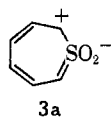


tion. The aforementioned properties suggest the resonance energy (if any) acquirable from charge-separated canonical forms (e.g., **3a**, presumably involving d-orbital participation) is insufficient to compensate for the angle strain required to form a planar conjugated system. Final conclusions must await



study of the reactions of thiepin 1,1-dioxide and its derivatives.

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Possible Fluoronium Ion Intermediates in the Reaction of Trifluoroacetic Acid with 5-Fluoro-1-pentyne and 5-Fluoro-2-pentyl Tosylate¹

Sir:

Fluoronium ion intermediates have not been postulated. However, in one very recent study an unsymmetrical, cyclic, donor-acceptor complex was observed by nmr spectroscopy of succinyl fluoride in a 1,1,2-trifluorotrichloroethane-SbF₅ solution.^{2a} Fluorocarbenium ions, having a partial positive charge on fluorine, are under active investigation.^{2b} We wish to report evidence for fluorine participation and a fluoronium ion intermediate or transition state in the reaction of 5-fluoro-1-pentyne with trifluoroacetic acid. The reaction products and their percentages are given in Scheme I.³

Since the reaction of 5-chloro-1-pentyne with trifluoroacetic acid leads to ~85% of a stable vinyl chloride⁴ analogous to **3**, our original expectation was that any fluorine shift in the reaction of 5-fluoro-1-pentyne would lead to **3**. When **4**, but no detectable **3**, was found as a reaction product, we realized that the participation pathway of Scheme I would be tenable only if the secondary reaction **3** → **4** was markedly more facile than the analogous reaction involving the vinyl chloride. Independent evidence supporting the postulated reactivity difference was provided by a determination of the rates of reaction of 2-halopropenes with trifluoroacetic acid to give 2-halo-2-propyl trifluoroacetates (cf. Table I). The 200-fold greater reactivity of fluoropropene, compared to chloropropene, provides strong assurance that **4**, not **3**, is the *expected* ultimate

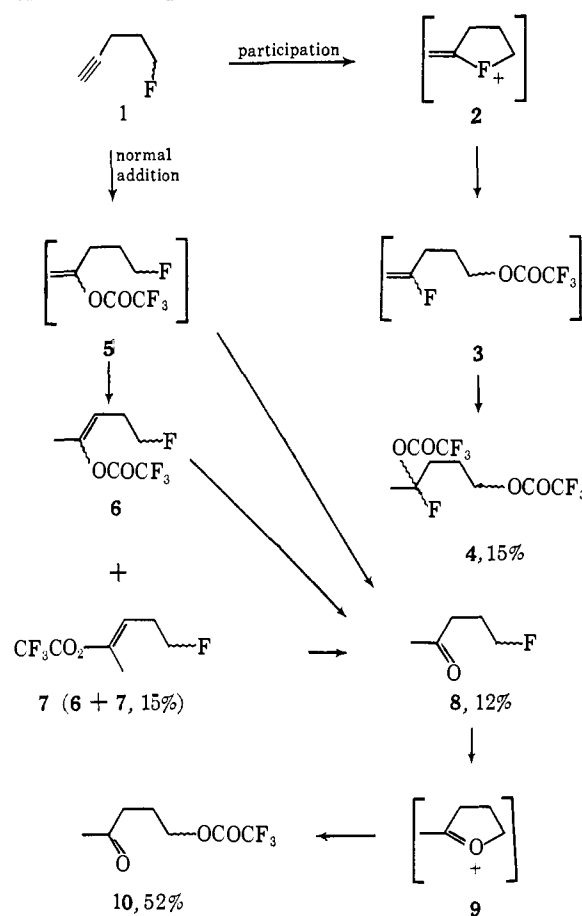
(1) (a) This work was supported in part by National Science Foundation Grant GP 2917. Award of a NASA traineeship is gratefully acknowledged by R. J. Bopp. (b) Reported in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12-16, 1966, Organic Abstracts, paper 3.

(2) (a) G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 3313 (1966); (b) G. A. Olah, C. A. Cupas, and M. B. Comisarow, *ibid.*, **88**, 362 (1966).

(3) Percentages are based on areas of gas chromatographic peaks (flame detector) of a flash distillate. Analysis by nmr gave closely similar results. Identification of preparative gas chromatographic fractions was accomplished by nmr analysis. Identifications of **8** and **10** were confirmed by comparison with authentic samples. The structure of **4** was confirmed by carbon and hydrogen analysis, by prolonged solvolysis to give **10**, and by the close correspondence of the nmr spectrum with that of 2-fluoro-2-trifluoroacetoxypropane, CH₃ doublet at δ 1.90, *J*_{HF} = 18 cps.

(4) (a) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966). (b) The chloride undergoes slow further reaction with trifluoroacetic acid.

Scheme I. Reaction of 5-Fluoro-1-pentyne with Trifluoroacetic Acid



product of 1,4-fluorine shift in the reaction of 5-fluoro-1-pentyne. Furthermore, the relative rates in Table I provide a striking illustration of the effectiveness of 2p-2p overlap in stabilizing the 2-fluoropropyl cation. These data suggest that fluorine may stabilize a carbonium ion in solution, compared to hydrogen. Previously this thermodynamic stability order has been strongly indicated only in gas-phase mass spectroscopic studies.⁵

Table I. First-Order Rate Constants for Reaction of Trifluoroacetic Acid with Propenes at 25.0°

Compound	10 ⁶ <i>k</i> , sec ⁻¹	<i>k</i> _X / <i>k</i> _H
	4.81	1
	340	71
	1.70	0.35
	0.395	0.082




Turning our attention to the proposed normal addition pathway (Scheme I), we note that reactions of 1-hexyne and/or 5-chloro-1-pentyne with trifluoroacetic acid^{4a} provide analogies for the formation of all of the observed products including the, at first sight, surprising major product, 5-trifluoroacetoxy-2-penta-

(5) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 1353 (1966).

none (10). A separate experiment showed that 8 was, in fact, converted to 10 under our reaction conditions sufficiently rapidly to account for the 10 obtained from 5-fluoro-1-pentyne. We also observed the conversion of 4 to 10, but the rate of reaction was insufficient for an appreciable proportion of the 10 obtained from 5-fluoro-1-pentyne to have arisen *via* the 4 → 10 pathway. That a special mechanism such as that of Scheme I is needed to account for loss of terminal fluorine (in 10) was evident from a control experiment in which 1-fluorohexane was shown to be stable in trifluoroacetic acid-sodium trifluoroacetate. Perhaps our most important control experiment was a clear demonstration that 4 was not formed from 10 under carefully simulated reaction conditions involving added sodium fluoride and trifluoroacetic anhydride in addition to sodium trifluoroacetate. All of these results lend support to the postulated competition between "normal addition" and "fluorine-shift" pathways.

In a separate series of experiments the ω -fluoroalkyl tosylates shown in Table II were solvolyzed in trifluoroacetic acid in order to obtain possible rate evidence for fluorine participation. Analysis of these

Table II. First-Order Rate Constants for Solvolysis of ω -Fluoroalkyl Tosylates at 25°

Tosylate	$10^5 k$, sec ⁻¹	k_H/k_X
	0.0502	291
	2.14	8.87
	7.37	3.38

results depends on our earlier demonstration that large inductive effects upon rates of reaction of approximately 40 alkenes with trifluoroacetic acid⁶ (also shown by the tosylates) could be correlated with an uncertainty of approximately $\pm 10\%$ by "attenuation plots," allowing even small participation effects to be evaluated.

The data in Table II, treated in this way, lead to a value of k_{Δ}/k_s (the ratio of rate constants for participation and for normal solvolysis) of 2.4. This modest but, in our judgment,⁷ probably significant effect was approximately that which we expected, based on unpublished studies of the more strongly participating chloroalkyl tosylates. We conclude that our studies have provided moderately good rate evidence for fluorine participation in tosylate solvolyses and, in the reaction of 5-fluoro-1-pentyne, a probable example of a

(6) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Am. Chem. Soc.*, **87**, 5163 (1965).

(7) We are aware that our judgment will be disputed, especially by those who make a comparison between our results and those obtained from solvolysis of cyclic and bicyclic systems, where interpretation of rate variations by factors as large as 10^2 or even 10^8 may be controversial. Our own studies have taken advantage of the very much greater predictability of rates in aliphatic systems, as evidenced especially by our discovery of 1,4-halogen shifts based originally on observation of an eightfold rate effect.

1,4-fluorine shift which arises *via* a fluoronium ion intermediate or transition state.

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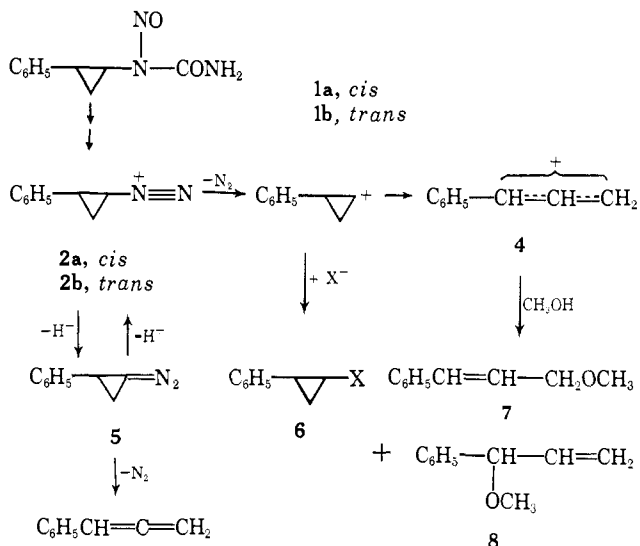
Received December 23, 1966

The Decomposition of Cyclopropyldiazonium Ions

Sir:

The solvolysis of cyclopropyl tosylates has recently been classified as a concerted process, with ring opening occurring in the transition state.¹ The cyclopropyl cation, presumably a highly energetic intermediate, is bypassed in the solvolysis of cyclopropyl tosylates.

We have studied the decomposition of cyclopropyldiazonium ions as a more promising route to cyclopropyl cations. Our arguments rest on product stereochemistry rather than kinetics. Therefore, two possible sources of error had to be eliminated: (i) acid-catalyzed equilibration of the (allylic) products; (ii) base-catalyzed equilibration of isomeric diazonium ions (*e.g.*, 2a,b) *via* diazoalkane (*e.g.*, 5). This type of reaction is readily detected in deuterated solvents. Intervention of the diazoalkane leads to incorporation of deuterium, while products free of deuterium result from decomposition of the diazonium ions prior to deprotonation.



Treatment of N-nitroso-N-2-phenylcyclopropylurea (*cis*- and *trans*-1a,b) with excess sodium formate in CH₃OD afforded phenylallyl methyl ethers (7, 8) with 0.25 g-atom of D/mole (nmr).² Consequently, only 25% of the diazonium ions 2a,b may have suffered *cis-trans* isomerization *via* 5. However, both 1a and 1b afforded *trans*-cinnamyl methyl ether (*trans*-7) with only a trace of the *cis* isomer (Table I). If the decomposition

(1) C. H. De Puy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4007 (1965); **88**, 3343 (1966); P. von R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(2) With KDCO₃-CH₃OD the deuterium content of 7 and 8 rose to 0.65 g-atom of D/mole; the yield of phenylallene was 0.5–0.8%. With 1 equiv of NaOCH₃ phenylallene was the major product (78–84%). Phenylallene results from the thermolysis of 5; *cf.* W. M. Jones, *et al.*, *J. Am. Chem. Soc.*, **82**, 6200 (1960); **85**, 2754, 3309 (1963); **86**, 912 (1964).