

case, it may cyclize in two possible manners to form methylvinylcyclobutanols [III] as well as methylcyclohexenol [IV] according to the following scheme:

When a solution of 6-hepten-2-one in pentane was irradiated with a low pressure mercury resonance quartz lamp,<sup>6</sup> acetone (32%), butadiene (23%) and an alcohol fraction (7.5%) isomeric with the starting ketone (found: C, 74.63; H, 10.48) were formed among some unreacted ketone (20%) and high molecular weight material. The major alcohol (6%), separated by gas chromatography, was identified to be 1-methyl-2-vinylcyclobutanol [III] (found: C, 74.88; H, 10.77;  $n_D^{25}$  1.4598;  $\gamma_{\max}$  3320, 3060, 1635, 990 and 910  $\text{cm}^{-1}$ ). The n.m.r. spectrum exhibits a singlet at 8.85  $\tau$  ( $-\text{CH}_3$ ), a multiplet at 7.90–8.70  $\tau$  ( $-\text{CH}_2$ ), a quartet at 7.15  $\tau$  (allylic), a singlet at 6.56  $\tau$  ( $-\text{OH}$ ), a triplet at 5.52, 5.10 and 4.93  $\tau$  (terminal vinyl) and a multiplet at 3.50–4.45  $\tau$  (non-terminal vinyl) and the relative intensities of these peaks are 3:4:1:1:2:1, respectively. Its double bond region in the n.m.r. spectrum was essentially identical with that of a known allyl system.<sup>7</sup> The other alcohol component (1.4%) had been identified tentatively to be 1-methyl-3-cyclohexenol [IV],  $\gamma_{\max}$  3320 and 3005  $\text{cm}^{-1}$ ; 8.80  $\tau$  (singlet,  $-\text{CH}_3$ ) and 4.42  $\tau$  (singlet, vinylene). Upon hydrogenation the alcohol fraction absorbed one mole equivalent of hydrogen, and the hydrogenated mixture was separated by gas chromatography into 1-methyl-2-ethylcyclobutanol<sup>8</sup> and 1-methylcyclohexanol in 4:1 ratio, identical in all respects with the corresponding authentic samples.

The isolation of both III and IV in the present investigation conclusively substantiates the step-wise mechanism.<sup>2</sup> It also indicates that the reactive state responsible for this reaction may be a triplet since the intermediate radical was free to delocalize over an allylic system.<sup>9</sup>

**Acknowledgment.**—A part of this work was carried out in the Department of Chemistry at the University of Illinois where N.C.Y. was a visiting lecturer, during the summer of 1962. The hospitality and stimulation provided by various members of that Department, particularly by Professor Stanley Smith, are gratefully acknowledged. This work is supported by a grant from the Petroleum Research Fund, Grant No. 726.

(6) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 245 (1949).

(7) Varian N.m.r. Spectra Catalog, spectrum No. 136.

(8) Prepared by the photochemical reaction of 2-heptanone, D. H. Yang, unpublished result.

(9) G. S. Hammond, Abstracts of Papers, 17th National Organic Chemistry Symposium of the American Chemical Society, 1961, pp. 48–58.

(10) Fellow of the Alfred P. Sloan Foundation.

(11) U. S. Public Health Service Predoctoral Fellow.

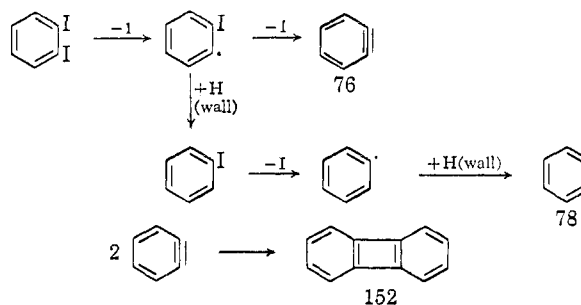
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RECEIVED FEBRUARY 7, 1963

### IONIZATION POTENTIAL OF BENZYNE

Sir:

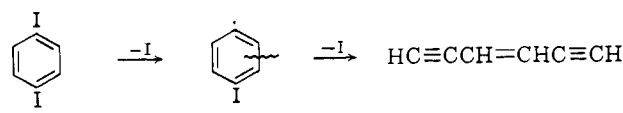
The chemistry of benzyne (1,2-dehydrobenzene) in solution has received considerable attention, and has been reviewed by a number of authors.<sup>1</sup> Recently, the transient spectrum of an intermediate has been observed in the flash photolysis of *o*-iodophenylmercuric iodide and other precursors,<sup>2</sup> which is almost certainly attributable to benzyne. We wish to report the detection of benzyne in the thermal decomposition of 1,2-diiodobenzene in a reactor coupled to a mass spec-

trometer.<sup>3</sup> The detection of free radicals and other products is carried out by ionization of a portion of the product stream with electrons of low energy, such that only parent ions are formed. The thermal decomposition of 1,2-diiodobenzene in this reactor at 960° (residence time  $\sim 10^{-3}$  sec., pressure  $\sim 10^{-3}$  mm.) leads to the formation of the following products: iodine atoms, iodophenyl radicals, phenyl iodide, phenyl radicals, benzene, a product of parent mass 76 and a product of parent mass 152. The reactions giving rise to these products are thought to be



These reactions are similar to those reported in the photolysis of 1,2-diiodobenzene in solution.<sup>4</sup> A comparison of the ionization efficiency curves for benzene, the product of mass 76 and an added xenon standard leads to the vertical ionization potentials: benzene, 9.50 v.; mass 76, 9.75 v. Identification of this species of mass 76 as benzyne by its parent mass alone is not sufficient, since three other structures for  $\text{C}_6\text{H}_4$  hydrocarbons can be written:  $\text{HC}\equiv\text{CCH}=\text{CHC}\equiv\text{CH}$  (I),  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{CH}_2$  (II) and  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CHC}\equiv\text{CH}$  (III). Formation of any of these three species from 1,2-diiodobenzene appears quite improbable. Formation of I would require one H-atom to migrate to a next-but-one carbon, II and III require the migration of two H-atoms. Moreover, the identity of the product of mass 76 with any of these can be ruled out on the basis of the expected ionization potentials. II and III, being substituted butatrienes, will have ionization potentials less than that of butatriene itself, 9.28 v.<sup>5</sup> The ionization potential of I can be estimated sufficiently closely for the present purposes by comparing the changes in ionization potential along the two series: ethylene, propylene, 2-butene; and ethylene, vinylacetylene and I. Substitution of H in ethylene by  $-\text{C}\equiv\text{CH}$  decreases the ionization potential slightly less (0.72 v.) than substitution by  $-\text{CH}_3$  (0.78 v.).<sup>6</sup> Comparison with 2-butene, derived from ethylene by a 1,2-disubstitution, gives the ionization potential of I to be 9.40 v. The observed value for mass 76 is clearly larger than expected values for I, II or III.

The thermal decompositions of 1,4- and 1,3-diiodobenzene under the same conditions were also examined. The former produced iodophenyl radicals, benzene, and again a compound of mass 76, but no product of mass 152. The ionization potential of the species of mass 76 in this case, however, was 9.46 v., in good agreement with the estimated value for I. The course of this reaction is evidently



(3) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955); F. P. Lossing, P. Kebarle and J. B. de Sousa in "Advances in Mass Spectrometry," Pergamon Press, London, 1959, p. 431.

(4) J. A. Kampmeier and E. Hoffmeister, *J. Am. Chem. Soc.*, **84**, 3787 (1962).

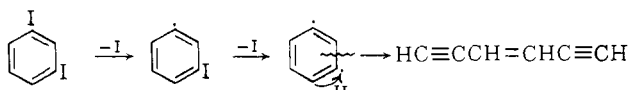
(5) A. Streitwieser, Jr., *ibid.*, **82**, 4123 (1960).

(6) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

(1) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); J. D. Roberts, *Chem. Soc. (London) Spec. Publ.*, **12**, 115 (1958); R. Huisgen, in "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Co., New York, N.Y., 1960; H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

(2) R. S. Berry, G. N. Spokes and R. M. Stiles, *J. Am. Chem. Soc.*, **82**, 5240 (1960); **84**, 3570 (1962).

The decomposition of 1,3-diiodobenzene also led to the formation of a product of mass 76, with the same ionization potential, 9.46 v. The formation of I in this case requires a H-atom migration



This migration may occur either before or after ring rupture.

The presence of a product of mass 152 in the decomposition of the *ortho* compound, and its absence in the decompositions of the *para* and *meta* compounds, supports the ionization potential evidence that the product of mass 76 from the *ortho* compound is benzyne.

Although the preliminary m.o. calculations of Berry, *et al.*,<sup>2</sup> do not permit an accurate prediction of I (benzyne), they indicate that the orbital of highest energy is a benzenoid orbital, and that the ionization potential of benzyne therefore should not be greatly different from that of benzene. Our observed value is in qualitative agreement with this conclusion. Electron impact ionization potentials correspond approximately to vertical transitions, and that observed here for benzene (9.50 v.) is 0.25 v. higher than the ionization potential obtained by spectroscopy (9.247 v.)<sup>7</sup> and photoionization<sup>8</sup> (9.245 v.). A further increase of  $0.25 \pm 0.1$  v. in the vertical ionization potential of benzyne over that of benzene may possibly represent merely a greater change in configuration between the neutral and charged species, rather than a change in adiabatic ionization potential.

(7) P. G. Wilkinson, *Can. J. Phys.*, **34**, 596 (1956).

(8) K. Watanabe, *J. Chem. Phys.*, **26**, 1773 (1957).

(9) Issued as N.R.C. No. 7319.

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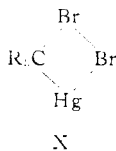
I. P. FISHER  
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RECEIVED FEBRUARY 23, 1963

**A PREFERRED INVERSION IN AN ELECTROPHILIC  
DISPLACEMENT: MERCURIDEBORONATION OF *exo*-  
AND *endo*-5-NORBORNENE-2-BORONIC ACIDS**

Sir:

The inherent stereochemical preference of electrophilic displacement at saturated carbon has been one of the most elusive of chemical problems. That retention is possible has long been known, inasmuch as all the familiar alkyl migrations to an electron-deficient atom may be so classified. Bromodemercuration proceeds with retention,<sup>1</sup> but the brominating agent may complex with the leaving mercuric ion, resulting in a cyclic transition state in which retention of configuration of the carbon atom would be inevitable. Related ex-

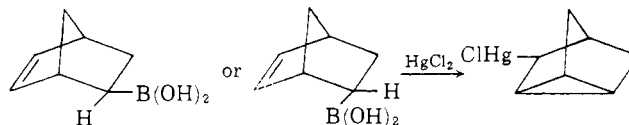


planations have been applied to the stereochemical preferences of carbanion intermediates, which range from retention to some net inversion, depending on the solvent.<sup>2</sup> We have now found what appears to be a concerted transannular electrophilic displacement in which *inversion is faster than retention*. The order of magnitude of the ratio is hundreds.

(1) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 148 (1960); a review of earlier literature is included. F. R. Jensen, L. D. Whipple, D. K. Wedegaertner and J. A. Landgrebe, *ibid.*, **82**, 2466 (1960); F. R. Jensen, *ibid.*, **82**, 2469 (1960).

(2) D. J. Cram, *et al.*, *ibid.*, **81**, 5740 (1959), *ibid.*, **83**, 3678, 3688, 3696 (1961).

We recently have reported the preparation, separation, unequivocal identification and analysis for isomer ratios of *exo*- and *endo*-5-norbornene-2-boronic acid.<sup>3</sup> Boiling either the *exo* or the *endo* boronic acid with an equimolar quantity of mercuric chloride in aqueous 83% acetone until most of the acetone evaporates yields 80–83% of nortricycylmercuric chloride, long needles, m.p. 140° dec.<sup>4</sup> *Anal.* Calcd. for C<sub>7</sub>H<sub>9</sub>HgCl: C, 25.54; H, 2.76; Hg, 60.93; Cl, 10.77. Found: C, 25.61; H, 2.83; Hg, 61.18; Cl, 10.61.



That the *exo* isomer, in which the carbon from which the boron is displaced must undergo inversion of configuration, reacts hundreds of times faster than the *endo* is established by the following observations. A solution 0.4 M in 93% *endo* acid and 0.4 M in mercuric chloride in aqueous 83% acetone was allowed to stand 26 hr. at 25°. The mercuric salts were precipitated with hydrogen sulfide, the acetone distilled and the organic material extracted with ether. The recovery of boronic acid with a few per cent impurity (checked by infrared) was 105%. Similarly, 0.4 M 96% *endo* acid and 0.2 M mercuric chloride refluxed 10 hr. led to 70% recovery of pure *endo* boronic acid and at least 20% conversion to boric acid. Thus, with 0.4 M reactants the first half-life of the *endo* isomer at 25° must be considerably greater than 26 but probably not more than a few hundred hours. In contrast, the half-life of the *exo* isomer under these conditions is 20–30 min. Nortricycylmercuric chloride crystallizes from the reaction mixture in 5–10 min., the recovery of impure *exo* acid after 30 min. was only 30%, and starting with a 5.83 *exo/endo* ratio (by weight), 0.39 M *exo* and 0.35 M mercuric chloride led in 22 min. to a 3.0 *exo/endo* ratio (by gas chromatography of derived dehydronorbornes). In other competition experiments run longer times with either *exo* or *endo* in excess, it appeared within experimental error that only the *exo* isomer was disappearing. We anticipate complexity in the detailed kinetics of the reaction,<sup>5</sup> and have first investigated a more crucial point.

The relative reactivities of the *exo* and *endo* boronic acids are relevant to the question of steric preference in electrophilic substitution only if the carbon-boron bond is being broken in the rate-determining step. That this is the case is shown by the B<sup>10</sup>/B<sup>11</sup> isotope effect, 1.7 ± 0.7% for the *endo*, 2.9% for the *exo* isomer. Measurements were made by degrading appropriate samples to boric acid and determining the neutron cross section. The method will be described in detail later.

The possibility exists that the deboronation is not transannular but involves direct displacement of boron followed by rapid rearrangement of the resulting norbornenylmercuric chloride. However, the reaction conditions used do not normally permit mercurideboronation of aliphatic boronic acids<sup>6</sup> and would require an unknown type of interaction between the double bond and the carbon atom undergoing displacement. In contrast,  $\pi$ -complex formation with HgCl<sup>+</sup> followed by transannular displacement seems straightforward.

(3) D. S. Matteson and J. O. Waldbillig, *J. Org. Chem.*, **28**, 366 (1963).

(4) The corresponding bromide and acetate have been reported by S. Winstein, E. Vogelfanger and K. C. Pande, *Chem. Ind. (London)*, 2060 (1962). We wish to thank Professor Winstein for verifying the identity of our chloride with his (by infrared) in advance of publication.

(5) H. G. Kuivila and T. C. Muller, *J. Am. Chem. Soc.*, **84**, 377 (1962).

(6) K. Torssell, *Acta Chem. Scand.*, **13**, 115 (1959).