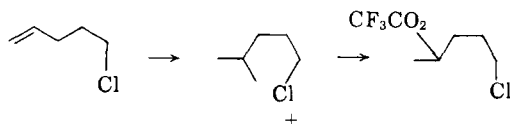


ingly, opens by attack at the primary carbon (to the extent of at least 85% as determined by gas chromatography). In contrast, addition of trifluoroacetic acid to 5-chloro-1-pentene (which probably also reacts *via* a cyclic ion, as shown later)⁹ gives exclusively (>95%) the product arising from reaction 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 SN_2 character in this case.

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PAUL E. PETERSON
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RECEIVED JUNE 17, 1963

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

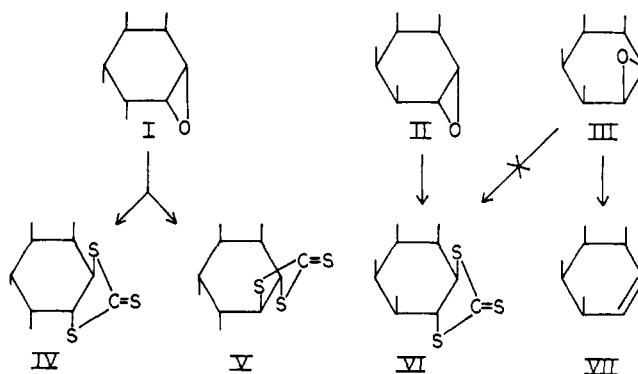
Sir:

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 $C_{12}H_{18}O_4$. A permanganate test for unsaturation was positive.

The product, m.p. 67–68°, was finally shown to be the *cis*-cyclohexanetetrol 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



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 Triarylcarbinol 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 triarylcarbinols.^{5,6} Wallis⁶ obtained *d*-phenylbiphenyl- α -naphthylcarbinol (*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.*, SN_2 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 triarylcarbinols 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).

(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.

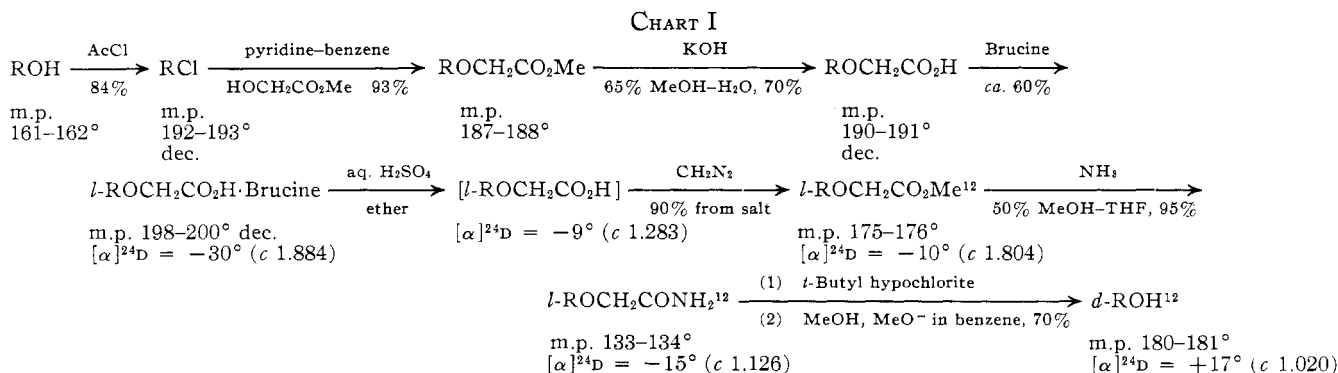
(4) (a) G. E. McCasland, S. Furuta, A. Furst, L. F. Johnson, and J. N. Shooley, *J. Org. Chem.*, **28**, 456 (1963); (b) S. Furuta, unpublished work.

(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.



carbon tetrachloride, rotation $+0.07^\circ$). Wallis⁶ reported for *l*-ROH $[\alpha]^{20}_D = -5.4^\circ$ (*c* 0.451 in carbon tetrachloride, rotation -0.05°). By fractional crystallization of this *d*-ROH from ether one can obtain *d*-ROH with $[\alpha]^{24}_D = +17^\circ$ (*c* 0.937), m.p. $180-181^\circ$, unchanged by three recrystallizations, and *d,l*-ROH, m.p. $161-162^\circ$, after crystallization from cyclohexane. Except for the possibility of anomalous racemates,¹¹ which are extremely rare, the evidence indicates that this alcohol is optically pure.

Our method of resolution is outlined in Chart I. Except as noted beyond, the reactions were carried out by standard methods with yields indicated beneath the arrows. Pilot experiments were carried out with both trityl- and *d,l*-phenylbiphenyl- α -naphthylmethyl derivatives. The acid was liberated from the brucine salt in the usual way⁶ and the ether solution was treated immediately with diazomethane. Treatment of triphenylmethoxyacetamide according to the usual method for preparing methyl carbamates¹³ (bromine in methanolic methoxide) afforded tritylmethyl ether in 85% yield. However, use of *t*-butyl hypochlorite by the procedure of Baumgarten¹⁴ for N-haloamine rearrangement led to the Hofmann rearrangement. *l*-Amide (0.0029 mole) dissolved in 300 ml. of benzene was treated with 0.006 mole of *t*-butyl hypochlorite. Care was exercised to exclude water. To the solution (65°) was added methanolic sodium methoxide (0.009, g.-atom of sodium in 30 ml. methanol) and the mixture was refluxed for 2 hr. Sodium chloride was removed by filtration and the solvent was removed *in vacuo*. The residue was triturated with ether. The solution was filtered and concentrated, whereupon crystals formed, $[\alpha]^{24D} = +14.5^\circ$ (*c* 2.046). The infrared spectrum of this material indicated that it was the alcohol contaminated with a carbonyl compound, probably the methylcarbamate.¹⁵ One recrystallization from ether afforded 0.78 g. of *d*-ROH, $[\alpha]^{24D} = +17.2^\circ$ (*c* 1.020), unchanged within experimental error by further recrystallizations.

Isolation of the alcohol from this last reaction gives assurance that the C-O bond at the asymmetric center has not broken during the reaction. Heterolysis of this bond to give either carbonium ion or carbanion would have resulted in formation of the ether (ROME) or the hydrocarbon (R-H), respectively. Homolysis

(10) Unless otherwise stated, all rotations were taken in chloroform in a 2-dm. cell such that observed rotations were greater than $\pm 0.2^\circ$.

(11) A. Fregda, *Tetrahedron*, **8**, 126 (1960); E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 106-110.

(12) Satisfactory analysis was obtained for this material.

(13) E. S. Wallis and J. F. Lane, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 282.

(14) H. E. Baumgarten, J. E. Dirks, J. M. Petersen, and D. C. Wolf, *J. Am. Chem. Soc.*, **82**, 4422 (1960).

(15) In the *d,l*-series, use of amide-*t*-BuOCl-NaOMe in the ratio 1:1:1 gave a yellow oil whose infrared spectrum is consistent with the carbamate structure. Treatment of this material with excess methoxide in methanol gave ROH.

would not be expected to give alcohol. The evidence indicates that this procedure is satisfactory for resolution of triarylcarbinols in high optical yield and its generality is under investigation. The optical purity of our alcohol is being checked by isotopic dilution studies.

Wallis⁶ converted l -RSCH₂CO₂H to d -ROH with silver nitrate in aqueous acetone and l -RSCH₂CO₂H to l -ROEt with silver nitrate in ethanol. Treatment of Wallis' d -ROH, $[\alpha]^{24D} = +10^\circ$, for 1 week with excess of ethyl iodide and silver carbonate¹⁶ yielded an oil, $[\alpha]^{24D} = -3.5^\circ$ (c 1.20), whose infrared spectrum indicated that it was a mixture of ether and alcohol. Alcohol $[\alpha]^{24D} = +9.4^\circ$ (c 15) was recovered from this mixture by crystallization from benzene-petroleum ether (b.p. 60–70°). This rotation shows that the alcohol was not racemized under the reaction conditions and, therefore, the d -ROH has the same configuration as l -ROEt. The active alcohol was converted *via* the potassium salt and methyl iodide to l -ROME $[\alpha]^{24D} = -5.8^\circ$ (c 1.72). Thus, the reactions of the thioacid with silver nitrate in aqueous and in alcoholic solution take the same stereochemical course. Our current working hypothesis is that these reactions proceed with net *retention* of configuration. This view is based on the reasonable assumption that the least soluble diastereomeric brucine salt of the thioacid (l -RSCH₂CO₂H) has the same configuration at the triarylmethyl carbon as that of the least soluble brucine salt of the oxygen acid (l -ROCH₂CO₂H). Experiments are in progress to establish this point by the method of quasiracemates¹¹ and to develop chemical means of stereochemical correlation for such compounds. For this purpose the thionbenzoate isomerization⁹ and the nitrosoamide deamination¹⁷ are being tested.

We are investigating other leaving groups and other triarylmethyl derivatives.

Acknowledgment.—The author expresses his appreciation to the following students of the graduate pre-research course who carried out several of the pilot experiments: L. DeBow, C. Elliger, J. Robbins, and N. Werstiuk.

(16) K. Mislow, *J. Am. Chem. Soc.*, **73**, 4043 (1951).

(17) E. H. White and J. E. Stuber, *ibid.*, **85**, 2168 (1963).

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BROWN L. MURR

RECEIVED JULY 23, 1963

The Structure of Telomycin

Sir:

The acidic hydrolysis of the antibiotic Telomycin¹ yields alanine, aspartic acid, glycine, β -hydroxyleu-

(1) M. Misiek, O. B. Fardig, A. Gourevitch, D. L. Johnson, I. R. Hooper, and J. Lein, *Antibiot. Ann.*, 852 (1957-1958).