

Iminosulfenes¹

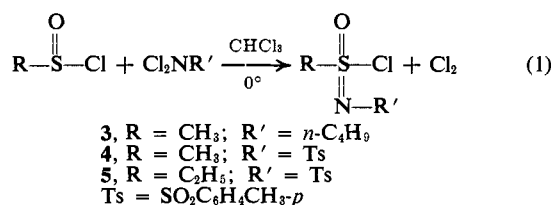
Sir:

Sulfenes (**1**) have been recognized through interception reactions as important transient reaction intermediates.² It occurred to us that related iminosulfenes (**2**) might be generated from appropriate precursors. Furthermore, the valency of nitrogen might afford an interesting opportunity to manipulate the polar character and, hence, reactivity of such intermediates (**2**) by variation of the nature of group X.



Several unsuccessful attempts to prepare iminosulfonyl chlorides have been reported; in 1960 Levchenko and Kirsanov³ succeeded in preparing the first derivatives of aromatic iminosulfonic acids. In this communication the first examples of esters and acid chlorides of aliphatic iminosulfonic acids⁴ are reported, and definitive evidence for the existence of an iminosulfene as a transient intermediate is described.

Alkaniminosulfonyl chlorides⁵ (**3-5**) have been prepared in 57-90% yield by the method employed by Levchenko⁶ for the preparation of areneiminosulfonyl chlorides (eq 1). N-Butylmethaniminosulfonyl chlo-



ride (**3**) is a very reactive, unstable liquid. The N-*p*-toluenesulfonyl derivatives **4** (mp 100-101°) and **5** (mp 44-45°) are less reactive and are stable solids at room temperature.

The alkaniminosulfonyl chlorides reacted with alcohols to give sulfonamides (see below). With **4** and **5** in the absence of added base, the reactions with alcohols were slow; heating for several hours was necessary to complete the reactions. However, the reactions of **4** and **5** with alcohols were very fast even at 0° in the presence of triethylamine. Base catalysis is consistent with the occurrence of an iminosulfene intermediate.

(1) Part XXV in the series Sulfoxides and Related Compounds. We gratefully acknowledge support by the National Science Foundation (Grant No. GP 8648).

(2) For a review of sulfene reactions, see G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967). For more recent references see J. F. King and T. W. S. Lee, *J. Amer. Chem. Soc.*, **91**, 6524 (1969); L. A. Paquette, J. P. Freeman, and R. W. Houser, *J. Org. Chem.*, **34**, 2901 (1969); W. E. Truce, J. W. Fieldhouse, D. J. Vrencur, J. R. Norell, R. W. Campbell, and D. G. Brady, *ibid.*, **34**, 3097 (1969).

(3) E. S. Levchenko and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 1553 (1960); *J. Gen. Chem. USSR*, **30**, 1562 (1960). In this paper it was established that the reported [J. von Braun and K. Weissbach, *Ber.*, **63**, 2836 (1930)] preparation of alkaniminosulfonyl chlorides was erroneous.

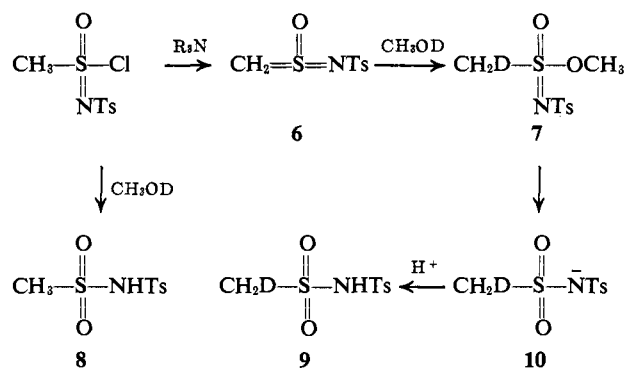
(4) R. G. Laughlin [*J. Amer. Chem. Soc.*, **90**, 2651 (1968)] has reported the preparation of aliphatic sulfonamide methylimines and bis(methylimines).

(5) All new compounds gave analytical values and nmr and ir spectra in agreement with the structures indicated.

(6) E. S. Levchenko, L. N. Markovskii, and A. V. Kirsanov, *Ukr. Khim. Zh.*, **33**, 337 (1967); *Chem. Abstr.*, **67**, 43517 (1968); *Zh. Org. Khim.*, **3**, 1273 (1967); *Chem. Abstr.*, **67**, 99792 (1968).

Conclusive evidence for a sulfene intermediate has been obtained in the base-promoted methanolysis of alkanesulfonyl chlorides; the methyl sulfonates were found to have incorporated one deuterium on the carbon α to the sulfonyl group when the reactions were carried out with methanol-O-*d*.⁷ When **4** dissolved in benzene was added to a solution of methanol-O-*d* and triethylamine in benzene, the product was found to be 80% **9** and 20% **8** by nmr and mass spectral analysis (Scheme I). When the reaction of **4** with

Scheme I

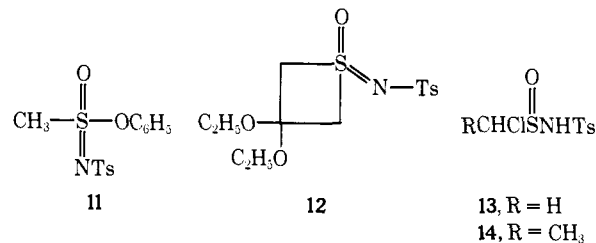


methanol-O-*d* was carried out (reflux, 3 hr) without added base, the product (**8**) contained no deuterium. These results clearly implicate an iminosulfene (**6**) in the base-promoted reaction (Scheme I).

In no cases have we yet succeeded in isolating the initially formed alkyl iminosulfonates (e.g., **7**). This is understandable since the anion of a disulfonamide (e.g., **10**) should be a superb leaving group. Sulfonates like **7** would not be expected to survive in the presence of nucleophiles. Aryl-oxygen cleavage is usually less favorable; phenyl methaniminosulfonate (**11**) (mp 70-72°) has been isolated from the reaction of **4** and phenol in the presence of pyridine.

When **4** was allowed to react with triethylamine (yield 10%) or, better, triethylenediamine (yield 46%) in the presence of ketene diethyl acetal, iminosulfene **6** was intercepted as the cycloaddition adduct **12** (mp 124-125°).

When iminosulfenes were generated from **4** and **5** in benzene without added trapping agents present, 1-chloroalkanesulfinamides **13**⁸ and **14** (a mixture of diastereomers) were isolated. These materials are the products of apparent 1,3 additions of HCl to iminosulfenes in which the α carbon acts as an electrophilic



center. In the addition of alcohols and in the cyclo-

(7) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **87**, 5684 (1965); W. E. Truce and R. W. Campbell, *ibid.*, **88**, 3599 (1966).

(8) At room temperature **13** decomposed to give *p*-toluenesulfonamide.

addition reaction, the α carbon of the iminosulfenes appears to be of nucleophilic character.^{9,10}

(9) For commentary on the various canonical structures as well as valence tautomers available to sulfenes and 1,2 vs. 1,3 addition reactions, the reader is referred to the review cited in ref 2.

(10) For other "abnormal" additions to sulfenes see J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. deMayo, *Chem. Commun.*, 31 (1969).

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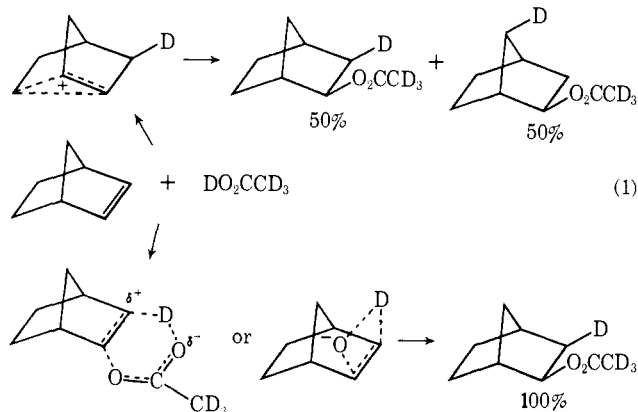
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exo-cis Addition of Trifluoroacetic Acid and Acetic Acid to 7,7-Dimethylnorbornene. Evidence for the Essential Absence of Molecular Cyclic Addition Processes

Sir:

The addition of deuteriotrifluoroacetic acid and of perdeuterioacetic acid to 7,7-dimethylnorbornene gives *exo*-3-*d*-7,7-dimethylnorbornyl *exo*-trifluoroacetate and the corresponding *exo*-acetate-*d*₃, respectively, with remarkably high *exo* stereoselectivity. According to the recently proposed generalization,^{1,2} the essential absence of *endo*-substituted product indicates that molecular cyclic addition processes cannot be significant in these additions.

The additions of deuterated acetic acid to norbornene³ and a number of its derivatives⁴ yield products with a distribution of the deuterium tag that is not consistent with the formation of a symmetrical non-classical ion as sole intermediate. Such distributions are consistent with the trapping of classical ions before they have attained full equilibration. However, it has been argued that the results can also be accommodated by postulating a dual mechanistic pathway, an ionic addition resulting in distribution of the tag to the *exo*-3 and *syn*-7 positions, and a concerted *cis* addition^{4,5} which places the tag exclusively at the *exo*-3 position (eq 1).



It was recently proposed that additions to 7,7-dimethylnorbornene provide an experimental test for the presence of cyclic additions. All additions examined, additions which are generally considered to

(1) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(2) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 3502 (1970).

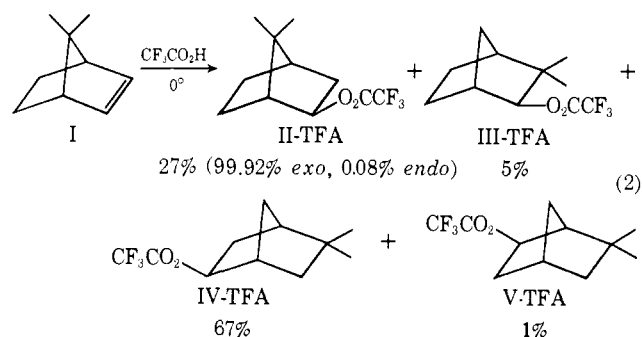
(3) E. Vogelfanger, Ph.D. Thesis, University of California, Los Angeles, Calif., 1963.

(4) S. J. Cristol, *et al.*, *J. Org. Chem.*, **31**, 2719, 2726, 2741 (1966); *ibid.*, **33**, 106 (1968).

(5) R. C. Fahey, *Top. Stereochem.*, **3**, 253 (1969).

proceed through cyclic transition states or intermediates, are markedly influenced by the presence of the 7,7-dimethyl substituents. Such reactions take a predominantly *exo* course for norbornene, but either take a preferential *endo* course or are so badly hindered that they fail to proceed with 7,7-dimethylnorbornene.^{1,2} Accordingly, it appeared desirable to examine the importance of the postulated concerted molecular processes by examining the addition of acetic acid and trifluoroacetic acid (and the deuterium tagged acids) to 7,7-dimethylnorbornene.

The addition of trifluoroacetic acid to olefins has been demonstrated to possess typical carbonium ion characteristics.⁶ We observed that the reaction of trifluoroacetic acid with 7,7-dimethylnorbornene (I) was quite fast, the addition being complete in 6–8 min at 0°. The product contained 27% 7,7-dimethylnorbornyl trifluoroacetate (II-TFA), consisting of 99.92% *exo* and 0.08% *endo*, and a great deal of Wagner–Meerwein and hydride shifted products (III-TFA–V-TFA), as indicated by glpc analysis (eq 2).^{7–9} The



formation of such large amounts of typical carbonium ion rearranged products, III-TFA–V-TFA, confirms the conclusion that the reaction must involve a major carbonium ion pathway. The insignificant amount of the *endo* isomer formed argues against the presence of any significant amount of cyclic addition, in accordance with the proposed generalization.^{1,2}

It was of interest to establish the stereochemistry for the addition of the proton in this reaction. Under the same conditions the addition of deuteriotrifluoroacetic acid to I yielded the same mixture of mono-deuterated trifluoroacetates (II-TFA-*d*-V-TFA-*d*). A mixture of II-TFA-*d* and IV-TFA-*d* was separated from the others by preparative glpc over a tricresyl phosphate column. After conversion to the alcohols, 7,7-dimethyl-*exo*-norbornanol-*d* was isolated by chromatography over alumina.

E2 elimination of a synthetic sample of *exo*-3-*d* tosylate proceeds with predominant loss of the *exo*-3 deuterium atom.¹⁰ Indeed, I obtained in the elimination retains only 5% of the original deuterium at

(6) P. E. Peterson, *et al.*, *J. Amer. Chem. Soc.*, **89**, 5902 (1967), and previous papers in this series.

(7) The mixture of the trifluoroacetates was reduced with lithium aluminum hydride to the corresponding alcohol mixture, which was analyzed by glpc with a 150 ft \times 0.01 in. UCON 50 LB 550X column on the Perkin-Elmer Model 226 chromatograph. The composition of the alcohol mixture was shown to be the same as the trifluoroacetates.

(8) All of the esters are stable to the reaction conditions.

(9) III-TFA–V-TFA are presumably the *exo* isomer predominantly, but no attempt was made to analyze the *exo:endo* ratio for other than II-TFA.

(10) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 200 (1970).