# Stable Carbonium Ions. CXVII.[1] Protonation of Sulfites and Sulfates and Their Cleavage Reactions in Fluorosulfuric Acid–Antimony Pentafluoride Solution

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*Received May 8, 1970*

Protonation of a series of alkyl sulfites and sulfates was examined in $FSO_3H$–$SbF_5$ solution. Protonated sulfites could not be directly observed even at −60° as sulfur–oxygen cleavage occurred with ease to give the corresponding protonated alcohols and subsequently stable carbonium ions. Protonated dialkyl sulfates were observed in the case of dimethyl and diethyl sulfate, each showing two isomeric forms. Higher homologs undergo fast carbon–oxygen cleavage to yield the corresponding alkylcarbonium ions.

No study of sulfites and sulfates in superacid media was reported so far in the literature. In continuation of our study of the protonation of organic sulfur compounds like sulfonyl halides,[1] sulfonic acids, sulfinic acids, alkyl sulfonates, alkyl sulfinates,[3] sulfoxides, and sulfones[4] we felt it of interest to study the protonation and cleavage reactions of alkyl sulfites and sulfates in $FSO_3H$–$SbF_5$ solution.

## Results and Discussion

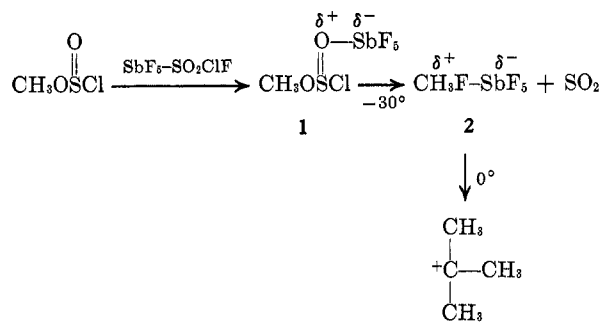
**Sulfides.**—The following sulfites were studied in $FSO_3H$–$SbF_5$–$SO_2$ solution at low temperature: dimethyl, diethyl, di-*n*-propyl, diisopropyl, di-*n*-butyl, diisobutyl, and dineopentyl sulfite.

Protonated sulfites could not be observed in $FSO_3H$–$SbF_5$ solution diluted with $SO_2$ even when the solutions were prepared and examined at −78°. Cleavage reactions had occurred.

The nmr spectrum of **dimethyl sulfite** in $FSO_3H$–$SbF_5$–$SO_2$ solution at −80° showed a sharp singlet at $\delta$ 5.63, a triplet at $\delta$ 4.66, and a quartet at $\delta$ 9.60. The latter two chemical shifts, assignable to protonated methanol, were reported previously.[5,6] This indicates that dimethyl sulfite in "magic acid" undergoes sulfur–oxygen cleavage to give protonated methanol and another species which gives a chemical shift of $\delta$ 5.63. At −40°, the resonance at $\delta$ 5.63 decreases and a new resonance appears at $\delta$ 4.40 which is assigned to the *tert*-butyl cation. Upon further raising the temperature, the nmr spectrum showed only the resonances for *tert*-butyl cation and protonated methanol.

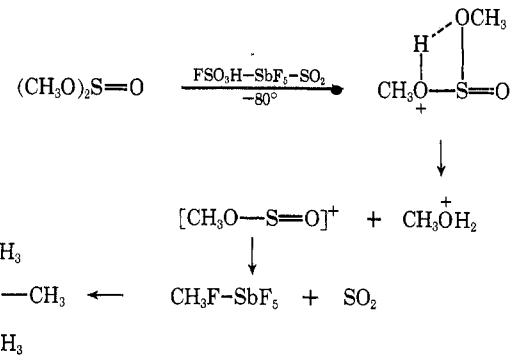
Methyl chlorosulfinate, $CH_3O$–S(=O)Cl, dissolved in antimony pentafluoride diluted with $SO_2ClF$, gave two sharp nmr singlets at $\delta$ 5.60 and 4.85. At −30°, the resonance at $\delta$ 5.60 increases at the expense of that at $\delta$ 4.85, which eventually disappeared completely. On further warming at 0°, a new peak which is assigned to the *tert*-butyl cation appeared at $\delta$ 4.50, and the resonance at $\delta$ 5.60 decreased with time. Finally, the nmr spectrum showed only one *tert*-butyl cation singlet at $\delta$ 4.50.

The resonance absorption at $\delta$ 5.60 is due to that of methyl fluoride–antimony pentafluoride complex. This assignment is made based on the fact that it not only has the same $^1H$ chemical shift as an authentic sample of methyl fluoride–antimony pentafluoride complex, but also has the same $^{13}C$ chemical shift (found at 119 ppm).[7] The resonance at $\delta$ 4.85 is in all probability due to that of the donor:acceptor complex **1**. At




−30°, **1** loses $SO_2$ to give methyl fluoride–antimony pentafluoride complex **2**. It is known that complex **2** goes to *tert*-butyl cation at higher temperature.

Data obtained indicate that the cleavage pathway for dimethyl sulfite in the superacid solution is as shown. The resonance absorption at $\delta$ 5.63 is due to the methyl fluoride–antimony pentafluoride complex which at higher temperature decomposes to the *tert*-butyl cation.




The site of protonation of sulfites cannot be directly detected based on the present data. There is indication in the low temperature (−100°) spectra of an nmr absorption at $\delta$ ~6.5 which could evolve at S protonation similar to that observed in the case of dimethyl sulfoxide. It is assumed, based on the ease of cleavage reactions, that protonation involves, at least in equilib-

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(1) Part CXVI: G. A. Olah, A. T. Ku, and J. O. Olah, *J. Org. Chem.*, **35**, 3925 (1970).

(2) National Institutes of Health Predoctoral Research Investigator, 1970.

(3) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3908 (1970).

(4) G. A. Olah, A. T. Ku, and J. A. Olah, *ibid.*, **35**, 3904 (1970).

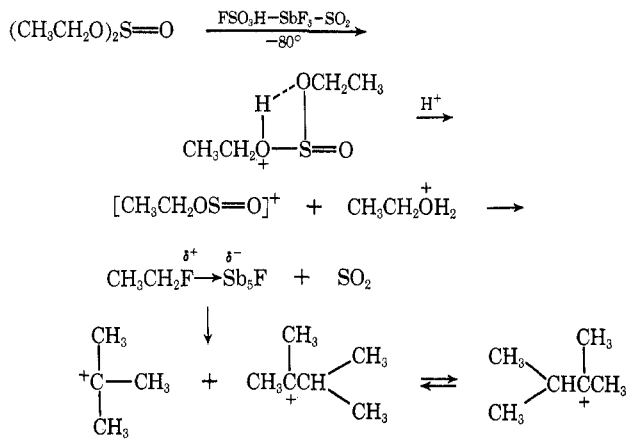
(5) G. A. Olah, J. Sommer, and E. Namanworth, *J. Amer. Chem. Soc.*, **89**, 3576 (1967).

(6) G. A. Olah and E. Namanworth, *ibid.*, **88**, 5327 (1966).

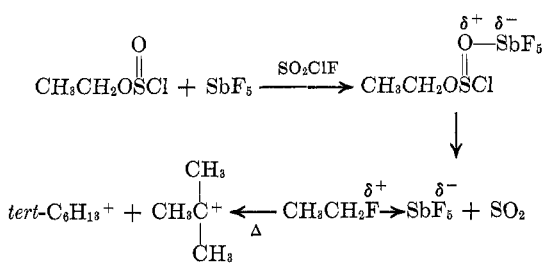
(7) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *ibid.*, **91**, 2112 (1969).

rium, the alkyl oxygen. The cleavage reaction (see subsequent discussion) is clearly O–S cleavage.

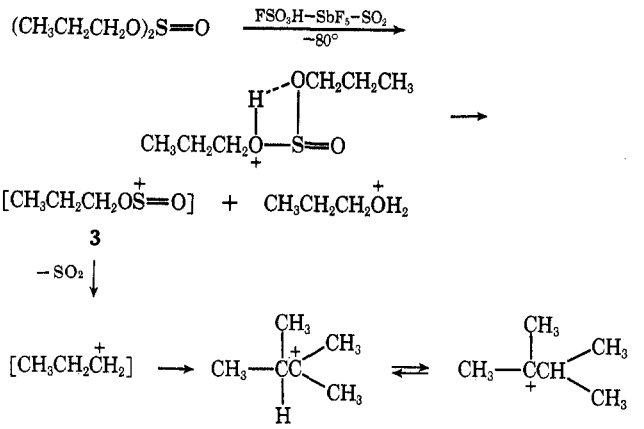
The nmr spectrum of **diethyl sulfite** in "magic acid," $FSO_3H$–$SbF_5$–$SO_2$, solution at −80° showed also that of the cleavage product protonated ethanol ($CH_3$ triplet at $\delta$ 1.56, $-CH_2-$ multiplet at 4.80 and $\overset{+}{O}H_2$ triplet at 9.20)[5,6] and the ethyl fluoride–antimony pentafluoride complex with $CH_3$ triplet at $\delta$ 1.93 and $-CH_2-$ quartet at 6.20. At higher temperature further cleavage reaction occurred and the nmr spectrum showed resonances for *tert*-butyl and *tert*-hexyl cations in addition to that of protonated ethanol. Thus the cleavage reaction of diethyl sulfite in "magic acid" is the same as that observed for dimethyl sulfite.



**Ethyl chlorosulfinate** in $SbF_5$–$SO_2ClF$ at −80°, as in the case of methyl chlorosulfinate, gives the donor:acceptor complex ($CH_2$ quartet at $\delta$ 5.20, $CH_3$ triplet at 2.23). In addition, the nmr spectrum also showed a quartet at $\delta$ 6.40 which we believe to be due to the $-CH_2$ of the ethyl fluoride–antimony pentafluoride complex. The chemical shift of the $CH_3$ protons of the complex is overlapped by that of the donor:acceptor complex at $\delta$ 2.23. On warming, decomposition of ethyl fluoride–antimony pentafluoride complex to *tert*-butyl and *tert*-hexyl cations occurred. These data further proved the cleavage pathway of diethyl sulfite in "magic acid." The nmr spectrum of *di-n-propyl* sulfite in $FSO_3H$–$SbF_5$ solution diluted with $SO_2$ at −80° showed the absorptions for protonated propanol and that of *tert*-hexyl cations, indicating that both sulfur–oxygen and alkyl–oxygen cleavage had occurred. It is believed that di-*n*-propyl sulfite, as in the case of dimethyl sulfite, was first protonated and then underwent sulfur–oxygen cleavage to give protonated propanol and



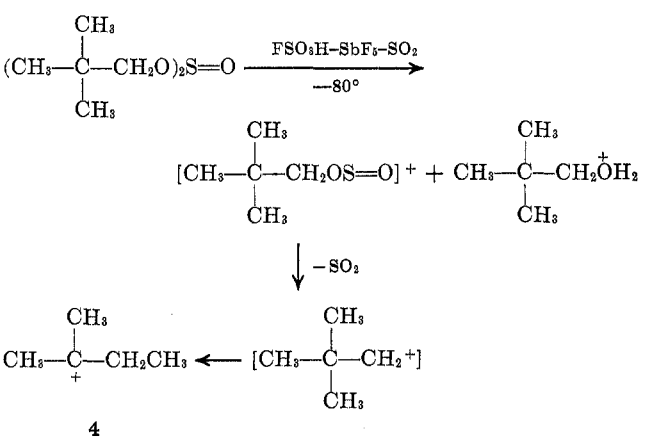
**3** which is not observed and undergoes further cleavage to give the *n*-propyl cation which in turn rearranges to the more stable *tert*-hexyl cation.



**Diisopropyl sulfite,** again, in $FSO_3H$–$SbF_5$–$SO_2$ solution undergoes both sulfur–oxygen and alkyl–oxygen cleavage to give the protonated isopropyl alcohol and *tert*-hexyl cation. The cleavage pathway is believed to be the same as that of di-*n*-propyl sulfite.

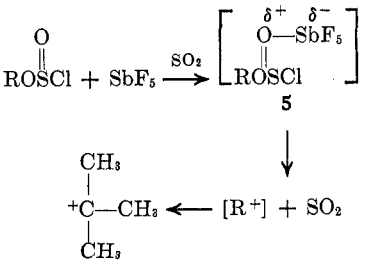
Accordingly, **di-*n*-butyl** and **diisobutyl sulfite** in $FSO_3H$–$SbF_5$–$SO_2$ solution undergo cleavages to give the corresponding protonated alcohol and *tert*-butyl cation.

The nmr spectrum of **neopentyl sulfite** in $FSO_3H$–$SbF_5$–$SO_2$ solution at −80° again showed no absorptions corresponding to the protonated species, but only that of the cleavage product, protonated neopentyl alcohol, and that of the *tert*-amyl cation (**4**). The cleavage is believed to be similar to that of di-*n*-propyl sulfite as shown in the following.



**4**

Ionization of isomeric **butyl chlorosulfinates**[8] in antimony pentafluoride–sulfur dioxide gave only the *tert*-butyl cation. In order to achieve the cleavage, warming of the samples to −10° was needed. Again, we feel that the reaction proceeds through intermediate **5**, although it was not directly observed.

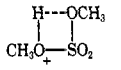
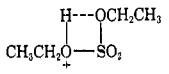


**5**

(8) Work done with J. M. Bollinger and previously unpublished.

TABLE I

PMR SPECTRAL PARAMETERS[a] OF THE PARENT AND PROTONATED SULFATES AT −60°

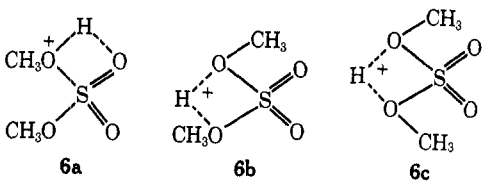
| Compd | Registry no. | Solvent | $CH_2$ | $CH_3$ |
|---|---|---|---|---|
| $(CH_3O)_2SO_2$ | 77-78-1 | $SO_2$ | | 3.73 |
|  | 26402-44-8 | $FSO_3H$–$SbF_5$ | | 4.86 |
| | | $SO_2ClF$ | | 4.70 |
| $(CH_3CH_2O)_2SO_2$ | 64-67-5 | $SO_2$ | 4.10 (q, 7.0) | 1.15 (t, 7.0) |
|  | 26402-45-9 | $FSO_3H$–$SbF_5$ | 5.53 (q, 7.0) | 1.95 (t, 7.0) |
| | | $SO_2ClF$ | 5.33 (q, 7.0) | |

[a] Chemical shifts are in parts per million from external TMS. Coupling constants in hertz are given in parentheses following the multiplicities: t = triplet, q = quartet.

It is of interest to mention that the conversion of alcohols into chlorosulfites or haloformates and their subsequent cleavage in $SbF_5$–$SO_2$/$SO_2ClF$ represents a useful fragmentation method to generate carbonium ions.[9] It is also of interest to note that the chlorosulfite cleavage reactions provide further proof for the mechanism of the conversion of alcohols into chlorides by thionyl chloride.[10]

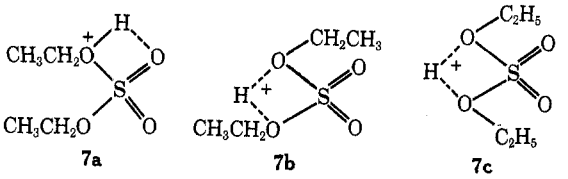
**Sulfates.**—The following sulfates were studied in $FSO_3H$–$SbF_5$–$SO_2ClF$ solution at low temperature: dimethyl, diethyl, di-*n*-propyl, and di-*n*-butyl sulfate.

The nmr spectrum of **dimethyl sulfate** in $FSO_3H$–$SbF_5$–$SO_2ClF$ solution at −80° showed a strong singlet at δ 4.85 and a small peak (*ca.* 1/5th of that at δ 4.85) at δ 4.66. These chemical shifts are much more downfield than those of the parent compound in $SO_2$ (see Table I), indicating that dimethyl sulfate is protonated presumably on alkyl oxygen although no proton on oxygen could be directly observed due to obvious fast exchange. These two singlets could be assigned to the methyl protons of any or all possible isomers **6a**, **b**, and **c**, of protonated dimethyl sulfate. No coupling was observed between the proton on oxygen and the methyl



**6a** **6b** **6c**

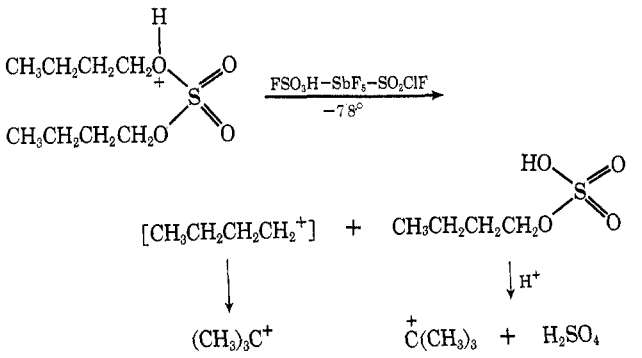
protons; hence no structural assignment could be made. The absence of coupling indicates rapid exchange which could not be frozen even at the lowest temperatures observable, −120°. The dotted lines used in the formulas are intended to denote oxygen sites between which proton equilibration can take place and not distinct species (of course, intramolecular exchange with the solvent also must be considered). Similar observations were also made for protonated diethyl sulfate in the same acid solvent system. Again, no proton on oxygen and no coupling was observed between the proton on oxygen and the α-alkyl protons, and no structural assignment could be made. The chemical shifts and coupling constants of the parent and protonated dimethyl and diethyl sulfates are given in Table I.



**7a** **7b** **7c**

The nmr spectrum of both protonated dimethyl and diethyl sulfate in $FSO_3H$–$SbF_5$–$SO_2ClF$ showed no significant change from −80° to room temperature.

However, **protonated di-*n*-propyl** and **di-*n*-butyl** sulfate could not be observed. The nmr spectrum of di-*n*-propyl and di-*n*-butyl sulfate in $FSO_3H$–$SbF_5$–$SO_2ClF$ showed only the resonances of the most stable cation, *tert*-hexyl and *tert*-butyl cation, respectively. This indicates that alkyl oxygen cleavage occurred, for example




The difference in the superacid protolytic cleavage reactions of dialkyl sulfites and sulfates can be found in the fact that the former undergo oxygen–sulfur cleavage (in good accordance with available data on acid-catalyzed hydrolysis of dialkyl sulfites)[11] whereas the latter only undergo carbon–oxygen cleavage (again in accordance with hydrolysis behavior of dialkyl sulfates).[12] Primary alkyl groups, particularly methyl and ethyl, are poor leaving groups in the alkyl–oxygen cleavage reaction, thus the stability of dimethyl and diethyl sulfate, as compared to their sulfites.

(9) G. A. Olah, *Chem. Eng. News*, **45**, 77 (1967).

(10) E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, **74**, 308 (1952), and references cited therein.

(11) For a summary, see H. F. Van Woerden, *Chem. Rev.*, **63**, 562 (1963), and references given therein.

(12) E. T. Kaiser, M. Ranar, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **85**, 602 (1963); E. T. Kaiser, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1959; R. E. Robertson and S. E. Sugamori, *Can. J. Chem.*, **44**, 1728 (1966).

## Experimental Section

**Materials.**—*n*-Propyl, isopropyl, *n*-butyl, isobutyl, *n*-pentyl, and neopentyl sulfite were prepared by the reaction of the corresponding alcohol with thionyl chloride.[13] Dimethyl and diethyl sulfite were commercially available. Alkyl chlorosulfinates were prepared by the reaction of alcohols with excess thionyl chloride.[14]

Di-*n*-propyl and di-*n*-butyl sulfate were prepared by the reaction of the corresponding sulfite with sulfuryl chloride. Dimethyl and diethyl sulfate were commercially available materials.

(13) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 112; p 111.

(14) P. D. Bartlett and H. F. Herbrandson, *J. Amer. Chem. Soc.*, **74**, 5971 (1952).

**Nmr Spectra.**—Varian Associates Model A-56/60A spectrometer, equipped with a variable temperature probe, was used for all spectra. Chemical shifts are reported in ppm ($\delta$) from external (capillary) tetramethylsilane, as in previous publications in this series.

**Preparation of Solutions.**—The procedure used for the preparation of solutions of the protonated sulfites and sulfates was identical with that described previously.[15]

**Acknowledgment.**—Support of our work by a grant from the National Institutes of Health is gratefully acknowledged.

(15) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967)

# The Synthesis of 1,8-Di-*tert*-butylnaphthalenes

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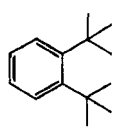
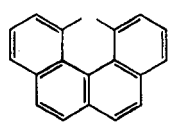
*Received June 26, 1970*

A direct synthetic route to *peri*-di-*tert*-butylnaphthalenes, **23**, **24**, and **25**, is described. A key step involves Diels–Alder reaction of a benzene with *tert*-butylfurans. Reaction of the naphthalenes with acid serve to demonstrate behavior that is different from the di-*tert*-butylbenzene case. Thus, crowding in **23** results in diminished reactivity at the peri position due to hindrance rather than increased reactivity resulting from relief of strain. Similarly, **25** is 1–2 orders of magnitude less reactive than **21** under identical acid conditions. Extreme structural perturbation is also detected *via* nmr and uv spectroscopy.

One approach to the study of van der Waals repulsion effects has been to synthesize aromatic hydrocarbons where the geometric requirements for $\pi$ orbital overlap force crowding of bulky substituents located on the aromatic ring. The resulting balance between relief of strain and distortion of the planar aromatic framework has been examined by both physical and chemical probes. Examples of structures that have been studied are *o*-di-*tert*-butylbenzene (**1**)[2] and 1,12-dimethylbenzo[*c*]phenanthrene (**2**),[3] as well as related

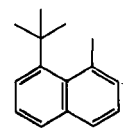


**1**

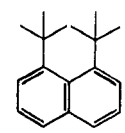


**2**

systems such as *o*-di-*tert*-butylquinoxaline[4] and $\beta,\beta'$-dihydroxy-2,3-di-*tert*-butylnaphthalene.[5] The present work on *peri*-*tert*-butylnaphthalenes developed from the principle stated by Newman to estimate qualitatively the steric effects of ortho substituents in aromatic compounds:[6] (1) a fused aromatic ring is equivalent to a methyl group, and (2) either (a) a fused aromatic ring containing a methyl group in the adjacent peri position, or (b) two continuously angularly fused aromatic rings is equivalent to a *tert*-butyl group. Thus it was our estimate that a 1-*tert*-butyl-8-methylnaphthalene (**3**) is comparable in its crowding to *o*-di-*tert*-butylbenzene (**1**) and that a 1,8-di-*tert*-butylnaphthalene (**4**) is more crowded than **1** or **3**. A strain energy of 22 kcal/mol has been determined for **1**,[2a] and using a value of 6–7 kcal/mol for the strain in *o*-*tert*-butyltoluene, one can assign a 15–16 kcal/mol increment for the replacement of methyl by *tert*-butyl.[7] Thus we can estimate that the substitution of the methyl in **3** by *tert*-butyl in **4** would result in a strain energy of 37–38 kcal/mol.



**3**



**4**

Syntheses of 1-*tert*-butylnaphthalene have been reviewed recently.[8] Our experience with the use of a *tert*-butylbenzyne–furan reaction followed by aromatization to afford 1,4-di-*tert*-butylnaphthalene led us to extend the method to the peri-crowded series.[9] The sequence shown below was developed for the preparation of a *tert*-butylbenzyne **8**, with the critical step being the aprotic diazotization and decarboxylative elimination of the anthranilic acid (**7**).[10]

Two results of some interest, although not germane to the naphthalene problem have been obtained with **7** and **8**. When acid **7** was treated with dicyclohexylcarbodiimide, the benzoxazine **9** (20% yield) was

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(1) (a) Portions of this work have been previously reported: R. W. Franck and E. G. Leser, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN 167; R. W. Franck and E. G. Leser, *J. Amer. Chem. Soc*, **91**, 1577 (1969). (b) This paper is based on the Ph.D. Thesis of E. G. L., Fordham University, 1970. (c) This research was supported in part by Fordham University funds, NSF Grant GP 7754, and an NSF Traineeship for E. G. L.

(2) (a) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5389 (1967); (b) A. W. Burgstahler, P. Chien, and M. O. Abdel-Rahman, *ibid.*, **86**, 5281 (1964).

(3) M. A. Frisch, C. Barker, J. L. Margrave, and M. S. Newman, *ibid.*, **85**, 2356 (1963).

(4) G. J. Visser, A. Vos, A. deGroot, and H. Wynberg, *ibid.*, **90**, 3253 (1968).

(5) L. R. C. Barclay, G. R. Nixon, H. M. Foote, and S. L. Barclay, *Can. J. Chem.*, **47**, 4313 (1969).

(6) M. S. Newman and W. H. Powell, *J. Org. Chem.*, **26**, 812 (1961).

(7) H. C. Brown, *J. Chem. Soc.*, 1248 (1956); (b) J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958); (c) H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

(8) H. Van Bekkum, T. J. Nieuwstad, J. Van Barneveld, P. Klapwijk, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas.*, **88**, 1028 (1969).

(9) R. W. Franck and K. Yanagi, *J. Org. Chem.*, **33**, 811 (1968).

(10) L. Friedman and F. M. Logullo, *ibid.*, **34**, 3089 (1969).