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## NOTE

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# OXYMERCURATION OF OPTICALLY ACTIVE *trans*-CYCLOOCTENE

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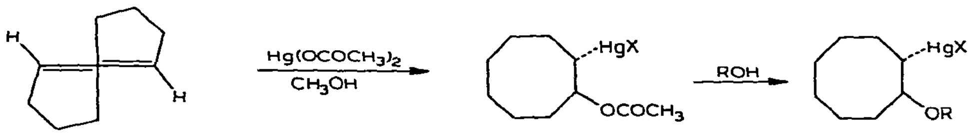
*trans*-Cyclooctene is a very rigid molecule with extremely restricted internal rotation as follows from the optical stability of its enantiomeres[1,2] and NMR-spectra[3]. Some years ago we reported[4] that it added mercuric acetate in various solvents to give at first *trans*-2-acetoxy-cyclooctylmercuric acetate by way of a tentative *cis*-reaction*. We have now succeeded in oxymercuration of the optically active *trans*-cyclooctene (−)I and have obtained the corresponding optically active organomercurials**.



(I, $[\alpha]^{20}_{D}$ − 426°)

(II, X=Cl$^-$, $[\alpha]^{20}_{D}$ + 38°)

(III a, R=OCH$_3$, $[\alpha]^{20}_{D}$ + 18°;
III b, R=OH, $[\alpha]^{20}_{D}$ + 16°)

Since the absolute configuration of *trans*-cyclooctene was established by Cope and Mehta[6] as *R* for (−)I then the configuration of the two asymmetric carbons in (+)II*** can be clearly assigned as *S*. This conclusion is in qualitative agreement with that expected from Brewster's theory[7]. Moreover, the calculations for a cyclohexane analogue[8] give $[M]_D$ 130°, in fair agreement with an experimental 165° for II, as the angles in cyclooctanes are greatly distorted from the usual values.

The acetoxy-adduct II is known[4] to be converted into IIIa or b on exposure in methanol or aqueous acetone for some hours. It is of interest that the optical activity is partly retained which seems to exclude a symmetrical mercurinium ion derived from *cis*-cyclooctene as a single intermediate in the II→III step. Some details of this reaction and the significance of these findings for the oxymercuration mechanism will be discussed elsewhere.

We have now observed a Cotton effect in a methanolic solution of (−)I and

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* Dr. W. L. Waters (University of Montana, U.S.A.) has recently informed us that he and Prof. T. G. Traylor have also observed *cis*-oxymercuration of this racemic olefin.

** A related case of oxymercuration was recently reported for enantiomeric allenes[5].

*** All rotations were measured in dichloromethane, c=0.5–0.7.

silver nitrate believed to be due to a complex formed from these compounds*. Only the first maximum at 232 mμ $[M]_{232} \sim -12000°$ could be clearly observed. Wrixon, Premujic and Scott[10] have recently published details of a similar investigation of some platinum complexes by the circular dichroism technique. In this way they were able to resolve the absolute configuration of olefinic ligands. The silver complexes are said to be suitable also for this technique. Indeed, a negative Cotton effect is correlated with the same effect of a platinum complex and an *R*-configuration of a (−)olefin.

REFERENCES

1 A. C. Cope, C. R. Ganellin, H. W. Johnson, T. V. Van Auken and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 85 (1963) 3276.
2 A. C. Cope and B. A. Pawson, *J. Amer. Chem. Soc.*, 87 (1965) 3649.
3 V. I. Sokolov, O. A. Reutov *et al.*, *Dokl. Akad. Nauk SSSR*, in press.
4 V. I. Sokolov, L. L. Troitskaya and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 166 (1966) 136.
5 W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, 89 (1967) 6261 and private communication from Dr. Waters.
6 A. C. Cope and A. S. Mehta, *J. Amer. Chem. Soc.*, 86 (1964) 5626.
7 J. H. Brewster, *J. Amer. Chem. Soc.*, 81 (1959) 5475, 5483, 5493.
8 V. I. Sokolov and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 148 (1963) 867.
9 A. C. Cope, R. A. Pike and C. F. Spencer, *J. Amer. Chem. Soc.*, 75 (1953) 3212.
10 A. D. Wrixon, E. Premujic and A. I. Scott, *Chem. Commun.*, (1968) 639.

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* To our knowledge, this complex, which has been known for some time[9], has never been isolated as a solid. We obtained it from aqueous solution as fairly stable crystals, m.p. 61–64° (dec.), with a satisfactory analysis for $C_8H_{14} \cdot AgNO_3$.