isomerized thermally to *trans*-IVa at room temperature. The thermal stability of *cis*-IIIa and -IVa was found to be concentration dependent. They were relatively stable when formed by irradiation at room temperature in alcoholic solvents in 10^{-4} *M* ($t_{1/2} \sim$ 24 hr). The uv spectrum of the photostationary mixture of IVa was similar to that obtained by dilution of the concentrated solution irradiated in the nmr tube to the photostationary state at −60°. The uv spectrum of *cis*-IVa[11] was determined from the photoequilibrium composition and the isosbestic point for cis → trans thermal isomerization.

The ratio of *cis*- and *trans*-IVa at the photostationary state is very different from the ratio of *cis*- and *trans*-IVb formed at the end of the photocyclization reaction. For this reason the quantum yields of the photoreactions for each isomer were determined at 23° (10^{-4} *M*) and are reported in Table I. From the quantum yields of formation of *trans*- and *cis*-IVa[12] and of IVb formation from *cis*- and *trans*-IVa, the calculated ratio of IVb isomers formed after the photostationary state was reached, assuming stereospecificity, is 68% cis:32% trans. After the IVa photostationary state was reached on irradiation at −60°, the ratio of IVb isomers found by nmr was 71% cis:29% trans. Therefore, these results indicate stereospecificity in the nitrone photocyclization reaction.

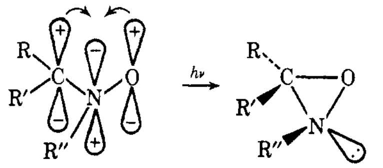
Table I. Quantum Yields for Products at 23° [a]

Reaction	Solvent	ϕ
trans-Ia → *trans*-Ib	Isopropyl alcohol	0.26
trans-IVa → IVb[b]	Methanol	0.016
trans-IVa → *cis*-IVa[c]	Methanol	0.18
cis-IVa → *trans*-IVa[d]	Methanol	0.46
cis-IVa → IVb[b]	Methanol	0.087

[a] Wavelength, 366 nm; concentration, 10^{-4} *M;* ferrioxalate actinometry. [b] Determined by decrease in optical density at 327 nm, isosbestic point of the nitrone isomers. [c] Determined by change in ratio of optical density at 357 and 317 nm. [d] Calculated from the photostationary state relation, $\phi_{t\rightarrow c}\epsilon_t X_t^{\infty} = \phi_{c\rightarrow t}\epsilon_c X_c^{\infty}$, where X_t^{∞} and X_c^{∞} are the mole fractions of the isomers at photoequilibrium.

For the reverse thermal cleavage of oxaziridine to nitrone, Ib in CD_3OD gave a 50:50 mixture of *cis*- and *trans*-Ia with a first-order rate constant, 6.8 × 10^{-4} sec^{-1} at −8°, by nmr spectroscopy.[13] The first-order rate constant for *cis*- → *trans*-Ia under these conditions was 2.9 × 10^{-5} sec^{-1} at 23°. Only in alcoholic solvents was the rate of the thermal *cis*- → *trans*-Ia isomerization slower than the rate of the Ib ring-opening reaction.[14] The photostationary state composition of Ia was confirmed to be 100% *trans*-Ia.

The *trans*-Ib thermal cleavage to *cis*- and *trans*-Ia is clearly in accordance with the predictions of the orbital symmetry rules. The observed stereospecificity in the nitrone photocyclization is consistent with the symmetry of the nitrone antibonding molecular orbital. As the carbon–oxygen σ bond forms in disrotatory motion, the nitrogen π orbital rehybridizes to a lone-pair sp^3-hybridized orbital in the opposite direction, giving an oxaziridine with the same configuration as the initial nitrone.



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(11) *trans*-IVa: λ_{max}^{MeOH} 338 nm (ϵ 14,800). *cis*-IVa: λ_{max}^{MeOH} 325 nm (ϵ 13,750). Although the uv of the IIIa photostationary state was similar to that of IVa, the photostationary state composition could not be determined because of the lesser solubility of IIIa in CD_3OD.

(12) The combined $\phi_{t\rightarrow c}$ and $\phi_{c\rightarrow t}$ suggest, in addition to oxaziridine formation, the efficient formation of a common twisted state analogous to the twisted state in the stilbene direct photoisomerization: (a) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90,** 3907 (1968); (b) J. Saltiel and E. D. Megarity, *ibid.*, **91,** 1265 (1969); **90,** 4759 (1968).

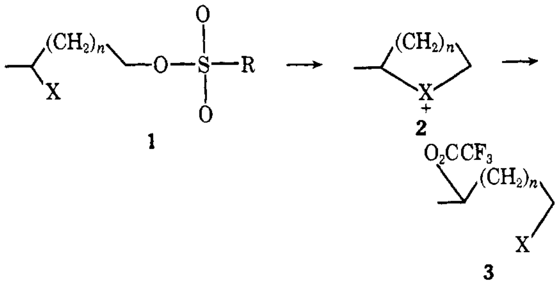
(13) *trans*-Ia: α-CH, τ 2.19; NCH_3, τ 6.27. *cis*-Ia: α-CH, τ 1.94; NCH_3, τ 6.15. No *cis*-Ia was detected in the partial irradiation of *trans*-Ia.

(14) At 23° in isopropyl alcohol (10^{-4} *M*) the ring cleavage rate was 3.4 × 10^{-4} sec^{-1}; the *cis*- → *trans*-Ia thermal rate was 4.0 × 10^{-7} sec^{-1}.

1,3-Halogen Shifts Occurring *via* Four-Membered Ring Halonium Ion Intermediates in the Solvolyses of 3-Halo-1-butyl Trifluoromethanesulfonates

Sir:

The trifluoroacetolysis of primary sulfonate–secondary halides has proved[1] to be an especially advantageous reaction for observing halogen shifts presumed to result from ring opening of halonium ion intermediates (eq 1). According to our analysis of the



(1)

products and rates of *p*-nitrobenzenesulfonate solvolyses (eq 1, R = *p*-$NO_2C_6H_4$), 1,2, 1,4, and 1,5 participations predominate over competing normal solvolyses by the ratios (k_Δ/k_s) 2000, 760, and 7.1, respectively.[1] In contrast with the postulated intermediacy in these reactions of halonium ions consisting of three-, five-, and six-membered rings, evidence was lacking for formation of a four-membered chloronium ion ring.[1] We now report that the 1,3-halogen shift occurs in the trifluoromethanesulfonates **1** (n = 1, R = CF_3).[2] Participation tendencies decrease in the sequence I > Br > Cl, the amount of Cl shift being no more than a few per cent. These results complement those of Reineke and McCarthy,[3] who have reported a 1,3-bromine migration

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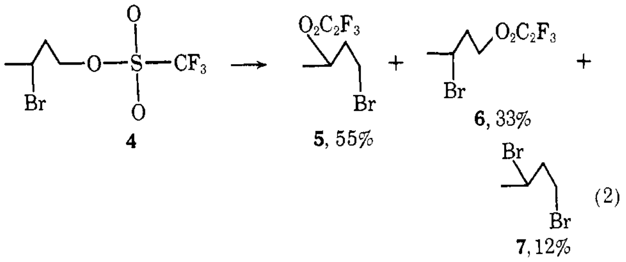
(1) (a) P. E. Peterson and J. F. Coffey, *Tetrahedron Lett.*, 3131 (1968); (b) J. F. Coffey, Ph.D. Thesis, St. Louis University, 1969; P. E. Peterson and J. F. Coffey, *J. Amer. Chem. Soc.*, in press; (c) see G. A. Olah and P. E. Peterson, *ibid.*, **90,** 4675 (1968), for references to observation by nmr to three-membered and five-membered ring halonium ions.

(2) For applications of the enhanced reactivity of triflates see T. M. Su, W. F. Sliwinski, and P. Schleyer, *ibid.*, **91,** 5386 (1969), and references cited therein.

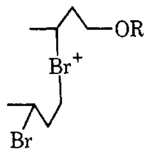
(3) C. E. Reineke and J. R. McCarthy, Jr., *ibid.*, **92,** 6376 (1970).

during a deamination of 3-bromo-2,2-bis(bromomethyl)-1-d_2-propylamine perchlorate. A four-membered ring halonium ion intermediate has been postulated in the bromination of a substituted bicyclo[2.2.1]-heptane[4a] and in the bromination of bicyclo[2.1.0]-pentene.[4b]

Our results for the trifluoroacetolysis of 0.1 *M* bromotriflate at 60° in the presence of 0.125 *M* sodium trifluoroacetate are summarized in eq 2. Also given are relative mole per cent yields, estimated by analysis of time-averaged nmr spectra at 100 MHz of the trifluoroacetic acid solution from solvolysis of 0.1 *M* triflate. Analysis of distilled material (58% yield) gave similar results (eq 2). In addition to the formation of 55% 1,3-halogen shifted product, the presence in the product of substantial amounts of 1,3-dibromobutane (7) was of interest as an unanticipated result. The "disproportionation product" 1,3-butanediol bistrifluoroacetate was shown to be absent. The relative yield of 7 was shown to be independent of the per cent reaction and of the initial concentration of 4. These observations rule out formation of 7 *via* the dialkylhalonium ion 8. Presumably, therefore, 7 is derived from the reaction of 4 with bromide ions in the solution. Bromide ions may result from elimination in 4 to give highly reactive allylic bromide or, less likely, *via* the 1,3 cleavage of 4 or cycloreversion of the intermediate halonium ion (suggested by the results of ref 3). The absence of the anticipated products of β cleavage[3] or cycloreversion[3] of the halonium ion intermediate, ethylene bromide, and acetaldehyde, serve to support the first alternative for the formation of 7. Acetaldehyde was stable under the reaction conditions and detectable by nmr at a concentration equivalent to a 2% yield. In support of the postulated origin of dibromide 7, triflate 4 reacted rapidly with tetraethylammonium bromide in trifluoroacetic acid–sodium trifluoroacetate to give 7. Furthermore, the dibromide 7 was stable under the conditions of solvolysis of triflate 4. For the reaction of 4, $t_{1/2}$ was approximately 4 hr. Identification of 6 and 7 was accomplished by glc and nmr analysis, using authentic samples.



(2)



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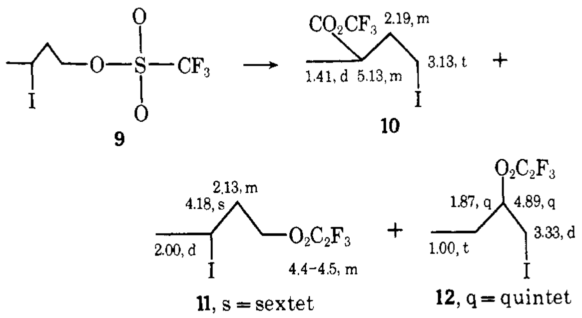
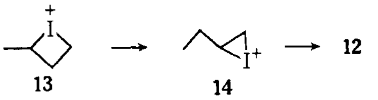
The reaction of 3-iodo-1-butyl triflate showed qualitative evidence of modest rate enhancement ($t_{1/2}$ approximately 20 min, 60°). Nmr analysis (100 MHz) of the reaction mixture before or after extraction into CCl_4 surprisingly indicated the presence of a tentatively identified rearranged component **12**, in addition to the expected product of iodine shift, **10**. The relative mole per cents (nmr analysis) of **10**, **12**, and **11** were 58, 36, and 6, respectively. A reference sample of **11** was available, but identification of **10** and **12** was based on the clean multiplets observed in early and late platinum spinning band distillation fractions (yield of distillate, 38%), exhibiting increased proportions of **12** and **10**, respectively. (*Cf.* nmr data, eq 3.) Gas chromatography of the distillate using stainless steel columns failed. Tentatively, the formation of **12** is ascribed to the rearrangement shown in eq 4.[5]



(3)



(4)

The time-averaged nmr spectrum (100 MHz) of the products of solvolysis of 3-chloro-1-butyl triflate indicated the presence of only approximately 5% of primary chlorides, possibly a mixture of compounds analogous to 5 and 7. According to the results we have given, the relative halogen reactivity in 1,3 participation is intermediate between that for 1,2 participation (I >> Br >> Cl)[6] and that for 1,4 participation (I ≥ Br ≥ Cl).[7]

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[4] (a) M. M. Avram, I. Pogany, F. Badea, I. G. Dinulescu, and C. D. Nenitzescu, *Tetrahedron Lett.*, 3851 (1969); (b) R. T. Lalonde, *J. Amer. Chem. Soc.*, **87**, 4217 (1965).

(5) For a related case see ref 1c.

(6) (a) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948); (b) E. Grunwald, *ibid.*, **73**, 5458 (1951).

(7) For references see (a) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *ibid.*, **92**, 2834 (1970); (b) P. E. Peterson, *Accounts Chem. Res.*, in press.

(8) (a) Address correspondence to this author after Sept 1, 1971 at: Department of Chemistry, University of South Carolina, Columbia, S.C. 29208. (b) A. B., June 1971.

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Synthesis and Decarbonylation of Pyruvoylpentacarbonylmanganese

Sir:

The carbonylation of $CH_3Mn(CO)_5$ to give $CH_3COMn(CO)_5$ has been extensively studied[1,2] and shown

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(1) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

(2) K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968), and references therein.