

of material melting at 88–94°. In a subsequent experiment the crude material was decolorized once with Darco G-60 and was recrystallized twice from absolute ethanol giving pure 10, m.p. 106–107°, $[\alpha]_D^{25} +4.5^\circ$ (c 0.10, water).

Anal. Calcd. for $C_6H_{13}O_5N$: C, 36.44; H, 6.71; N, 7.17. Found: C, 36.94; H, 6.50; N, 7.07.

Conversion of the Deoxynitrohexitol (10) to 2-Deoxy-D-allose (11).—The 506 mg. (2.6 mmoles) of crude hexitol (10) obtained in the preceding preparation was dissolved in 4 ml. of 2 N sodium hydroxide and the solution was added without delay to 4 ml. of a stirred, 40% (v./v.) aqueous solution of sulfuric acid. The product was worked up in the same manner as given for the preparation of 11 by the alkaline procedure (*vide supra*). After decolorizing with Darco G-60, the material was recrystal-

lized once from absolute ethanol giving 170 mg. (40%) of 2-deoxy-D-allose (11), melting at 130–133°. Two additional recrystallizations raised the melting point of 11 to 140–142°.

Acknowledgment.—The authors wish to thank Miss Paula M. Parisius of the Microanalytical Laboratory, NIAMD, National Institutes of Health, under the direction of Mr. H. G. McCann, for the elemental analyses. They are especially grateful to Dr. Nelson K. Richtmyer, for generous gifts of D-allose and D-altrose which were of much value in comparison studies.

The Disproportionation of Some Chlorofluoroalkyl Nitroso Compounds¹

D. E. O'CONNOR AND PAUL TARRANT

Department of Chemistry, University of Florida, Gainesville, Florida

Received November 20, 1962

Fluorochloroalkyl nitroso compounds have been shown to disproportionate into nitro and chloro derivatives with the evolution of some nitrogen. A kinetic study of the decomposition of α - and β -chloro nitroso compounds has been made and a mechanism postulated.

The preparation of nitroso compounds by the addition of nitrosyl chloride to fluoroolefins usually results in the formation of some nitro and chloro derivatives of the olefin.



For example, the addition of nitrosyl chloride to tetrafluoroethylene at 100° yielded a mixture of 1-chloro-2-nitrotetrafluoroethane and 1,2-dichlorotetrafluoroethane, but no nitroso compound.² It was postulated that the nitroso compound was formed initially and was subsequently oxidized by nitrosyl chloride to the nitro compound. Under milder conditions using catalysis, these two reactants yield primarily 1-chloro-2-nitrotetrafluoroethane, but some of the corresponding nitro and chloro compounds are also obtained.³ In this laboratory it was observed that certain fluorochloroalkyl nitroso compounds decomposed slowly on standing at room temperature. Furthermore, attempts to carry out reactions of these nitroso compounds with other materials by heating resulted in the formation of the corresponding nitro and chloro compounds⁴ and very little else. Our observations suggested that disproportionation was occurring approximately according to the following equation.

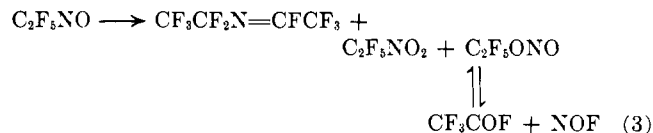


Equation 2 obviously does not balance and does not account completely for the products of the reaction, but it does describe the gross features of it. Our study was undertaken to learn more about this interesting reaction.

The only other data concerning the disproportionation of fluoroalkyl nitroso compounds have been obtained with perfluoroalkyl nitroso compounds. Haszeld-

dine and co-workers have investigated rather thoroughly the reactions of nitrosotrifluoromethane, the thermal reactions of which follow quite different courses under different conditions. Irradiation of nitrosotrifluoromethane with ultraviolet light yields a dimer, $(CF_3)_2NONO$,⁵ while heating nitrosotrifluoromethane over activated charcoal yields a mixture of nitrotrifluoromethane and hexafluoroazoxymethane⁶ analogous to the reaction Bamberger reported for nitrosobenzene.⁷ However, when nitrosotrifluoromethane is heated alone, a 48% yield of nitrotrifluoromethane is obtained along with the products of reaction of trifluoromethyl radicals with glass.⁸ This last reaction was run under conditions similar to our experiments, the major difference being that theirs was a gas-phase reaction while ours was carried out in the liquid phase.

Andreades⁹ has found that nitrosopentafluoroethane undergoes the following reaction when heated.



We postulate that the course of the thermal disproportionation of fluorochloroalkyl nitroso compounds is that shown in eq. 4, 5, and 6. Our arguments are based on the products of the reaction, the effect of added reagents (NO and NOCl), and the relative thermal stabilities of four chlorofluoroalkyl nitroso compounds.

The relative thermal stabilities of 1,2-dichloro-1-nitrosotrifluoroethane (I), 1,1-dichloro-1-nitrosotrifluoroethane (II), 1-chloro-1-nitrosotetrafluoroethane (III), and 1-chloro-2-nitrosotetrafluoroethane (IV) at 78.2° were measured. Compounds I and IV were made by

(1) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961.

(2) R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

(3) J. D. Park, A. P. Stefani, and J. R. Lacher, *J. Org. Chem.*, **26**, 4017 (1961).

(4) Throughout this paper the term chloro compound refers to the chloro-fluorocarbon obtained by replacement of the nitroso group by chlorine.

(5) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1741 (1957).

(6) J. Jander and R. N. Haszeldine, *ibid.*, 919 (1954).

(7) E. Bamberger, *Ber.*, **33**, 1939 (1900).

(8) D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J. Chem. Soc.*, 1351 (1961).

(9) S. Andreades, 2nd International Fluorine Symposium, Estes Park, Colo., July 17–20, 1962.

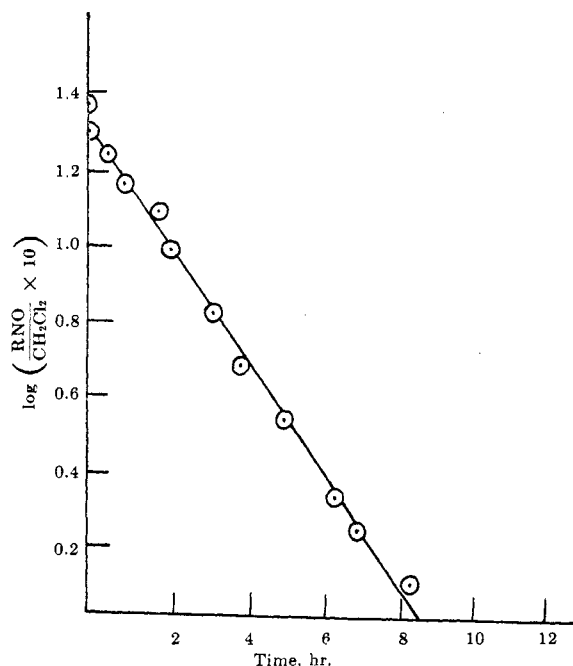


Fig. 1.—First-order plot: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane at 78.2°.

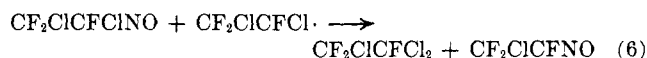
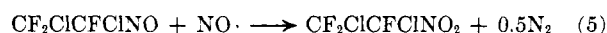
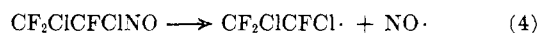
adding nitrosyl chloride to chlorotrifluoroethylene and tetrafluoroethylene, respectively.^{10a} Compounds II and III were prepared by reacting the corresponding fluoroalkylmercury compound with nitrosyl chloride by a procedure to be discussed in a forthcoming publication.^{10b} The thermal stabilities were determined by placing, in the vapors of refluxing 95% ethanol, sealed ampoules containing approximately equimolar amounts of nitroso compound and internal standard (methylene chloride for I and II, methyl bromide for III and IV). After a specified period of time the ampoules were cooled in Dry Ice-acetone and opened; a sample of their contents was injected into a vapor-phase chromatographic (v.p.c.) apparatus. From the v.p.c. curves it was possible to determine the rate of disappearance of nitroso compound and the quantities of nitro and chloro compound formed.

A first-order plot of the rate of disappearance of I is shown in Fig. 1. Comparable plots were obtained for compounds II, III, and IV, but with more scatter of points. The reaction was carried to >90% completion during which time the reaction medium changed from a mixture of roughly equimolar amounts of I and methylene chloride to a mixture of methylene chloride, 1,1,2-trichlorotrifluoroethane, 1,2-dichloro-1-nitrotrifluoroethane, and I. In spite of the change of solvent during the course of the reaction, the same first-order rate of disappearance was obtained throughout. Furthermore, when the reaction was carried out using carbon tetrachloride in place of methylene chloride, the same rate of disappearance of I, within experimental error, was observed. These results suggest that there is very little solvent effect in this reaction. Repeat runs with I in which the ratio of I to internal standard was varied by a factor of 2 gave essentially the same results.

(10) (a) A sample of IV was kindly furnished by Dr. E. C. Stump of Peninsular ChemResearch, Inc.; (b) P. Tarrant and D. E. O'Connor, *J. Org. Chem.*, **29**, 2012 (1964).

Compounds II, III, and IV exhibited similar behavior, although first-order plots of their rates of disproportionation showed more scatter. The data for each of the four compounds were subjected to first-order plots and from these plots half-lives were obtained for the purpose of comparing the four compounds. Since the data were obtained using quite concentrated solutions whose compositions changed significantly during the course of the reactions, no further significance was attached to the half-lives.

The products from the disproportionation of I are 1,2-dichloro-1-nitrotrifluoroethane (36%), 1,1,2-trichlorotrifluoroethane (34%), nitrogen (20%), nitric oxide, and a material, b.p. 51–53° (23 mm.), mol. wt. 416 ± 20, which was not identified.¹¹ The quantity of nitrogen evolved in the reaction was measured only once, and in a separate experiment from the rate determinations. The value obtained was a little over half the value predicted in the equations below.



↓
other products

Table I lists some of the data obtained in this study, the important aspects of which will be cited here for emphasis. (1) The three compounds containing an α -chlorine atom (I, II, and III) disproportionate at a significantly faster rate than does IV, which has no α -chlorine atom. (2) No chloro compound is obtained from IV, while with each of the three α -chloro compounds it is a major product. (3) The addition of nitric oxide greatly increases the rate of reaction of I and presumably would have a similar effect on the other nitroso compounds. (4) The addition of nitrosyl chloride increased the rate of disproportionation of I somewhat but not greatly, did not drastically change

TABLE I
SUMMARY OF THERMAL STABILITIES AND PRODUCT RATIOS
FOR DISPROPORTIONATION OF NITROSO COMPOUNDS AT 78.2°

Compound	Relative half-life ^a	RCI-RNO ₂ ^b	RCI + RNO ₂ average % of total product ^c
CF ₃ CCl ₂ NO (II)	1.3	2.1 ^c	88 ^c
CF ₂ ClCFClNO (I)	1.95	0.9–0.95	70
CF ₂ CFCINO (III)	4.0	1.1	62
CF ₂ ClCF ₂ NO (IV)	49	0.0	44
CF ₂ ClCFClNO + NOCl	1.4	0.74	97
CF ₂ ClCFClNO + NO	<0.25 ^d	0.08 ^e	ca. 100

^a The constants for I and II were determined using CH₂Cl₂ as internal standard, III and IV in CH₃Br. When I was run with CCl₄ as internal standard, the half-life was found to be 1.98 thus indicating the absence of solvent effect. ^b The values contained in these columns are average values. ^c These values are gross approximations because of difficulties in measuring the areas under v.p.c. curves. ^d This value was not obtained by a first-order plot. It is based on the time required for more than half of 1.1 mmole of I to react with 0.7 mmole of NO. ^e After 1 hr; the ratio was smaller during earlier parts of the run.

(11) An empirical formula of C₇O₄Cl₃F₇N was calculated for this compound from elemental analysis results, but was not very accurate. This material has two strong, sharp bands at 5.49 and 5.62 μ in the infrared and it hydrolyzed very slowly in distilled water to yield an acidic solution. These data as well as a fluorine nuclear magnetic resonance spectrum suggest that the compound contains an acyl fluoride functional group.

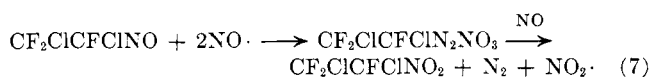
the ratio RCl-RNO₂, but did increase the amount of RCl and RNO₂ in the product to almost 100%.

It appears that the disproportionation of I, II, and III are accommodated by the reaction scheme illustrated by eq. 4, 5, and 6.

The initial step in the reaction is probably the homolytic cleavage of the C-N bond as shown in eq. 4. The nitric oxide thus formed can then react with more of the nitroso compound to form the corresponding nitro compound and nitrogen as shown in eq. 5. The chlorofluoroalkyl radical formed in eq. 4 can react with more nitroso compound to form the chloro compound as shown in eq. 6. The radical formed by the process shown in eq. 6 probably goes on to form the C₇Cl₃-F₇NO₄, the only other fluorine-containing product isolated from the reaction.

The presence of nitric oxide among the products is good evidence for a homolytic cleavage of the C-N bond. Evidence that nitric oxide is the oxidizing species was obtained by carrying out the reaction of I at 78.2° with nitric oxide. Under the conditions employed (NO-RNO = *ca.* 0.7:1.1), over half of the nitroso compound had been consumed in less than 15 min. indicating that I reacts readily with nitric oxide. Furthermore the nitro compound is formed in essentially 100% yield, the small amount of chloro compound formed being accounted for by some disproportionation according to the scheme postulated above. These facts strongly support the postulate that nitric oxide is the oxidizing agent.

The reaction of nitroso compounds with nitric oxide to form diazonium nitrates was reported by Bamberger¹² many years ago, and more recently Haszeldine and co-workers³ postulated that a diazonium nitrate was an intermediate in the oxidation of nitrosotrifluoromethane by nitric oxide, the diazonium nitrate being formed by the reaction of the nitroso compound with two molecules of nitric oxide and subsequently reacting with a third molecule of nitric oxide to yield nitrosotrifluoromethane, nitrogen, and nitrogen dioxide, analogous to eq. 7. Although they offered no direct evidence

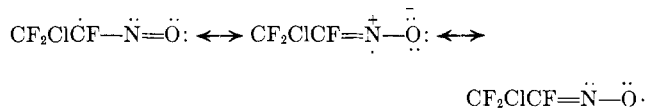


for such an intermediate, it seems quite reasonable in view of Bamberger's findings. Hence, it seems likely that eq. 5 is more accurately represented as shown in eq. 7. The net reaction would not be changed, since the NO₂ radical formed could couple with a fluoro-chloroalkyl radical. The oxidation of nitrosomethane by nitric oxide has also been reported,¹³ but no details were given.

Equation 6 is indicated by the fact that each of the three nitroso compounds containing an α -chlorine yields substantial quantities of the corresponding chloro compound (RCl), whereas the nitroso compound which contains no α -chlorine, *i.e.*, IV, yields no chloro compound. These data indicate that the chlorine in the RCl formed comes from the α -carbon of the nitroso compound, contrary to the recent postulate by Park and co-workers³ that the initial steps in the disproportionation of I are the stepwise elimination of the

nitroso group and chlorine from adjacent carbon atoms with formation of a fluoroolefin. If their postulate were true, then IV should give products similar to I, whereas III should behave quite differently. Actually, III behaved very much like I (similar thermal stability and similar product composition), whereas IV was quite different (formed no RCl and greater thermal stability).

That a chlorofluoroalkyl radical will abstract the α -chlorine but not the β -chlorine seems quite reasonable in view of the difference in resonance stabilization available to the two radicals.¹⁴ The nitroso group attached to the radical-bearing carbon can stabilize the radical through the following resonance forms



while a radical formed on the β -carbon would receive no resonance stabilization by the nitroso group.

The fact that addition of nitrosyl chloride increases the combined yield of the nitro and chloro compounds from *ca.* 70 to *ca.* 100% and lowers the ratio of RCl-RNO₂ but does not alter the rate drastically lends further support to the proposed reaction path. The presence of nitrosyl chloride provides an alternative to reaction 6 for the chlorofluoroalkyl radical. Instead of abstracting a chlorine atom from a molecule of the nitroso compound, the chlorofluoroalkyl radical can abstract a chlorine atom from nitrosyl chloride. Thus, the reaction which produces the higher boiling unidentified product is essentially eliminated and all of the nitroso compound reacts to form the corresponding nitro and chloro compounds. The fact that an additional molecule of nitric oxide is produced when the alkyl radical reacts with nitrosyl chloride accounts for the decrease in the ratio of RCl-RNO₂. Ideally this ratio should be 0.5, but experimentally we observed a ratio of 0.74. It is, however, significantly less than the ratio observed for the disproportionation of the pure nitroso compound, which should be 1.0.

The results may be summarized as follows. Disproportionation as illustrated in eq. 2 occurs when there is an available source of chlorine atoms such as an α -chloro nitroso compound or nitrosyl chloride. When no source of chlorine atoms is available, dissociation occurs as shown in eq. 4 and oxidation occurs as shown in eq. 5, but the fluoroalkyl radical must react by some different course, perhaps to form the azomethines observed by Andreades.¹¹ This explains why certain fluoroalkyl nitroso compounds, *e.g.*, IV, react with nitrosyl chloride to yield the chloro as well as the nitro compound, while alone they form no chloro compound, whereas others, *e.g.*, I, II, and III, form both the chloro and the nitro compound in the presence or in the absence of nitrosyl chloride. Equations 4-6 account for the gross features of the reaction. Furthermore, it is reasonable to expect that any fluoroalkyl nitroso compound would react with nitrosyl chloride to yield both the nitro and chloro compounds.

(12) E. Bamberger, *Ber.*, **30**, 506 (1897).

(13) J. B. Levy, *Ind. Eng. Chem.*, **48**, 762 (1956).

(14) See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 6, for a discussion of this subject and for leading references.

Experimental¹⁵

Disproportionation of 1,2-Dichloro-1-nitrosotrifluoroethane.—An ampoule (25-mm. o.d., 3-mm. wall, ca. 140-ml. volume) was charged with 1,2-dichloro-1-nitrosotrifluoroethane (9 g., 0.05 mole) and was sealed under vacuum. The tube was heated at 75° for several hours until the blue color had faded. Then the tube was cooled in liquid nitrogen and was opened into the vacuum line. The pressure rose immediately indicating the presence of nitrogen, in 20% yield. The nitrogen was swept out and a molecular weight of the most volatile gas remaining was 31.1 (calculated for NO, 30.0). In addition, this colorless gas became brown when it was exposed to the air. The tube was then immersed in Dry Ice-acetone and the volatile material was pumped off. Then, an infrared spectrum of the remaining volatile material had bands at 5.52 and 5.59 μ , indicating the presence of nitrogen dioxide. A separate run was similarly made using 1,2-dichloro-1-nitrosotrifluoroethane (30 g., 0.16 mole). From this run was obtained 2.5 g. of material, b.p. 51–53° (23 mm.).

Anal. Calcd. for $C_2Cl_2F_2NO_2$: C, 20.9; H, 0.00; Cl, 26.5; F, 33.10; N, 3.48. Found: C, 19.52; H, 0.43; Cl, 27.3; F, 32.34; N, 3.40.

The molecular weight was 416 ± 20 , determined cryoscopically. The nitro and chloro compounds were determined chromatographically during the rate studies described below. They were identified by comparing their retention times by v.p.c. with known samples.

Determination of the Thermal Stabilities of the Nitroso Compounds.—The relative rates of disproportionation at 78.2° of four chlorofluoroalkyl nitroso compounds were determined with a vapor-phase chromatographic column using an internal standard.

The nitroso compounds were purified by passing each of them through a vapor-phase chromatographic column packed with material prepared from 0.6 g. of dinonyl phthalate per gram of Johns Mansville "Chromosorb," 35–80-mesh size, and were subsequently stored at –78° until they were used.

Methylene chloride was used as an internal standard for the studies of the disproportionation of I and II and methyl bromide was used as an internal standard for the studies of III and IV. Carbon tetrachloride was also used as internal standard for I.

(15) Analyses were by Galbraith Laboratories, Knoxville, Tenn.

The nitroso compound and the internal standard were mixed in the desired ratio. Aliquot portions of approximately 0.1 ml. of the mixture were then transferred to glass tubes (5-mm. o.d., ca. 4-cm. length) which had previously been swept out with nitrogen. The tubes were sealed and were kept in Dry Ice-acetone until they were used. For the run in which the effect of added nitric oxide was determined, the tubes were filled in the usual manner, after which nitric oxide (ca. 0.7 mmole) was added and they were sealed under vacuum.

The disproportionations were carried out at $78.2 \pm 0.1^\circ$ by placing the tubes in the vapors of refluxing 95% ethanol for the desired length of time. When each tube was removed, it was cooled in Dry Ice-acetone and opened, and a sample of its contents was introduced into the vapor-phase chromatographic column. It was necessary to maintain the column at a temperature at which the rate of disproportionation of the nitroso compound was negligible. The temperatures chosen for the individual compounds were I, 60°; II, 45°; III, 35°; and IV, 35°.

The area under each curve was computed by multiplying the height of the peak by the width at the half-height point. This method was checked by accurately weighing a sample of methylene chloride and I, mixing them, and then determining their molar ratios from both their weights and from their areas under the curve. The results were ratio of CH_2Cl_2 -I from weights—2.86, 1.26; from v.p.c.—2.84, 1.30. The differences in the ratios are probably due to weighing errors. Accurate weights of these materials were difficult to obtain because of their high volatility.

The major source of error was in transferring the aliquots to the individual tubes. In the case of I and II, the errors were not large, but with III and IV, which have boiling points of –5 and –4°, errors in transferring resulted in considerable scattering of the points.

Acknowledgment.—We are grateful to the Quartermaster Research and Engineering Command, U. S. Army, Natick, Massachusetts, for the support of the research for which Dr. J. C. Montermoso and Mr. C. B. Griffis served as the scientific officers for the Army.

The Addition Reaction of Bromotrichloromethane to Compounds with Vinyl and Perfluorovinyl Groups

HIROSHIGE MURAMATSU¹ AND PAUL TARRANT²

Department of Chemistry, University of Florida, Gainesville, Florida

Received January 3, 1964

The light-initiated reaction of bromotrichloromethane with olefins containing vinyl and trifluorovinyl groups has been studied. In cases where both groups are present in the molecule, the attack of trichloromethyl radical occurs preferentially on the methylene carbon. 1,4-Addition takes place with 1,1,2-trifluorobutadiene. In cases where a chlorine atom was located on a carbon atom adjacent to the carbon-bearing double bond, the chief product was generally not the 1:1 adduct but an olefin containing the trichloromethyl group. Some unusual dehydrohalogenations of the adducts are noted.

A number of reports have appeared in the literature³ on the free-radical addition reaction of halo alkanes to olefins and fluorine-containing olefins. However, very little information has been published on the relative reactivity of vinyl and perfluorovinyl groups, or allyl and perfluoroallyl groups toward free-radical addition. In order to obtain information on their relative reactivities, we have carried out the sunlight-initiated reactions of bromotrichloromethane and compounds containing a vinyl or a perfluorovinyl group, or both of them either conjugated or separated. The addition

reaction to 3,3-difluoroallyl bromide was also studied to compare the reactivity of fluorine-containing unsaturated groups in allylic structure with ordinary allyl groups.

Kharasch and his co-workers^{4–6} obtained predominantly 1:1 adducts, 5-bromo-1,1,1-trichloro-3-pentene (1,4-addition) and 3-bromo-5,5,5-trichloro-1-pentene (1,2-addition), by the peroxide-induced reaction of 1,3-butadiene and bromotrichloromethane. Recently Pyne⁷ reported that only the 1,4-addition product

(1) On leave from Government Industrial Research Institute, Nagoya, Japan.

(2) To whom requests for reprints should be sent.

(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 249.

(4) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

(5) M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

(6) M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953).

(7) W. J. Pyne, *ibid.*, **27**, 3483 (1962).