The known spectrum[12] of NH_2 in solid rare gas was observed in the visible region. The NH_2 absorption intensity in experiment II after 3 hours of photolysis is approximately five times more intense than it is after 6 hours of photodeposition. In II, the intensity of NH_2 in Kr is roughly twice that in Xe when the photolysis times are the same. This indicates that diffusion or steric orientation effects are important to some extent in the formation of NH_2.

The integrated intensity of NH_2 (Xe, Expt. II) was about 1/200 that of NH. Assuming all the NH_2 to be formed from the reaction of NH with a nearest neighbor HN_3, taking this reaction to be 100% efficient, and using the known oscillator strength of NH, the oscillator strength of the NH_2 ($^2A_1\pi_u$—$^2B_1$) transition is estimated to be 2×10^{-4}. In experiments where free radicals are trapped from electrical discharges[4,5] the intensities of NH and NH_2 spectra are comparable. The presence of weak, broad features in the region near 2600 Å. give rise to the suspicion that the N_3 radical is also trapped in detectable quantities.

[12] Ref. 4 and unpublished work.

[13] National Science Foundation Predoctoral Fellow.

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TRICHLOROMETHANESULFONYL CHLORIDE AS A SELECTIVE CHLORINATING AGENT[1]

Sir:

Trichloromethanesulfonyl chloride has been found to be an effective free radical chlorinating agent. Specificity in the site of chlorination makes it preferable in certain instances to such chlorinating agents as chlorine and sulfuryl chloride. The reaction can be initiated either photochemically or with benzoyl peroxide. The products of the reaction are equimolecular amounts of the chlorinated substrate, chloroform and sulfur dioxide.

$$Cl_3CSO_2Cl + RH \longrightarrow RCl + HCCl_3 + SO_2$$

The free radical chain sequence shown is suggested to account for these products and their distribution

$$Cl_3C\cdot + RH \longrightarrow HCCl_3 + R\cdot$$

$$R\cdot + Cl_3CSO_2Cl \longrightarrow RCl + Cl_3C\cdot + SO_2$$

In a reaction photo-initiated with a 275-watt General Electric sun lamp, an excess of toluene and 0.10 mole of trichloromethanesulfonyl chloride maintained at 110–115° for eight hours yielded 0.08 mole of sulfur dioxide and 0.08 mole of benzyl chloride (b.p. 79–81° at 25 mm.; $n^{25}D$ 1.5240). In a repetition of this reaction, 0.06 mole of chloroform and 0.06 mole of benzyl chloride were isolated. The infrared spectrum of the benzyl chloride obtained in these reactions was identical with that of an authentic sample. An excess of cyclohexane and 0.20 mole of trichloromethanesulfonyl chloride heated at 80° for 40 hours in the presence of 0.02 mole of benzoyl peroxide resulted in the formation of 0.20 mole of chloroform and 0.20 mole of cyclohexyl chloride (b.p. 140–142° at atm. press., $n^{25}D$ 1.4610). The infrared spectrum of this material was identical with that of an authentic sample of cyclohexyl chloride.

n-Alkylbenzenes are chlorinated only in the benzylic position by this reagent. A reaction mixture consisting of 1.00 mole of ethylbenzene and 0.20 mole of trichloromethanesulfonyl chloride maintained at 78–80° for 72 hours in the presence of 0.012 mole of benzoyl peroxide yielded on distillation 0.11 mole of chloroform and 0.10 mole of α-chloroethylbenzene (b.p. 77–78° at 17 mm.; $n^{25}D$ 1.5230). The infrared spectrum of this chlorinated product showed no absorption band at 718 cm.$^{-1}$, the position at which a very strong absorption band was found to be present in the spectrum of an authentic sample of β-chloroethylbenzene. The infrared spectrum of the chlorination product obtained by the photochlorination of ethylbenzene at this same temperature with chlorine indicated the product to contain about 10% of β-chloroethylbenzene. In a benzoyl peroxide initiated chlorination of ethylbenzene with sulfuryl chloride at 80°, infrared analysis showed that about 7% of the product was the beta isomer.

Trichloromethanesulfonyl chloride also can be used to chlorinate the alkyl side chain of compounds having an aromatically bonded bromine atom without replacement of this bromine by chlorine. Such substitutions are known to occur in chlorinations of *p*-bromotoluene as well as other aryl bromides with both chlorine and sulfuryl chloride.[2] In a photo-initiated reaction, 0.50 mole of *p*-bromotoluene and 0.115 mole of trichloromethanesulfonyl chloride heated at 110–115° for 10 hours gave on distillation 0.10 mole of chloroform and 0.11 mole of *p*-bromobenzyl chloride (m.p. 39–39.5°; reported, 38–39°[3]). There was no evidence of any replacement of the aromatically bonded bromine by chlorine in this reaction.

Selectivity also is noted in the chlorination of *n*-alkanes with this reagent, the hydrogens on a secondary carbon being more susceptible to subtitution than hydrogens on a primary carbon. Gas chromatographic analysis[4] of the reaction mixtures obtained in the chlorination of *n*-hexane with chlorine and sulfuryl chloride at 70° indicated the presence of two main mono-chlorinated products. The retention time of the larger chromatographic peak under the conditions specified was 12 minutes and that of the smaller peak, 17 minutes. These retention times were the same as those found for authentic samples of 2-chlorohexane and 1-chlorohexane, respectively.[5] The primary halide amounted to 22% of the mono-chlorinated products in the reaction with chlorine and 17% in the reaction with sulfuryl chloride. However, in both the photo-initiated and benzoyl peroxide initiated reactions of 0.30 mole of *n*-hexane with 0.10 mole of

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[1] Initial experiments performed in The E. C. Britton Research Laboratory, The Dow Chemical Co., Midland, Mich.

[2] B. Miller and C. Walling, THIS JOURNAL, **79**, 4187 (1957).

[3] G. Errera, *Gazz. chim. ital.*, **18**, 239 (1888).

[4] The gas chromatographic analysis were performed on a seven foot, 1/4 inch column packed with 15% di-*sec*-octyl sebacate on Chromosorb W. Column temperature was 78° and the carrier gas was helium with a head pressure of 10 p.s.i.g.

[5] The 2-chlorohexane and 3-chlorohexane were not separated by this chromatographic technique.

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).

DEPARTMENT OF CHEMISTRY
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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.

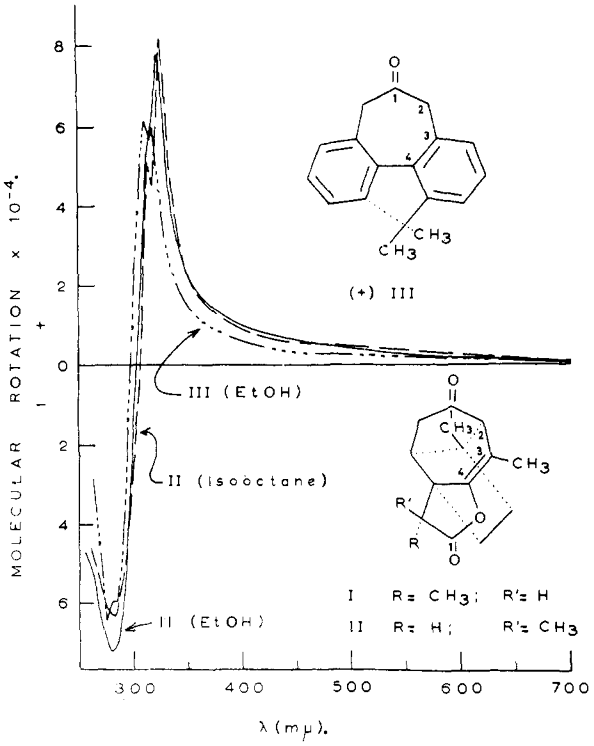

Fig. 1.

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.