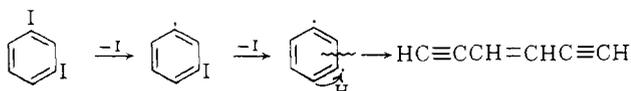


The decomposition of 1,3-diiodobenzene also led to the formation of a product of mass 76, with the same ionization potential, 9.46 v. The formation of I in this case requires a H-atom migration



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.*,² 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.⁷) and photoionization⁸ (9.245 v.). A further increase of 0.25 ± 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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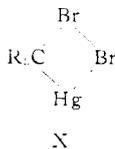
I. P. FISHER
F. P. LOSSING

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,¹ 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-

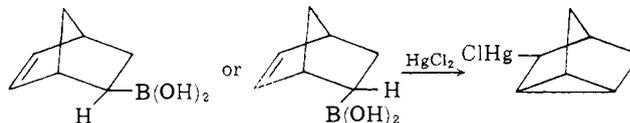


planations have been applied to the stereochemical preferences of carbanion intermediates, which range from retention to some net inversion, depending on the solvent.² We have now found what appears to be a concerted transannular electrophilic displacement in which *inversion is faster than retention*. 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.³ 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 nortricyclylmercuric chloride, long needles, m.p. 140° dec.⁴ *Anal.* Calcd. for C₇H₉HgCl: 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. Nortricyclylmercuric 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,⁵ 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 B¹⁰/B¹¹ 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.

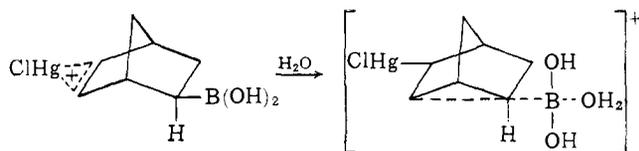
The possibility exists that the deboronation is not transannular but involves direct displacement of boron followed by rapid rearrangement of the resulting norbornenylmercuric chloride. However, the reaction conditions used do not normally permit mercurideboronation of aliphatic boronic acids⁶ and would require an unknown type of interaction between the double bond and the carbon atom undergoing displacement. In contrast, π -complex formation with HgCl⁺ 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).



Essentially the same mechanism has been proposed for the bromination of norbornylene.⁷

Quantum mechanically, preference for inversion in the above electrophilic displacement is reasonable. The carbon atom undergoing displacement would be somewhat electron-deficient (resembling a carbonium ion), and p character is preferred to s in an incompletely filled orbital. The essential difference between concerted electrophilic and nucleophilic displacement is the filling of orbitals, the system X—C—Y having only one electron pair in the bonding orbital during electrophilic displacement but having a second pair in a non-bonding orbital, to which the contribution of the central carbon atom is nearly zero, in nucleophilic displacement. Electron repulsion in the non-bonding orbital makes inversion practically mandatory in nucleophilic displacement, while its absence leaves the stereochemistry more flexible in electrophilic displacements. In electrophilic displacements where the carbon atom acquires considerable carbanion character, the central orbital would acquire more s character (sp^3) and retention would be favored. Any cyclic three-center bonding resulting from orbital overlap of X and Y would also tend to favor retention.

Because of the inherently tentative interpretation of any unprecedented results, we are searching for analogous reactions to support or revise our initial conclusions.

Acknowledgment.—We thank Drs. H. W. Dodgen and S. W. Peterson for helpful discussions and for making available neutron counting equipment at the Washington State University Nuclear Reactor, and the National Science Foundation for financial support (NSF-G 19906).

(7) J. D. Roberts, E. R. Trumbull, R. W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

DEPARTMENT OF CHEMISTRY DONALD S. MATTESON
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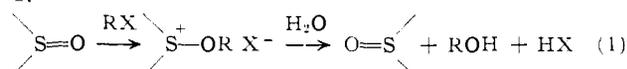
RECEIVED JANUARY 14, 1963

THE INVERSION OF SULFOXIDE CONFIGURATION

Sir:

The configurational stability of sulfoxides was confirmed in 1926 with the resolution of three sulfoxides by Harrison, Kenyon and Phillips.¹ Soon thereafter examples of geometrical isomerism attributable to the sulfoxide grouping were provided.² This communication now reports the first examples of the inversion of the configuration of the sulfoxide group.³

The recent report⁴ that alkyloxysulfonium salts hydrolyze in isotopically enriched water to yield the parent sulfoxide containing oxygen-18 suggested that such a reaction might proceed with inversion of configuration 1.



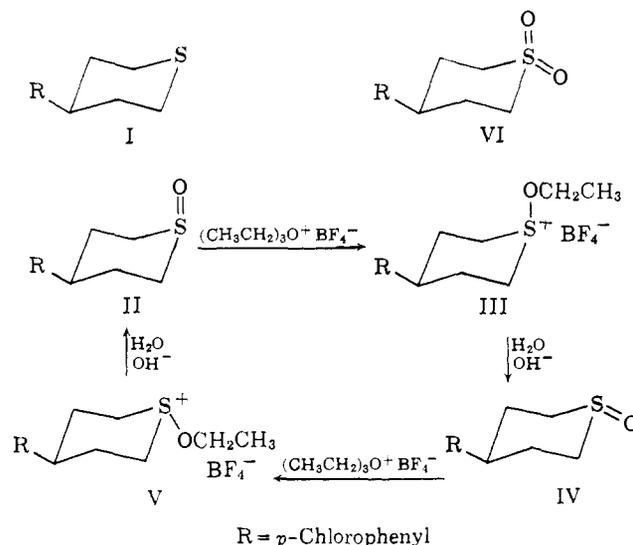
In the present study *cis*-4-(*p*-chlorophenyl)-thian-1-oxide (II) was transformed to the corresponding *trans*

(1) P. W. B. Harrison, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 2079 (1926).

(2) E. V. Bell and G. M. Bennett, *ibid.*, 1798 (1927).

(3) Walden inversion has been shown to occur during trans-esterification of sulfonic esters which have related molecular dissymmetry at the sulfur atom: H. Phillips, *ibid.*, **127**, 2552 (1925).

(4) N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).



isomer (IV) *via* hydrolysis of an intermediate O-alkyl sulfoxide adduct. To complete the cycle, the *trans* sulfoxide in like manner was converted to the *cis* as shown in the annexed scheme and described in detail below.

Cyclization of 3-(*p*-chlorophenyl)-1,5-dibromopentane⁵ was effected with sodium sulfide in absolute ethanol to provide 4-(*p*-chlorophenyl)-thiane (I), m.p. 70–71°. (*Anal.* Calcd. for $C_{11}H_{13}ClS$: C, 62.11; H, 6.16. Found: C, 62.10; H, 6.22.)

Oxidation of the sulfide I with aqueous sodium metaperiodate⁶ and recrystallization of the crude sulfoxide⁷ from ethyl acetate provided pure *cis*-4-(*p*-chlorophenyl)-thian-1-oxide, m.p. 172.5–173°, $\nu_{\text{max}}^{\text{CCl}_4}$ 1058 cm^{-1} , ($S = 0$). (*Anal.* Calcd. for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73; S, 14.04. Found: C, 57.78; H, 5.76; S, 13.81.) The dipole moment of II in benzene solution was found to be 3.98 ± 0.02 D,⁸ in fair agreement with 4.30 D. calculated⁴ from models and model compounds⁹ for the chair conformation of the *cis* sulfoxide.

Alkylation of II with triethyloxonium fluoroborate¹⁰ in methylene chloride afforded in 76% yield the desired kinetically-controlled alkylation product,¹¹ *cis*-4-(*p*-chlorophenyl)-1-ethoxythioniacyclohexane fluoroborate (III), m.p. 107–108°. (*Anal.* Calcd. for $C_{13}H_{18}BClF_4OS$: C, 45.32; H, 5.26; neut. equiv., 344.5. Found: C, 45.13, 45.55; H, 5.30, 5.22; neut. equiv., 347.)

When III was dissolved in dilute aqueous sodium hydroxide, one equivalent of base was consumed and shiny platelets of a new sulfoxide, m.p. 119–121°, precipitated in 93% yield. Recrystallization from ethyl acetate–hexane provided pure *trans*-4-(*p*-chlorophenyl)-thian-1-oxide (IV), m.p. 120–120.5°, $\nu_{\text{max}}^{\text{CCl}_4}$ 1054 cm^{-1} , ($S = 0$), dipole moment in benzene 2.60 D.⁸ (calcd. for chair conformation of *trans* sulfoxide, 2.24 D.). (*Anal.*

(5) N. L. Allinger and S. Greenberg, *ibid.*, **81**, 5733 (1959).

(6) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(7) It is noteworthy that oxidation of I with periodate provided a mixture consisting of 70% *cis* sulfoxide (II) and 30% *trans* sulfoxide (IV) as ascertained by infrared analysis. On the other hand, oxidation of I with hydrogen peroxide in acetone or with perbenzoic acid in chloroform yielded approximately 30% II and 70% IV. The implications of these and similar data bearing on the mechanism of oxidation of sulfides will be discussed in the full paper. At the same time detailed infrared studies of these compounds will be presented.

(8) The dielectric and density measurements were made by Mr. C. L. Neumann of these Laboratories.

(9) Thian-1-oxide, 4.19 D. [A. I. Vogel and C. W. N. Cumper, *J. Chem. Soc.*, 3521 (1959)] and *p*-chlorotoluene, 1.95 D. [N. L. Allinger, S. P. Jindal and M. A. DaRooze, *J. Org. Chem.*, **27**, 4290 (1962)].

(10) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willang, *J. prakt. Chem.*, **154**, 83 (1939).

(11) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).