[CONTRIBUTION FROM HUMBLE OIL AND REFINING CO. AND NORTHWESTERN UNIVERSITY]

Stereochemistry of the Removal of Sulfur from Episulfides by the Action of Phenyllithium and Triethyl Phosphite

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The treatment of *cis*- and *trans*-2-butene episulfides with phenyllithium or triethyl phosphite leads to greater than 97% stereoselective removal of sulfur from the three-membered ring with the formation of *cis*- and *trans*-2-butenes, respectively.

The reaction of episulfides with phenyllithium has been shown to result in the abstraction of sulfur to give lithium thiophenoxide and the corresponding olefin, presumably by nucleophilic attack of the incipient phenyl carbanion on sulfur.[1] Our interest in the stereochemistry of this reaction was aroused, first by the observation that *cis*-2-butene is the major product obtained on treating α-chloroethyl ethyl sulfone with alkali[2] (an olefin-forming reaction also presumed to involve nucleophilic attack on sulfur),[3] and second by our desire to use product analysis of the desulfurizations of the 2-butene episulfides as a measure of the relative amounts of the two diastereoisomeric 1-methyl-2-chloropropyl acetothiolates [$CH_3CHCl-CH(SCOCH_3)CH_3$; these form episulfides stereoselectively when treated with alkali] produced by free radical addition of acetothiolic (thiolacetic) acid to *cis*- and *trans*-2-chloro-2-butenes.[4]

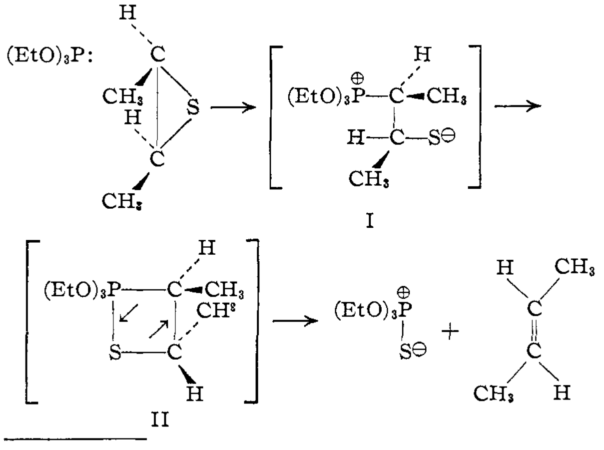
The *cis*- and *trans*-2-butene episulfides used in this study were prepared readily in high purity from *cis*- and *trans*-2-butenes *via* the bromohydrins and epoxides. The epoxides were converted in good yield to the episulfides on treatment with potassium thiocyanate.

The reaction with phenyllithium was originally carried out in ethyl ether. The 2-butenes obtained were contaminated with ether vapor and with ethylene, which made their precise analysis by infrared spectroscopy difficult. With the advent of vapor phase chromatography the presence of these materials no longer presented any difficulties and the experiments were repeated. It was found later that use of benzene as the solvent greatly facilitated the butene recovery, nearly quantitative yields then being obtained.

The composition of the butene mixtures was determined by vapor phase chromatography. From *cis*-2 butene episulfide *cis*-2-butene containing 2-3% of *trans*-2-butene was obtained. Similarly, *trans*-2-butene episulfide gave *trans*-2-butene containing only 1-2% of *cis* isomer. Thus a stereoselective sulfur removal of at least 97% was demonstrated. It is clear that phenyllithium was not effecting a slow equilibration of *cis*- and *trans*-2-butenes since the composition after 40-hour reflux was essentially the same as after 1.5 hours. The source of the small amount of isomerization in each instance is not clear. Though there was a small amount of the isomeric episulfide present in each sample, the quantity was less than that of the isomeric olefin in the product. It is possible that a small percentage of the reaction goes by a "carbanion" mechanism rather than a concerted process,[1] or that all the episulfide reacts to form a lithium derivative, $CH_3CHLiCH(SC_6H_5)CH_3$, which eliminates lithium thiophenoxide thirty to sixty times faster than it changes its conformation by rotation about the central carbon–carbon bond.

An interesting analogy to the desulfurization reaction is the removal of oxygen from epoxides by the action of triphenylphosphine[5] or triethyl phosphite.[6] Although ethene and propene epoxides quantitatively release their oxygen when treated with triethyl phosphite at 150-175°,[6] we found that the 2-butene epoxides undergo this reaction much less satisfactorily. Only small yields of butenes were obtained even on prolonged heating at 200°. Under these conditions the formation of ethene by decomposition of triethyl phosphite was appreciable. Mixtures of *cis*- and *trans*-2-butenes were obtained, but isomerization may have occurred.

In contrast to the 2-butene epoxides, *cis*- and *trans*-2-butene episulfides reacted smoothly with triethyl phosphite at 105-155° to give essentially quantitative yields of 2-butenes. The reactions appear to be stereospecific, over 99% of *cis*-2-butene being formed from *cis*-2-butene episulfide, and over 99% of *trans*-2-butene being formed from *trans*-2-butene episulfide. This result rules out a mechanism involving nucleophilic attack by phosphorus on carbon to give intermediates I and II, a path which is favored for the comparable reaction of epoxides involving oxygen,[5,6] since this would



I

II

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[1] F. G. Bordwell, H. M. Anderson and B. M. Pitt, THIS JOURNAL, **76**, 1082 (1954).

[2] L. Ramberg and B. Backlund, *Arkiv Kemi, Min. Geol.*, **13A**, No. 27 (1940); N. P. Neureiter, Ph.D. Dissertation, Northwestern University, June, 1957.

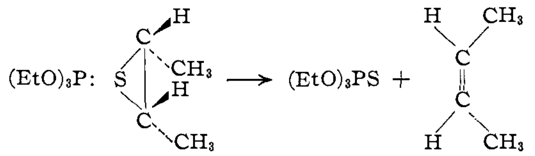
[3] F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5187 (1951).

[4] F. G. Bordwell and N. P. Neureiter, p. 10-O of the Abstracts of the Miami Meeting of the American Chemical Society, April, 1957.

[5] G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

[6] C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957).

lead to the opposite stereochemical result. Nucleophilic attack of phosphorus on sulfur is indicated. In view of the high stereoselectivity observed a concerted mechanism appears attractive



although a short-lived intermediate dipolar ion, $(\mathrm{EtO})_3\overset{\oplus}{\mathrm{P}}\mathrm{S{-}CH(CH_3)}\overset{\ominus}{\mathrm{C}}\mathrm{HCH_3}$, cannot be excluded. The fact that sulfur is more susceptible to nucleophilic attack than is oxygen has been rationalized previously.[1]

Experimental

***cis*-and *trans*-2-Butene Episulfides.**—From an aqueous suspension of N-bromosuccinimide and *cis*-2-butene was prepared *threo*-3-bromo-2-butanol by analogy with the method of Winstein and Lucas.[7] This bromohydrin was converted to the *cis*-2-butene oxide *via* the method of Wilson and Lucas.[8] The epoxide was converted to the episulfide by application of the method of Snyder, *et al.*[9] It had b.p. 51.0–51.5° (130 mm.), n^{20}_{D} 1.4765, and strong characteristic infrared absorption bands at 1029 and 1146 cm.$^{-1}$.[10]

The same sequence of reactions was repeated starting with *trans*-2-butene for preparation of the *trans*-2-butene episulfide. It had b.p. 43.0–43.2° (140 mm.), n^{20}_{D} 1.4624 and characteristic infrared bands at 1086 (medium strong) and 1290 cm.$^{-1}$ (medium).

Vapor phase chromatography of the episulfides through an 8-ft. by 0.25-inch column on a Kromo-Tog instrument using a tetra-*n*-propyl pyromellitate substrate on 40–50 mesh firebrick at 80° gave an excellent separation of the *cis*- and *trans*-episulfides. Each episulfide contained a trace of the corresponding epoxide and each case less than 0.15% of the isomeric episulfide.

Price and Kirk[11] have reported the synthesis of optically active *trans*-2-butene episulfide. It appears, however, that their material was contaminated with the corresponding epoxide. The strong infrared absorption bands at 9.8 and 11.27 μ and the medium band at 9.0 μ in their spectrum are characteristic of *trans*-2-butene oxide and were absent from our spectrum of the pure sulfide. Also, it was found in the present work that reaction under the conditions of Price and Kirk even for a period of several days led to only poor yields of sulfide and contamination of the product with large amounts of unreacted oxide. A reaction temperature of 40–44°, gave, on the other hand, very satisfactory conversions. These observations are consistent with the low index of refraction (n^{25}_{D} 1.4390) and the low sulfur analyses reported by the previous workers.

Desulfurization Reactions.—All the subsequent reactions were carried out in a single piece of apparatus, which consisted of a small round bottom flask equipped with a magnetic stirrer, a small efficient condenser which could be kept at any desired temperature (usually 10–18°), and a dropping funnel (if necessary). From the top of the condenser a short delivery tube led into a graduated cold trap cooled in Dry Ice and acetone. The yield of butenes was calculated from the volume, assuming a density of 0.67 g./ml. After collection the condensed products were vaporized into bulbs from which samples could be withdrawn by a syringe through serum caps for charging to a vapor phase fractometer. Analyses were done for the most part on a Fischer-Gulf instrument at 50° and 8 lb. of helium pressure using a 23 ft. by 0.25-inch stainless steel column packed with a benzyl Cellosolve substrate on 40–60 mesh C-22 acid-washed firebrick. The molar ratio of *cis*- and *trans*-2-butenes was assumed equal to the ratio of peak areas (determined by half-heights method). This assumption proved valid to within ±1.5% absolute over a range of 25:75 to 75:25 *cis* to *trans*. The method served to detect 0.3% of one isomer in the presence of the other. In general the reproducibility of the analyses was within 0.5%.

2-Butene Episulfides with Phenyllithium in Ether.—The sulfide (3.0 g.) was added dropwise to 130 ml. of an ethereal solution of phenyllithium (1.3 *M*), with vigorous stirring at room temperature. The heat of reaction caused the ether to boil throughout the addition. The condenser was kept at 5–8°. After complete addition (20 min.) the condenser temperature was raised to about 10° and the reaction mixture gently boiled. After a few minutes the 0.1 to 0.2 ml. of condensate collected was analyzed. Stirring was continued at room temperature for a total of 40 hours. Samples were collected by boiling the solution after 1.5, after 16, and after 40 hours. It seemed difficult to boil all the butene out of the ether even with the condenser at 10°. The gas samples contained in addition to the 2-butenes small amounts of ethylene (the amount increased with increased time of reaction), propane, propylene, isobutylene, *n*-butane and some ether. The hydrocarbon impurities amounted to as much as 5% of the total gaseous product, with ether as high as 15–20%. Of the four samples collected from the *cis*-2-butene sulfide, each of 0.1–0.2 ml., the first had 5.5%, the second 2.8%, the third 2.4%, and the fourth 2.7% *trans*-2-butene (the sum of *cis*- and *trans*-2-butenes being 100%).

From the *trans*-2-butene episulfide the four samples had: 3.2, 1.6, 2.1, and 1.5% *cis*-2-butene, respectively.

2-Butene Episulfides with Phenyllithium in Benzene.—Dry benzene was added to an ethereal solution of phenyllithium while continuously removing the ether by distillation through a short Vigreux column until the vapor temperature reached 79°. The solution still contained a small amount of ether. The precipitated lithium bromide was removed by filtration through a glass wool plug. Titration with sodium hydroxide solution of a hydrolyzed aliquot showed the solution to be 0.88 *M* in phenyllithium.

To 135 ml. of this solution was added with stirring 2.0 g. of the episulfide. Some heat development occurred during addition, but the reaction was clearly not as vigorous as it had been in ether. After addition had been completed (5 min.) the solution was heated to reflux and boiled gently for 20 min. with the condenser at 13–16°. An 80–90% yield of butenes condensed in the Dry Ice trap. In an experiment with 0.5 g. of episulfide, an essentially quantitative yield of butene was obtained. Two runs with the *cis*-episulfides gave values of 2.1 and 1.8% *trans*-2-butene. Runs with the *trans*-episulfide gave an average value of 1.1% of *cis*-2-butene.

2-Butene Episulfides with Triethyl Phosphite.—In the reaction flask was placed 10 g. of triethyl phosphite (Aldrich Chemical Co., Research Grade). From 0.65 to 1.7 g. (in various runs) of the sulfide was added and gentle heating begun. At about 105° slow gas evolution began. Heating was continued for 20–30 min. during which the temperature reached 155°. After 5 min. of refluxing at 155°, heating was discontinued. The yield of 2-butene recovered from the cold trap was 90–100%. From the *cis*-episulfide the product contained 0.4% (<0.5%) *trans*-2-butene. From the *trans*-episulfide the product contained 0.3% (<0.5%) *cis*-2-butene. The residue from the reaction of 2.6 g. of the episulfide with triethyl phosphite was distilled at atmospheric pressure through a short Vigreux column to remove the excess triethyl phosphite. The higher boiling material was distilled *in vacuo* giving 2.9 g. up to 105° (20 mm.) (n^{25}_{D} 1.4390) and 1.4 g., b.p. 105–110° (20 mm.), n^{25}_{D} 1.4408 to 1.4426 for three successive fractions. Triethyl phosphite had n^{25}_{D} 1.4119. From the refractive index it appeared that the triethyl thionophosphate was contaminated with about 10% of triethyl phosphite. This corresponds to 3.9 g. (90% yield) of triethyl thionophosphate. The infrared spectrum of the fraction with n^{25}_{D} 1.4420 was similar to that of the triethyl phosphite with a new band at 7.9 μ, and both of the intense bands at 10.8 and 13.4 μ shifted to 10.4 and 12.45 μ, respectively. Mastin, *et al.*,[12] gave b.p. 105–106° (20 mm.) for triethyl thionophosphate.

The presence of the 7.9-μ band may correspond to some of

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[7] S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1580 (1939).

[8] C. W. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

[9] H. R. Snyder, J. M. Stewart and J. B. Ziegler, *ibid.*, **69**, 2672 (1947).

[10] The infrared spectra were run on a Baird Associates double beam infrared spectrometer equipped with a cam by Dr. E. M. Amir making the spectrum linear with respect to wave number. The reported frequencies are uncorrected.

[11] C. C. Price and P. F. Kirk, THIS JOURNAL, **75**, 2396 (1953).

[12] T. W. Mastin, G. R. Norman and E. A. Weilmuenster, *ibid.*, **67**, 1662 (1945).

the isomeric thiolophosphate in the product.[13] It is possible that some of the initially formed thionophosphate has rearranged during the distillation.[14] However, the thiolophosphate should have b.p. 122° (20 mm.).[15]

Acknowledgment.—This investigation was supported in part by American Petroleum Institute Project 48B. The authors would like to express their thanks to Messrs. W. C. Jones, H. C. Reeder, H. C. Williams and H. T. Taylor of The Humble Oil and Refining Co. for help with the butene analyses.

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(13) L. J. Bellamy, "Infrared Spectra of Complex Molecules," second edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 322, attributes the 7.7 to 8.0 μ region to the P=O bond.

(14) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 5.

(15) Pischimuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Synthesis of *p*-Vinylphenylboronic Acid and Some of its Derivatives

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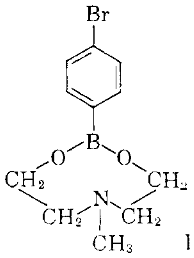
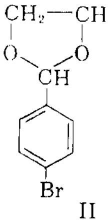
The synthesis of *p*-vinylphenylboronic acid, iminodiethyl *p*-vinylphenylboronate, *p*-vinylphenylboroxine and di-*n*-butyl *p*-vinylphenylboronate is described. These compounds are new monomers.

A wide variety of boron compounds may be classed as either demonstrated or potential monomers. Polymers of such compounds contain boron atoms whose bonds either form part of the polymer skeleton as in glycol borates, or are non-integral to the polymer skeleton. Molecules containing a polymerizable vinyl group and a boron moiety unaffected by vinyl polymerization conditions could lead to the latter type of polymer. Representative compounds of this type include β-chlorovinylboronic,[1] allylboronic,[2] and styrylboronic acids,[3] B-tri-(β-chlorovinyl)borazine,[4] potassium tetrastyrylborate[3] and the vinylborines.[5] No detailed information regarding the polymerization of this monomer class has, however, been reported.

The synthesis of a boron-containing vinyl monomer was undertaken to provide information relating to the electronic influence of boron on a reactive vinyl group under polymerization conditions. Factors such as air-oxidative stability and hydrolytic stability, coupled with the known behavior of styrene under a wide variety of conditions, led to our choice of *p*-vinylphenylboronic acid as a model compound for this study. Accordingly, this paper presents the synthesis of this monomer and some of its derivatives. In an attempt to obtain *p*-(β-hydroxyethyl)-phenylboronic acid as a precursor of the desired monomer, N-methyliminodiethyl *p*-bromophenylboronate (I) was prepared from *p*-bromophenylboronic acid.[6] Attempts to form a Grignard reagent from I failed as did also attempts to form the lithium or sodium derivatives by reaction of I with the metals in ether.

A similar approach employing 2-*p*-bromophenyldioxolane (II) also failed because of resistance to Grignard-reagent formation. A "direct reaction" was attempted with this halide but no significant metal consumption occurred under these conditions.[7]


I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Since a procedure was desired which could lead to relatively large amounts of monomer, failure of I and II to easily form Grignard reagents prompted an approach avoiding such unreactive halides. Although arylboronic acids are known to undergo electrophilic displacement reactions resulting in cleavage of the aryl–boron bond,[8] no information regarding similar displacements by free radicals was available. In the hope that such a displacement by a bromine atom would not be significantly competitive with α-hydrogen abstraction from a *p*-ethylphenyl-substituted boron-containing group, bromination of N-methyl-iminodiethyl *p*-ethylphenylboronate by N-bromosuccinimide was attempted. N-Methyliminodiethyl *p*-ethylphenylboronate was prepared from *p*-bromoethylbenzene as starting material. When brominated with N-bromosuccinimide, it afforded only a brown tar from which no brominated ester could be recovered. Bromination under the same conditions, however, of *p*-ethylphenylboroxine (III) led in excellent yield to the expected *p*-α-bromoethylphenylboroxine.

Recently, Torssell[9] reported brominating *p*-tolylboronic acid with N-bromosuccinimide and isolating *p*-ω-bromotolylboronic acid and not the corresponding boroxine.

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(1) H. R. Arnold, U. S. Patent 2,402,590, June 25, 1946.

(2) W. L. Ruigh, C. E. Erickson, F. Gunderloy and M. Sedlak, WADC Technical Report 55-26, Part II.

(3) V. A. Sazonova and N. Ya. Kronrod, *Zhur. Obshchei Khim.*, **26**, 1876 (1956).

(4) W. L. Ruigh, A. D. Olin, N. G. Steinberg and P. A. Van Der Meulen, WADC Technical Report 55-26, Part IV.

(5) T. D. Parsons, M. B. Silverman and D. M. Ritter, THIS JOURNAL, **79**, 5091 (1957).

(6) F. R. Bean and J. R. Johnson, *ibid.*, **54**, 4415 (1932).

(7) Unpublished work by R. A. Clarke and S. J. Groszos of these laboratories has shown that alkyl and aryl halides react with metallic magnesium in refluxing *n*-butyl borate to form, respectively, di-*n*-butylalkyl- and or -arylboronates.

(8) A. D. Ainsley and F. J. Challenger, *J. Chem. Soc.*, 2171 (1930).

(9) K. Torssell, *Arkiv Kemi*, **10**, 507 (1957).