trichloromethanesulfonyl chloride, gas chromatographic analysis of the reaction mixtures indicated the presence of only the secondary chloride in the mono-chlorinated products. Distillation of the photo-initiated reaction mixture yielded 0.028 mole of chloroform and 0.026 mole of the secondary chloride (b.p. 56° at 65 mm.).

The high degree of specificity noted in chlorinations with trichloromethanesulfonyl chloride results from the selectivity of the trichloromethyl radical in hydrogen abstraction reactions.[6] Precluding any hydrogen migrations in the free radical which results from the hydrogen abstraction reaction and is subsequently chlorinated in reacting with the chlorinating agent, the site of hydrogen abstraction is the location of the chlorine atom in the reaction product. In chlorinations with chlorine, hydrogen abstraction is performed by a chlorine atom, a free radical more reactive and less selective than a trichloromethyl radical. In the case of sulfuryl chloride chlorinations, the sulfur dioxide complexed chlorine atom, which is less reactive and somewhat more selective than a chlorine atom,[7] is involved in the hydrogen abstraction reaction.

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(6) E. S. Huyser, THIS JOURNAL, **82**, 391 (1960).

(7) G. A. Russell and H. C. Brown, *ibid.*, **77**, 4031 (1955).

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RECEIVED AUGUST 19, 1960

THE ABSOLUTE CONFIGURATION OF BIARYLS BY ROTATORY DISPERSION COMPARISON WITH A SESQUITERPENE[1]

Sir:

The extraordinary optical activity of santonide (I) and parasantonide (II) has been the subject of some comment.[2] We now report a striking coincidence: *the rotatory dispersion (RD) curves*[3] *of I and II are virtually superimposable (see Fig. 1)*[4] *on the RD curve of the bridged biphenyl ketone (+)-III,*[5] *while the relative asymmetric disposition of double bond and carbonyl π-electrons in all three compounds (carbon atoms 1–4) is the same.* Since the absolute configurations of I and II are assured,[6] we are led to the conclusion that (+)-III has the (R)-configuration, as shown. *The previously established*[5,7] *absolute configurations of the biaryls have thus been independently corroborated.* A configurational correlation of two different stereoisomeric *types* by the RD-method[8] appears to be without precedent.

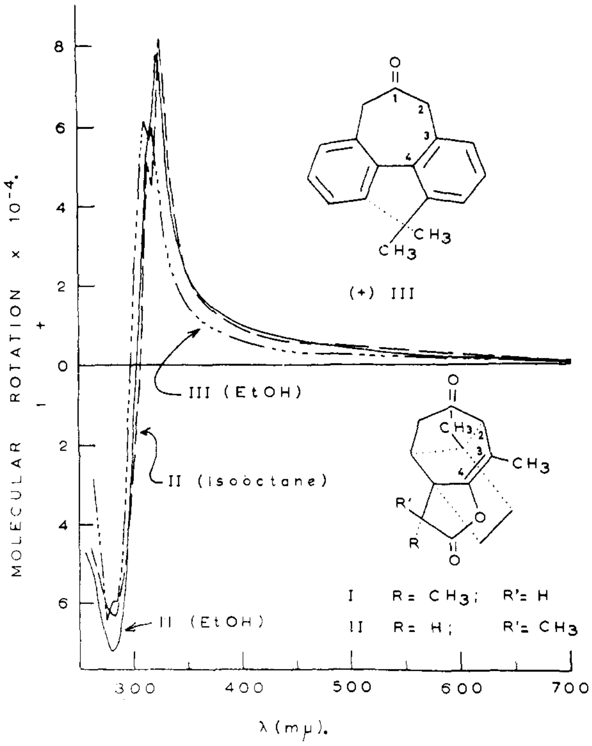

Fig. 1.

We hope to explore the generality of this observation.

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(1) "Configurational Studies in the Biphenyl Series. X." "Optical Rotatory Dispersion Studies. XL." For preceding papers see ref. 5.

(2) R. B. Woodward and E. G. Kovach, THIS JOURNAL, **72**, 1009 (1950); R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

(3) S. Mitchell and K. Schwarzwald, *ibid.*, 889 (1939).

(4) The RD curve of parasantonide (II) in ethanol solution measured in our laboratory (Fig. 1) on a sample kindly provided by Prof. R. B. Woodward, is in good agreement with that published earlier (ref. 3). The corresponding curve in isoöctane solution (Fig. 1) is characterized by the same type of fine structure as was recorded (ref. 5) for the isoöctane curve of III and has been attributed to homoconjugation of the carbonyl and benzene π-electrons.

(5) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg and C. Djerassi, THIS JOURNAL, **82**, 4740 (1960).

(6) R. B. Woodward and P. Yates, *Chem. & Ind.*, 1391 (1954); H. Bruderer, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 858 (1956).

(7) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

(8) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960.

(9) Fellow of the Alfred P. Sloan Foundation.

(10) Financial support has been provided by the National Cancer Institute (grant No. CRTY-5061) of the National Institutes of Health, U. S. Public Health Service. The rotatory dispersion measurements were made by Mrs. Ruth Record.

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RECEIVED JULY 25, 1960

PRODUCTION OF BENZYNE INTERMEDIATES FROM PERCHLORYL AROMATIC COMPOUNDS[1]

Sir:

We have examined the reactions of some perchloryl aromatic compounds with amide ions in liquid ammonia,[2] using anilide ions as a convenient trap for any benzynes produced.[3] Perchlorylbenzene (Ia) undergoes a very vigorous reaction with amide and anilide ions in liquid ammonia at −33°, so vigorous that extensive formation of carbonaceous matter can result unless addition is carefully controlled.[4] The major product iso-

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(1) Presented at the 138th National A.C.S. Meeting, New York, N. Y., Sept. 1960.

(2) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956); J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenow, *ibid.*, **78**, 611 (1956).

(3) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958).

(4) The perchloryl aromatic compound was always added portionwise, and cautiously, to the liquid ammonia medium.