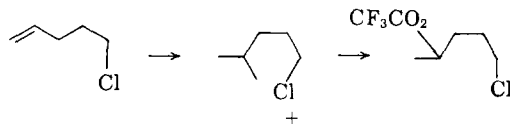


ingly, opens by attack at the primary carbon (to the extent of at least 85% as determined by gas chromatography). In contrast, addition of trifluoroacetic acid to 5-chloro-1-pentene (which probably also reacts *via* a cyclic ion, as shown later)⁹ gives exclusively (>95%) the product arising from reaction of trifluoroacetic acid at the secondary carbon, suggesting car-



bonium ion character in the transition stage for product formation. An analogous interpretation of the product determining step in the reaction of 5-chloro-1-pentyne can be adopted provided the incipient primary carbonium ion formed by ring opening of the cyclic intermediate is *more stable than the vinyl cation* which would be formed by the other mode of ring opening.¹⁰

(9) P. E. Peterson and G. Allen, *J. Am. Chem. Soc.*, in press.

(10) Alternatively the ring opening reaction may possess S_N2 character in this case.

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Anomalous Reduction of an Epoxycyclohexanetetrol to a Cyclohexenetetrol by Potassium Methyl Xanthate¹

Sir:

The normal product from reaction of an epoxide with potassium methyl xanthate is a trithiocarbonate.² For example, the anhydroinositol diketal³ I gives a mixture of the trithiocarbonate diketals IV and V.^{4a} The diastereomer II similarly gives the trithiocarbonate diketal VI.^{4b}

It was expected that the product from similar treatment⁵ of diastereomer III^{6b} would also be VI. The actual product, surprisingly, was a colorless (not yellow) crystalline compound, containing no sulfur, with microanalysis corresponding to C₁₂H₁₈O₄. A permanganate test for unsaturation was positive.

The product, m.p. 67–68°, was finally shown to be the *cis*-cyclohexenetetrol diketal VII of the same reported^{6a,7} melting point. Its identity was established by hydrolysis and acetylation to give the enetetrol tetraacetate, m.p. 102–103° (lit.^{6a,7} 103° or 104°). The infrared spectrum was identical with that of an authentic sample,⁷ and a mixture melting point was not depressed. The quantity of pure VII actually isolated was 31% of theoretical.

Since few methods for regenerating an alkene from its epoxide are available,⁸ extension of this reaction should be useful. However, the most interesting feature at present is the striking stereospecificity which causes diastereomers I and II to form trithiocarbonates and little or no alkene, while III shows the opposite

(1) Aided by a grant (G-15893-R) from the National Science Foundation.

(2) L. Owen, *et al.*, *J. Chem. Soc.*, 1024 (1960); 1030 (1960).

(3) The tetrol formulas I–VII should be understood to represent the corresponding diacetone ketals.

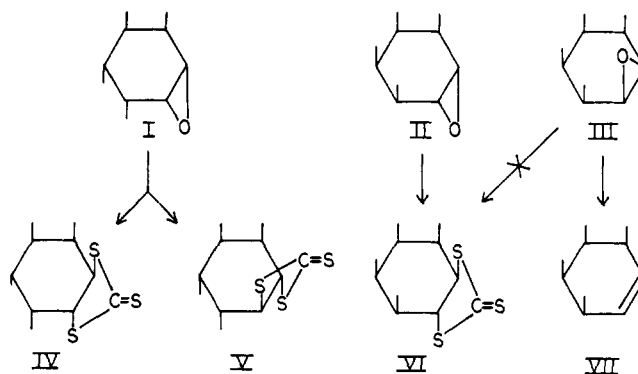
(4) (a) G. E. McCasland, S. Furuta, A. Furst, L. F. Johnson, and J. N. Shooley, *J. Org. Chem.*, **28**, 456 (1963); (b) S. Furuta, unpublished work.

(5) A mixture of epoxide diketal, carbon disulfide, potassium hydroxide, and methanol was boiled under reflux for 5 hr. or longer.

(6) (a) S. J. Angyal, *et al.*, *J. Chem. Soc.*, 375 (1958); (b) *ibid.*, 3691 (1957).

(7) R. Criegee and P. Becher, *Chem. Ber.*, **90**, 2516 (1957). We wish to thank Professor Criegee (Düsseldorf) for a sample of his conduritol-D carbonate diacetate. This sample was hydrolyzed by us with aqueous ethanolic sodium hydroxide, and then acetylated, to provide our authentic sample.

(8) See S. Winstein and R. Henderson in "Heterocyclic Compounds," Vol. I, R. Elderfield Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 44.



behavior.⁹ Efforts to explain these steric effects in terms of configuration and conformation are in progress.

(9) The alkene formation possibly is due to desulfurization of an intermediate episulfide by attack of a nucleophile. See D. Denney and M. Boskin, *J. Am. Chem. Soc.*, **82**, 4736 (1960).

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RECEIVED JULY 23, 1963

Resolution of a Triarylcannabinol and Stereospecific Substitution Reactions

Sir:

Satisfactory methods of resolution have been reported for all types of alkyl and arylalkyl secondary^{1,2} and tertiary^{3,4} carbinols except for the triarylcannabinols.^{5,6} Wallis⁶ obtained *d*-phenylbiphenyl- α -naphthylcannabinol (*d*-ROH) by treating *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid (*l*-RSCH₂CO₂H) with silver nitrate in aqueous acetone, but this method was termed unsatisfactory.¹

The optically active trityl system appeared to us most attractive for studies of the stereochemistry of substitution processes involving ion pairs because the system appears to be free of complicating side reactions, *e.g.*, S_N2 type processes⁷ and elimination reactions. Kinetic and stereochemical studies of optically active trityl derivatives should provide helpful information concerning the mechanism of substitution of trityl compounds.⁷ Wallis recognized the value of such studies, and interest in stereochemical studies of trityl compounds is heightened by recent developments.^{8,9}

This note presents: (1) evidence that the method of Wallis has an optical yield of 60% and that by an extension of the method one can obtain optically pure alcohol; (2) a new method of resolution of triarylcannabinols with high optical yield; (3) proof that both of Wallis' stereospecific substitution reactions take the same stereochemical course; and (4) preliminary evidence that Wallis' reactions proceed with *retention* of configuration.

Alcohol (*d*-ROH) prepared by Wallis' method had $[\alpha]^{25}_D = +10^\circ$ (*c* 1.050),¹⁰ $[\alpha]^{25}_D = +4.4^\circ$ (*c* 0.8 in

(1) A. W. Ingersoll, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 376.

(2) G. H. Green and J. Kenyon, *J. Chem. Soc.*, 751 (1950).

(3) W. von E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **72**, 147 (1950).

(4) H. H. Zeiss, *ibid.*, **73**, 2391 (1951).

(5) C. L. Arcus, J. Kenyon, and S. Levin, *J. Chem. Soc.*, 407 (1951).

(6) E. S. Wallis and F. H. Adams, *J. Am. Chem. Soc.*, **55**, 3838 (1933). A second stereospecific reaction was the conversion of *l*-RSCH₂CO₂H to *l*-ROEt.

(7) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1220 (1957); S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958), and later papers in this series; C. G. Swain and E. E. Pegues, *ibid.*, **80**, 812 (1958).

(8) C. G. Swain and G. Tsuchihashi, *ibid.*, **84**, 2021 (1962), and references quoted therein.

(9) S. G. Smith, *Tetrahedron Letters*, **No. 21**, 979 (1962); A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, **No. 1**, 27 (1963).