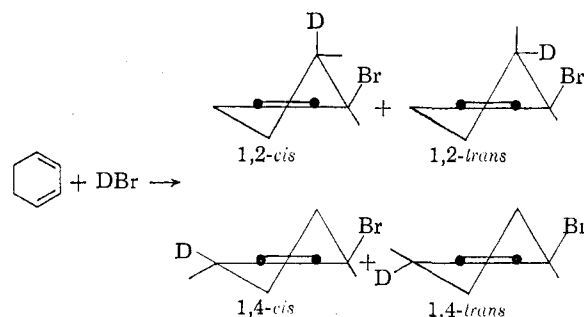
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The addition of deuterium bromide to 1,3-cyclohexadiene in pentane solution gives a mixture of products which probably include both *cis* and *trans* isomers of the 1,2- and 1,4-adducts; *cis* products predominate over *trans* products and the total 1,4-adduct exceeds the total 1,2-adduct by a small amount. Although the results are not compelling, they suggest that addition occurs by a 1,4-*cis* process and a 1,2-*trans* process and that some jumbling of products occurs by stereospecific allylic rearrangements.

The polar addition of hydrogen bromide to 1,2-dimethylcyclohexene<sup>2</sup> and of hydrogen chloride to 1,2-dimethylcyclopentene<sup>3</sup> have been shown to proceed by a stereospecific, *trans* process. The present study was undertaken to determine the steric course of addition to a conjugated diene. The substrate chosen for the study was 1,3-cyclohexadiene and the addend was deuterium bromide.

### Results and Discussion

Four addition products can conceivably be formed in the addition reaction as is shown by the equation

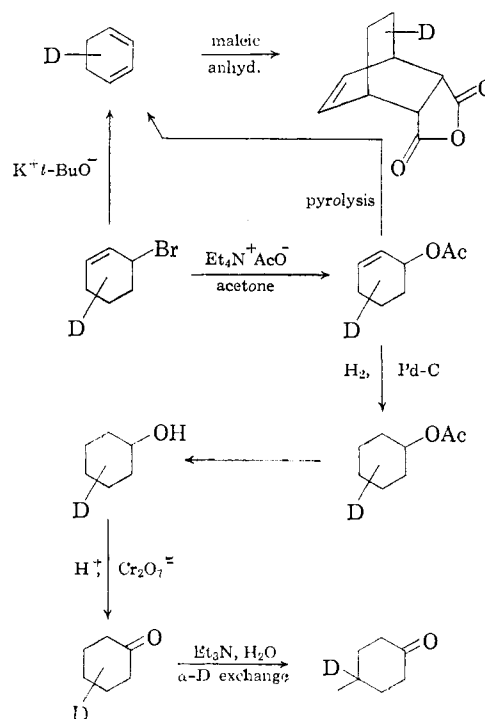


The deuteriobromocyclohexene was partially analyzed by the scheme

(1) Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, Calif.

(2) G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **76**, 4121 (1954).

(3) G. S. Hammond and C. H. Collins, *ibid.*, **83**, in press (1961).



Results of the degradative experiments are gathered in Table I and show that the reaction must have taken more than one course. Both elimination sequences remove 12.5% of the deuterium. This implies that the original product contained only 12.5% of the 1,2-*trans*-adduct. The

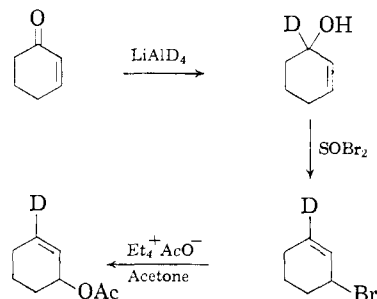
argument supporting this view is somewhat tortuous since it is not *a priori* certain that the elimination reactions do not involve some 1,4-reactions. If this possibility is not considered, the results are consistent since 1,2-elimination by the  $E_2$  mechanism is known to be *trans*-stereospecific<sup>4</sup> and

TABLE I  
DEUTERIUM CONTENT OF DEGRADATION PRODUCTS

Compound	Gram atom of deuterium per mole
3-Bromocyclohexene	0.721 ± 0.002
3-Acetoxy-cyclohexene	.716 ± .005
Bicyclo(2,2,2)- $\Delta^5$ -octene-2,3-dicarboxylic anhydride	.632 ± .004 <sup>a</sup>
Cyclohexanone (after exchange)	.62 ± .01 <sup>b</sup>
Cyclohexanone (after exchange)	.390 ± .003

<sup>a</sup> From product of potassium *t*-butoxide elimination. <sup>b</sup> From product of acetate displacement and pyrolytic elimination.

acetate pyrolysis is known to be *cis*-stereospecific.<sup>4</sup> Since inversion should occur in the acetate displacement, the two sequences should give the same result if no 1,4-reactions are involved. It was possible to show that the acetate displacement does not involve any  $SN_2'$  reaction by means of the reaction sequence



The position of the deuterium throughout the sequence was followed by infrared measurements. The reaction of 3-cyclohexenol-3-*d* with thionyl bromide was carried out under conditions designed to give an  $SN_1'$  reaction.<sup>5</sup> The strongest C-D stretching frequency in the alcohol was found at 2128  $cm^{-1}$  and that in the bromide appeared at 2245  $cm^{-1}$ . Reaction of the bromide with tetraethylammonium acetate gave a product having a strong absorption maximum at 2245  $cm^{-1}$  and no absorption near 2130  $cm^{-1}$ . Obviously no migration of deuterium from the vinylic to an allylic position occurred during the nucleophilic substitution. Since deuterium that is *trans* to bromine in cyclohexenyl bromide becomes *cis* to acetoxy in the acetate, the coincidence of results of the two elimination reactions implies that both involve exclusively 1,2-eliminations. There is, of course, the possibility that both processes involve just the same mixture of 1,2- and 1,4-elimination. The possibility of such a coincidence seems remote.

The total amount of deuterium in 2-positions was determined by base-catalyzed exchange between cyclohexanone, derived from cyclohexenyl acetate and excess, normal water. The results indicate

(4) See D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 5.

(5) F. C. Caserio, G. E. Dennis, R. H. DeWolfe and W. G. Young, *J. Am. Chem. Soc.*, **77**, 4182 (1955); W. G. Young, F. C. Caserio and D. Brandon, *Science*, **117**, 473 (1953).

that 46% of the total deuterium is alpha to the carbonyl group. The distribution of deuterium in the cyclohexenyl bromide is: 12.5%, 1,2-*trans*; 33.5%, 1,2-*cis*; and 54%, 1,4-*cis* plus 1,4-*trans*.

Two results stand out. First, insufficient allylic reshuffling has occurred to equilibrate completely deuterium among 1,2- and 1,4-positions. Second, there is far less than the statistical amount of *trans*-1,2-adduct. These results compel the conclusion that the addition does not involve the free cyclohexenyl cation as an intermediate and strongly suggest that at least two more concerted processes are involved. Since we have shown that 1,2-addition to monoolefins shows a *trans*-stereospecificity,<sup>2,3</sup> we are reluctant to attribute the large amount of 1,2-*cis*-adduct to 1,2-*cis*-addition. It seems to us more probable that the compound is produced by 1,4-*cis*-addition followed by allylic rearrangement (of bromine) to give the 1,2-*cis*-product. That *cis*  $\rightarrow$  *cis* rearrangement might occur at a rate faster than that of *cis*  $\rightarrow$  *trans* rearrangements is reasonable in view of the carefully documented report by Goering, Nevitt and Silversmith<sup>6</sup> of the racemization of *cis*-5-methyl-2-cyclohexenyl chloride by "across-the-face" allylic rearrangement.

If we adopt the view that the initial addition involves 1,2-*trans* and 1,4-*cis* reactions, we can use the ratio of 1,2-*cis* to 1,2-*trans* to estimate a minimum value for the relative rates of these two processes. The data indicate that *cis* addition is at least 2.7 times as fast as *trans* addition. The actual difference is probably slightly larger since the data indicate that 1,2  $\rightleftharpoons$  1,4 equilibration is not quite complete. Furthermore, any *cis*  $\rightleftharpoons$  *trans* isomerization would tend to decrease the ratio even further.<sup>7</sup>

The hypothesis also demands that the ratio 1,4-*cis*/1,4-*trans* should be slightly higher than the ratio 1,2-*cis*/1,2-*trans* since 1,4-*trans* and 1,2-*cis* are believed to be secondary products. We were unable to carry through a degradative scheme acceptable for establishing this ratio by chemical means. However, study of the C-D stretching frequencies in various products, especially cyclohexyl acetate produced by hydrogenation of cyclohexenyl acetate, indicated that the *cis* isomer was certainly the predominant 1,4-adduct. Corey and co-workers<sup>8</sup> recently introduced characterization of C-D stretching frequencies as a tool for determination of the stereochemistry of deuteriocyclohexanes, which also bear other, configuration-determining substituents. In the spectra of each set of epimers studied they found that the highest frequency C-D stretch of the isomer having equatorial C-D occurred at higher frequency than the highest frequency C-D stretch of the axial isomer. A simple monocyclic deuteriocyclohexane such as one of the 1-deuterio-4-phenylcyclohexanes has only a single

(6) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *J. Am. Chem. Soc.*, **77**, 5026 (1955).

(7) The discussion has tacitly ignored secondary isotope effects on rates and equilibria. For example, we assume that the rate 1,2-*trans*  $\rightarrow$  1,4-*trans* is the same as the rate 1,4-*cis*  $\rightarrow$  1,2-*cis*. While the assumption is surely not precisely correct, it is doubtless adequate for the purposes of our present discussion.

(8) E. J. Corey, M. G. Howell, A. Boston, R. L. Young and R. A. Sneed, *ibid.*, **72**, 5036 (1950).

C-D frequency. More complex C-D spectra were obtained for deuterated steroid derivatives. All of the frequencies observed in the 2050-2250  $\text{cm}^{-1}$  region of the spectra of our deuterio compounds are listed in Table II. Some weak bands were not assigned.

TABLE II  
ASSIGNMENT OF C-D STRETCHING FREQUENCIES

Compound	Bands, $\text{cm}^{-1a}$	Assignment
Deuterio-3-bromocyclohexene <sup>b</sup>	2217(w)	Not assigned
	2179(s)	4-Equatorial
	2163(s)	4-Axial
	2136(w)	6-Pseudoequat.
	2127(m)	6-Pseudoaxial
	2103(w)	Not assigned
Deuterio-3-acetoxycyclohexene <sup>b</sup>	2250(w)	Not assigned
	2188(m)	4-Equatorial
	2180(m)	4-Axial
	2154(s)	6-Pseudoequat.
	2126(m)	6-Pseudoaxial
Cyclohexyl acetate <sup>b</sup>	2169(s)	4-Equat., 2-equat.
	2155(sh)	4-Axial
	2147(s)	2-Axial
	2120(w)	Not assigned
3-Deuterio-3-hydroxycyclohexene	2181(m)	Not assigned
	2154(m)	Allylic, pseudoequat.
	2128(s)	Allylic, pseudoaxial
	2099(m)	Not assigned
1-Deuterio-3-bromocyclohexene	2245(s)	Vinyl
	2216(m)	Not assigned
1-Deuterio-3-cyclohexenyl acetate	2245(s)	Vinyl
	2181(m)	Not assigned
<i>trans</i> -2-Deuteriocyclohexyl bromide	2178(s)	Equatorial
	2143(w)	Axial
	2124(m)	Not assigned
<i>cis</i> -2-Deuteriocyclohexyl acetate	2174(s)	Equatorial
	2145(s)	Axial
	2122(sh)	Not assigned

<sup>a</sup> Bands are characterized as weak (w), medium (m), strong (s) and shoulder (sh). <sup>b</sup> Prepared from adduct of DBr to cyclohexadiene.

We can estimate the positions expected for C-D stretching frequencies in the spectra of mixed 2- and 4-deuteriocyclohexyl acetates. First, the spectrum of *trans*-4-deuteriophenylcyclohexane<sup>8</sup> has a strong band at 2169  $\text{cm}^{-1}$  and that of the *cis* isomer has a similar strong band at 2158  $\text{cm}^{-1}$ . These are surely characteristic of equatorial and axial C-D, respectively, in cyclohexanes containing remote substituents. It is by no means certain that 2-substituted compounds should have the same spectral characteristics. Therefore, 2-deuteriocyclohexyl bromide was prepared by addition of deuterium bromide to cyclohexene in pentane solution. Radical scavengers, chloranil and 2,6-di-*t*-butyl-*p*-cresol were added to suppress addition by the radical mechanism; so it is presumed that the product was the *trans* isomer.<sup>9</sup> The spectrum of the product had a strong band at 2178  $\text{cm}^{-1}$ , a weak band at 2143  $\text{cm}^{-1}$ , and a band of medium intensity at 2124  $\text{cm}^{-1}$ . The high frequency

(9) It is reasoned that cyclohexene, which can only give a secondary carbonium ion, will be less likely to undergo non-stereospecific, polar addition than 1,2-dimethylcyclohexene, which is known to give *trans*-addition.<sup>7</sup>

band should doubtless be assigned to the equatorial C-D of the *trans*-bromide. Assignment of the other two absorptions is uncertain. One should be attributed to the less stable conformer of the *trans*-bromide in which deuterium and bromine are both axial. The third may be due to a small amount of *cis*-bromide, or it may be due to some motion in which C-D stretching is coupled with another mode. If the latter is correct, the 2143  $\text{cm}^{-1}$  band is probably characteristic of axial C-D. A low yield of cyclohexyl acetate was obtained by treatment of *trans*-2-deuteriocyclohexyl bromide with tetramethylammonium acetate. Presumably the reaction involved a Walden inversion, so the product should be predominantly *cis*-acetate. The product showed fairly strong absorption at 2174 and 2145  $\text{cm}^{-1}$ , and there was a suggestion of a shoulder near 2125  $\text{cm}^{-1}$ . However, the 2145 absorption was stronger than that at 2174. This is consistent with the view that 2174 absorption is due to equatorial C-D and that absorption at 2145  $\text{cm}^{-1}$  is characteristic of axial C-D. The fact that the two bands are more nearly equal in intensity than are the two bands in the spectrum of the bromide implies that the bromide is more nearly conformationally pure than the acetate.

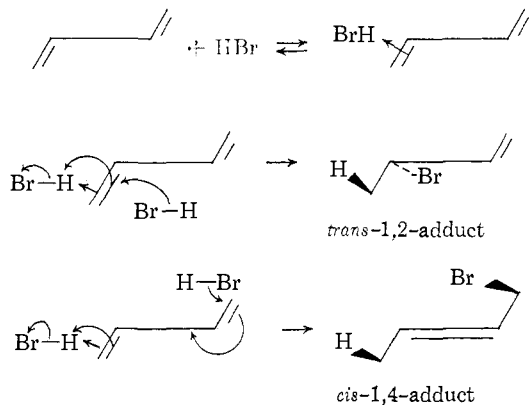
The spectrum of deuteriocyclohexyl acetate obtained from deuteriocyclohexenyl bromide has strong maxima at 2169 and 2147  $\text{cm}^{-1}$ , a shoulder at 2155  $\text{cm}^{-1}$ , and a low-intensity maximum at 2120  $\text{cm}^{-1}$ . The 2169 band indicates that the sample must be rich in *trans*-4-deuteriocyclohexyl acetate; although the band, which is broad on the high frequency side, probably has some contribution from absorption by the axial conformer of the *cis*-2-deuterioester (expected near 2174  $\text{cm}^{-1}$ ). Axial 4-D should absorb near 2155  $\text{cm}^{-1}$ . The absorption at 2147  $\text{cm}^{-1}$  must be due to 2-axial deuterium. Qualitative comparison of the intensities of the various bands leads to the conclusion that the sample must contain a preponderance of species containing equatorial C-D. It also appears that the amount of 4-axial C-D is rather small. As a result we conclude that a major fraction of the 54% deuterium shown by chemical analysis to be in the 4-position is *trans* with respect to the acetoxy group. This in turn implies that the 6-deuterio-3-bromocyclohexene was predominantly *cis*.

Other assignments listed in Table II are based upon analogy. Since groups in the allylic positions in a cyclohexene derivative are pseudoaxial and pseudoequatorial, we cannot expect exact analogs to the absorption characteristics of their saturated analogs. We have assumed that absorption by pseudoequatorial C-D will occur at higher frequency than that of pseudoaxial C-D.

**Mechanism.**—The hypothesis that *cis*-addition of deuterium bromide occurs by preliminary 1,4-addition leads to interesting mechanistic speculations. Young, Hall and Winstein<sup>10</sup> showed that the reaction of bromine with cyclopentadiene gives *cis*-1,4-adduct as a major product. They pointed out that this result could be explained by a variety

(10) W. G. Young, H. K. Hall and S. Winstein, *J. Am. Chem. Soc.*, **78**, 4338 (1956).

of mechanisms. However, an inviting possibility is the opening of a bromonium ion by SN2' attack by bromide since the SN2' reaction is *cis*-stereospecific.<sup>11</sup> This type of reaction would be a logical extension of the mechanism commonly accepted for *trans*-1,2-addition.<sup>12</sup> It is interesting to note that a similar extension of the mechanisms previously proposed<sup>2,3</sup> for *trans*-1,2-addition of hydrogen halides to alkenes can be extended in a similar manner to include *cis*-1,4-addition.



### Experimental

**Materials.**—Acetone was dried over anhydrous potassium carbonate for several days, decanted onto anhydrous calcium sulfate, and distilled through a 6-in. Vigreux column; b.p. 55°. Acetyl bromide (Eastman Kodak Co., White Label Grade) was used without further purification. Bromobenzene (Allied Chemical and Dye Corp.) was washed with 10% aqueous sodium hydroxide and with water. It was dried over calcium chloride and distilled through an Oldershaw column operating at an efficiency of 17 theoretical plates; b.p. 154° at 749 mm. 3-Bromocyclohexene, derived from the reaction of cyclohexene with N-bromosuccinimide, was distilled through a spinning band column. The fraction boiling at 54–59° at 13–15 mm. was redistilled in a Claisen flask to remove the yellow color; b.p. 58° at 14 mm.,  $n_D^{20}$  1.5298 (lit.<sup>13</sup> b.p. 80–82° at 35 mm.,  $n_D^{20}$  1.4829). Cyclohexen-3-one (Aldrich Chemical Co., Technical Grade) was distilled through a Vigreux column; b.p. 62–65° at 14 mm.,  $n_D^{18}$  1.4829. Deuterium oxide of purity greater than 99.5% was obtained from the Stuart Oxygen Co. Kerosene was stirred with concentrated sulfuric acid for several hours. The organic layer was separated, and the treatment was repeated with fresh acid until the latter no longer became discolored after contact with the hydrocarbon. The kerosene was then washed with water, dried over potassium hydroxide, and distilled from a Claisen flask. The fraction boiling in the range 180–210° at 749 mm. was used. Maleic anhydride (Eastman Kodak Co., White Label Grade), m.p. 55–56°, was used directly. Pentane (Matheson, Coleman and Bell, Technical Grade) was distilled through a 1.5-ft. insulated Vigreux column; b.p. 34–35° at 750 mm. Quinoline (Matheson, Coleman and Bell, Synthetic) was distilled from zinc dust. Colorless material, b.p. 227° at 735 mm., was collected for use. Thionyl bromide was prepared according to the directions given in reference 14. The yellow product boiled at 47–48° at 22 mm.

**Cyclohexadiene.**—Two hundred and fifty ml. of quinoline was heated to the reflux temperature in a 500-ml. round-bottomed flask and 100 g. of 3-bromocyclohexene was added dropwise. The diene was distilled out through a 6-in.

Vigreux column and was dried over calcium carbonate and redistilled. The yield of cyclohexadiene boiling at 79–80° at 742 mm. was 40.4 g. (92%),  $n_D^{20}$  1.4733 or lower (lit. 1.4742<sup>13</sup> and 1.4739<sup>14</sup>). The ultraviolet spectrum of a sample having  $n_D^{20}$  1.4720 was measured with a Beckman model DU spectrophotometer. The absorbance between 240 and 275 m $\mu$  was a smooth curve with an indicated minimum value of log  $\epsilon$  3.70 at 257 m $\mu$ . This value of the extinction coefficient is somewhat lower than that reported in the literature.<sup>15</sup>

**Tetraethylammonium Acetate.**—Silver oxide, prepared from 580 g. (3.25 moles) of silver nitrate and 160 g. (4 moles) of sodium hydroxide, was added in small portions to a solution of 630 g. (3 moles) of tetraethylammonium bromide in one liter of water. The precipitated silver halide was removed by filtration and the filtrate was tested for bromide ion. Addition of silver oxide was continued until the filtrate no longer contained bromide. Acetic acid was added to neutralize the solution. Water was removed by vacuum evaporation at the temperature of a steam-bath. The crude acetate was recrystallized by dissolution in hot, anhydrous acetone followed by chilling in a Dry Ice-acetone-bath. The product obtained in this manner was a white, crystalline material free of bromide ion. When the solid was dried over phosphorus pentoxide it slowly liquified. Owne and Smith<sup>17</sup> have shown that the solid form is the tetrahydrate and that the liquid is a monohydrate. Unless otherwise specified, the monohydrate was used in reactions.

**3-Deuteriocyclohexene-3-ol.**—A solution of cyclohexene-3-one was added dropwise, with stirring, to a slurry of lithium aluminum deuteride (0.76 g., 0.02 mole) in 50 ml. of ether. The mixture was heated overnight under reflux. Water and dilute hydrochloric acid were added cautiously. The ether layer was separated and washed with aqueous base. The ether solution was dried, first over sodium sulfate, and then over calcium sulfate. Distillation gave 5.0 g. of labeled cyclohexanol, b.p. 55–58° at 8 mm.

**1-Deuterio-3-bromocyclohexene.**—A cold solution of the labeled alcohol (5.0 g., 0.05 mole) in 50 ml. of ether was added to thionyl bromide (11.0 g., 0.053 mole). The mixture was allowed to stand at 0° for 1 hour. Ether was then removed at 15-mm. pressure without heating. A solid, which was probably bromosulfite, was precipitated as the volume of the liquid in the flask decreased. When the flask was heated at 50° the solid decomposed and turned black. The yield of labeled bromocyclohexene boiling at 48° (8 mm.) was 3.2 g. (34%).

**trans-2-Deuteriocyclohexyl Bromide.**—Deuterium bromide, generated from 5.0 g. (0.25 mole) of heavy water and 50 g. (0.33 mole) of acetyl bromide, was passed into a solution of 30 g. (0.36 mole) of cyclohexene in 200 ml. of pentane. Chloranil (0.05 g.) and di-*t*-butyl-*p*-cresol (0.05 g.) were added to suppress addition by the radical chain mechanism. All the deuterium bromide was added during 1 hour. The pentane solution was washed thoroughly with aqueous sodium carbonate and dried over calcium chloride. Distillation gave unreacted cyclohexene and 7.1 g. of deuteriocyclohexyl bromide, b.p. 47–50° at 15 mm. Infrared spectra of the recovered cyclohexene obtained by concentration in carbon tetrachloride solution (200 mg. per ml. of solvent) showed a very weak absorption band at 2080 cm.<sup>-1</sup>. This limited allylic C–D absorption shows that very little addition-elimination occurred but does mean that a small amount of the deuterio bromide probably contained more than one deuterium per molecule.

**cis-2-Deuteriocyclohexyl Acetate.**—*trans*-2-Deuteriocyclohexyl bromide (5.76 g., 0.039 mole) was added to a solution of 16.5 g. (0.080 mole) of tetramethylammonium acetate monohydrate in 100 ml. of anhydrous acetone. The mixture was heated under reflux for 15 hours, and the precipitated tetramethylammonium bromide was removed by filtration. Ether (150 ml.) and water (150 ml.) were added to the acetone solution, and the organic layer was separated. It was washed thoroughly with water and dried over potassium carbonate. Distillation gave 0.6 g. (13%) of labeled ester, b.p. 62° at 16 mm.

**Generation of Deuterium Bromide.**—Deuterium bromide was generated by dropping deuterium oxide into acetyl bromide. The gas was stored in three gas burets of 500-

(11) G. Stork and W. White, *J. Am. Chem. Soc.*, **78**, 4609 (1956).

(12) See, for example, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 137.

(13) J. D. Park, H. J. Gerjovich, W. R. Lycan and J. R. Lacher, *J. Am. Chem. Soc.*, **74**, 2189 (1952).

(14) H. Hibbert and J. C. Pullman, *Inorg. Syntheses*, **1**, 113 (1939).

(15) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **6**, 55 (1938).

(16) V. Henri and L. W. Pickett, *ibid.*, **7**, 439 (1939).

(17) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4035 (1952).

100- and 10-ml. capacity, which were preflushed with dry, oxygen-free nitrogen.

**Typical Addition of Deuterium Bromide to Cyclohexadiene.**—A solution of cyclohexadiene (15.0 g., 0.187 mole) in 300 ml. of pentane was placed in the painted reaction cell. Chloranil (0.015 g.) and 2,6-di-*t*-butyl-*p*-cresol (0.015 g.) were added, and the stirrer was started to hasten dissolution of the inhibitors. Deuterium bromide was generated from 49.2 g. (0.40 mole) of acetyl bromide and 7.5 g. (0.375 mole) of deuterium oxide. The burets were filled first and then the gas from the burets was passed through a fritted disk into the reaction mixture under about 12 mm. pressure. When 1165 ml. (0.052 mole) of deuterium bromide had been passed through the reaction mixture, a 0.5-ml. aliquot from the latter was removed and analyzed for residual cyclohexadiene by ultraviolet spectrophotometry. The amount of diene consumed was 0.052 mole, indicating 1:1 stoichiometry. After the reaction had reached 50% completion, the decrease in remaining cyclohexadiene during the addition of known volumes of deuterium bromide was 10 or 15% less than calculated. This is attributed to a decrease in the rate of addition as the concentration of the diene decreased, rather than to a deviation from the expected stoichiometric relationship. No dibromocyclohexane was detected in any run.

When the reaction was 95% complete, the addition of deuterium bromide was stopped and nitrogen was bubbled through the solution to flush out any unreacted deuterium bromide. The pentane was then stripped off under about 70 mm. pressure with the flask at about 0°. When all the pentane had been removed the pressure was decreased to 0.2 mm. Distillation of 3-bromocyclohexene-*d* occurred without application of heat. The product was obtained in 83% yield,  $n_D^{20}$  1.5262.

Unreacted cyclohexadiene was isolated from a run carried to about 80% completion. The infrared spectrum of a solution of the diene in carbon tetrachloride (about 40 mg. per ml. in 1-mm. cells) showed no absorption bands in the C-D region.

The procedure for addition of deuterium bromide at -78° was slightly modified. The large amount of deuterium bromide dissolved in pentane at the low temperature could not be removed by purging with nitrogen. Therefore, the solution was distilled under vacuum with the flask at -50°.

**Reaction of Tetraethylammonium Acetate with 3-Bromocyclohexene-*d*.**—3-Bromocyclohexene (4.0 g., 0.025 mole) and tetraethylammonium acetate monohydrate (9.9 g., 0.048 mole) were dissolved in 170 ml. of anhydrous acetone and heated under reflux for 11 hours. The precipitated tetraethylammonium bromide was removed by filtration and washed with acetone. To the acetone was added 200 ml. of ether and 150 ml. of water, and the organic layer was separated and washed with 10% aqueous potassium carbonate and with water. The product was distilled through a 6-in. insulated Vigreux column yielding 3.2 g. (90%) of 3-cyclohexenyl acetate, b.p. 79–83° at 25 mm.

**Typical Hydrogenation of 3-Cyclohexenyl Acetate.**—A solution of 3-cyclohexenyl acetate (3.1 g., 0.022 mole) in 65 ml. of cyclohexane was hydrogenated at atmospheric pressure in the presence of 1 g. of 5% palladium-on-charcoal. The mixture took up 103% of the calculated amount of hydrogen. The catalyst was removed by filtration and washed with a few ml. of cyclohexane. The solution was then washed with a 10% aqueous potassium carbonate to remove any acetic acid that might have been formed by hydrogenolysis.<sup>18</sup> The cyclohexane layer was dried over potassium carbonate, and the solvent was removed by distillation. Distillation of the residue under reduced pressure gave 2.54 g. (82%) of cyclohexyl acetate, b.p. 75–80° at 25 mm. The infrared spectrum showed no absorption at 6.10  $\mu$ , indicating that little or no unsaturated ester was present.

**Saponification of Cyclohexyl Acetate.**—Cyclohexyl acetate (4.0 g., 0.028 mole) was heated under reflux with 15%

(18) When a platinum catalyst was used in ethyl acetate, cyclohexenyl acetate took up more than the calculated volume of hydrogen. The reaction was stopped after 130% of the calculated amount of hydrogen had been absorbed. Distillation of the solution gave a substantial amount of acetic acid, boiling from 118–130°, and only a 16% yield of crude cyclohexyl acetate. Hydrogenolysis occurred to the extent of about 50% when it was carried out using palladium-on-charcoal and tetrahydrofuran as the solvent.

aqueous potassium hydroxide solution for 3.5 hours. Some material was lost when bumping occurred near the end of the heating period. The solution was extracted with ether, and the ether extract was washed once with water and dried, first over potassium carbonate, and then over calcium sulfate. Distillation gave 2.26 g. (80%) of cyclohexanone boiling near 70° at 20 mm.,  $n_D^{20}$  1.4601 (lit.<sup>19</sup> 1.4656 at 22.6°).

**Oxidation of Cyclohexanol.**<sup>20</sup>—Sodium dichromate dihydrate (3.0 g.) in 5.5 ml. of glacial acetic acid was cooled to 10° and poured into a solution of cyclohexanol (3.0 g.) in 5 ml. of acetic acid at 10°. The mixture was stirred briefly with a thermometer. A maximum temperature of 52° was attained after 15 minutes. The mixture was allowed to stand at room temperature for 10 more hours. Water was then added and the mixture was subjected to steam distillation until no more oil was volatilized. Extraction of the distillate with ether, drying of the ether solution with potassium carbonate, and distillation gave 1.5 g. (51%) of cyclohexanone boiling in the range 54–58° at 20 mm. Deuteriocyclohexanone samples were subjected to equilibration with aqueous base prior to distillation.

**Exchange Reaction with Cyclohexanone.**—Cyclohexanone (1.52 g.) was allowed to stand at room temperature for 18 hours with 4 ml. of heavy water (approximately 60% deuterated) containing 10 drops of triethylamine. The milky suspension was then extracted with ether, and the ether layer was dried with potassium carbonate. All of the ether and most of the triethylamine were then removed by distillation at atmospheric pressure by heating the distilling flask to 100° with an oil-bath. The residual cyclohexanone was analyzed qualitatively for deuterium by infrared measurements. Spectra of solutions containing 100 mg. of the exchanged cyclohexanone in 1 ml. of carbon tetrachloride showed a strong absorption band at 4.60  $\mu$  with a shoulder at 4.70  $\mu$ .

The procedure used to determine  $\alpha$ -deuterium in labeled cyclohexanone was similar to that described above. About 15 ml. of water was used for every gram of cyclohexanone, and one drop of triethylamine was added for every 3 ml. of water. Equilibration times were again 18 hours.

**Elimination of Hydrogen Bromide from 3-Bromocyclohexene-*d*.**—In a typical run 5.0 g. (0.031 mole) of 3-bromocyclohexene, which had been stored at -78°, was added to 110 ml. of 0.297 *N* potassium *t*-butoxide in benzene at 20°. The mixture was shaken for 15 minutes, and the liquid was decanted into a distilling flask. Cyclohexadiene and benzene were distilled under reduced pressure with a maximum pot temperature of 50°. The distillate was then treated with maleic anhydride as is described in the following section.

**Preparation of Bicyclo[2,2,2]- $\Delta^5$ -octene-2,3-dicarboxylic Anhydride.**—To the solution of cyclohexadiene in benzene (*vide supra*) was added 2.7 g. (0.027 mole) of finely divided maleic anhydride. The mixture was swirled to dissolve the anhydride and was then heated to 100° for about 5 hours. Skellysolve B (petroleum ether) was added to precipitate the adduct which was removed by filtration. The product was recrystallized from hot Skellysolve B. The yields of adduct after three or four recrystallizations, which were required to raise the melting point of the adduct above 140° (m.p. of pure adduct, 146.5–147°), were 30–60% based on 3-bromocyclohexene.

**Pyrolysis of Cyclohexenyl Acetate.**—The pyrolysis was carried out in a Pyrex tube of 200-mm. i.d. packed with 1/8-in. Pyrex helices. The packed section, which was 15-cm. long, was heated to 500° by an electric furnace. Samples of the ester weighing from 1–2 g. were dropped into the top of the vertically mounted pyrolysis tube at the rate of one drop in 5 seconds. Oxygen-free nitrogen was passed into the top of the tube at the rate of one bubble in 2 seconds. The pyrolysis products were collected in a trap cooled by a Dry Ice-acetone-bath. Toluene was added to the pyrolysis products, and the solution was washed with dilute aqueous base. The toluene layer was dried over potassium carbonate and treated with maleic anhydride as described above.

**Analysis for Deuterium.**—To analyze a compound for its deuterium content a sample large enough to yield about

(19) "Handbook of Chemistry and Physics," 39th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1958, p. 888.

(20) I. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., New York, N. Y., 1955, p. 94.

0.25 g. of water was burned with oxygen in an ordinary combustion apparatus consisting of a 1.8-cm. Vycor tube, containing cupric oxide and a plug of silver wool, and a macro combustion furnace. Cylinder oxygen was dried by bubbling it through two washing bottles filled with concentrated sulfuric acid. The gas was then passed through a 3-ft. 1.5-in. i.d. tube packed with potassium hydroxide pellets, a plug of glass wool and anhydrous calcium sulfate. The water was collected in a U-tube that was cooled in a Dry Ice-acetone bath. The apparatus was prepared for combustion by passing oxygen through the combustion tube while the latter was heated to dull redness. Solids were introduced in a porcelain boat and liquids were stored in glass ampules. Just before introduction into the furnace the top of the ampule was cut off and the ampule was pushed, tip first, into the tube until it touched the copper oxide packing. Heat transferred to the ampule from the packing was sufficient to produce slow volatilization of the liquid samples allowing burning of liquids with no "flash backs."

Water samples were purified by the method of Keston, Rittenberg and Schoenheimer,<sup>21</sup> which involves refluxing

(21) A. S. Keston, D. Rittenberg and R. Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1937).

with and distillation from potassium permanganate. The purified water was transferred to a clean, dry serum vial equipped with a self-sealing serum stopper.

The falling drop method<sup>22</sup> was used to analyze the water. The falling drop tube was filled with a mixture of bromobenzene and kerosene having a density of 0.9988 at 26.2°, the temperature of the thermostat. A micro pipet constructed by drawing out 0.5-mm. capillary tubing, was used to deliver water samples. Very reproducible rates of fall were obtained, showing that the drop size was uniform. The rate of fall through a marked 20-cm. length was observed with a cathetometer. An empirical calibration curve was established using water samples of known deuterium content.

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(22) U. Kirshenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 324-343.

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## Restricted Rotation in Aryl Amines. XXII. Effect of *meta* Substitution on the Optical Stability of Some N-Benzenesulfonyl-N-carboxymethylmesidines

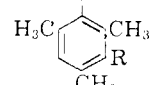
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The half-life of optically active N-benzenesulfonyl-N-carboxymethyl-*t*-butylmesidine was shown to be very short (1.5 hr.) in comparison with the half-lives of the corresponding methyl, ethyl, *n*-propyl and isopropyl derivatives (7.3-11.4 hr.).

The possible inductive and steric influences on the optical stability of 3-substituted N-benzenesulfonyl-N-carboxymethylmesidines have been reported.<sup>1</sup> The influence of field effect alone on the half-lives of such systems has also been studied.<sup>2</sup> More recently, research on 3-substituted mesidine derivatives was extended to a comparison of the stability of N-benzenesulfonyl-N-carboxymethyl-*t*-butylmesidine with the corresponding methylmesidine in order to determine whether the bulky *t*-butyl group<sup>3</sup> might have a buttressing effect in the molecule. It was found, however, that the *t*-butyl derivative exhibits a marked decrease in optical stability (half-life 1.49 hr.) as compared to that of the isoduridine homologs (half-life 7.3 hr.).

The purpose of the present investigation was to determine the optical stability of the 3-ethyl-, 3-isopropyl- and 3-*n*-propylmesidines and to correlate their stabilities with those of the methyl and *t*-butyl homologs. The values of the half-lives of the compounds studied in this investigation as well as of the methyl and *t*-butyl homologs are shown in Table I.

$C_6H_5O_2SNCH_2CO_2H$	R	Half-life, hr.
	CH <sub>3</sub>	7.3 <sup>3</sup>
	C <sub>2</sub> H <sub>5</sub>	9.6
	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	10.6
	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	11.4
	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	1.5 <sup>3</sup>

(1) R. Adams and M. J. Gortatowski, *J. Am. Chem. Soc.*, **79**, 5525 (1957).

(2) R. Adams and K. R. Brower, *ibid.*, **78**, 663 (1956).

(3) R. Adams and J. S. Dix, *ibid.*, **80**, 4579 (1958).

The regular increase of the optical stability in the sequence methyl, ethyl, isopropyl might be due merely to inductive effect but the unexpected value for the *t*-butyl homolog is inexplicable on this basis. In fact, to make certain that no experimental error was involved the *t*-butyl derivative was re-synthesized and the racemization experiment repeated. The value of the half-life found in this investigation (1.6 hr.) agrees closely with the value previously reported (1.5 hr.).<sup>4</sup>

A possible explanation is that the bulky *t*-butyl group pushes the adjacent methyl groups out of the plane of the benzene ring causing reduction of the interference to rotation around the ring-carbon to nitrogen bond and thus shortening the half-life. A Stuart-Briegleb model of the molecule indicates such an interference. Non-bonded interaction may also cause considerable angle distortion.<sup>5</sup> The possibility that a decomposition was being measured in the case of the *t*-butyl derivative rather than a racemization was eliminated by isolation of unchanged racemic product after racemization. Moreover, the racemic *t*-butyl derivative was subjected to very long heating under the conditions of the racemization experiments with no sign of decomposition, even though the corresponding ester by refluxing with dilute sulfuric and acetic acid is

(4) In previous studies on optically active compounds with restricted rotation, activation energies of a series of 2-nitro-6-carboxy-2'-alkoxy biphenyls were measured (C. C. Li and Roger Adams, *J. Am. Chem. Soc.*, **57**, 1565 (1935)). The results indicated that the heat of activation of each member of the series was the same, about 20,000 calories, within experimental error. The racemization half-lives thus appear to have more significance.

(5) R. F. Bryan and J. D. Dimitz, *Helv. Chim. Acta*, **43**, 3 (1960).