# Radical Reactions of Tetrafluorohydrazine. V. The Synthesis of β-Difluoramino-N′-fluorodiimide N-Oxides[1]

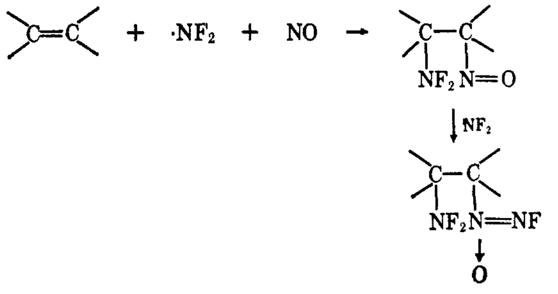
SAMUEL F. REED, JR.

*Gorgas Laboratory, Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama 35807*

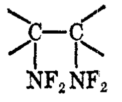
*Received June 6, 1967*

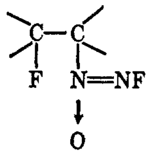
The reaction of olefins with tetrafluorohydrazine in the presence of nitric oxide leads to the synthesis of β-difluoramino-N′-fluorodiimide N-oxides through the intermediate formation of β-difluoraminonitroso compounds.

The addition of tetrafluorohydrazine to olefins to produce bis(difluoramino) compounds has been reported recently.[2] A free-radical mechanism fits the qualitative observations about olefin reactivity[2] and the kinetic behavior of the reaction.[3] It has now been found that in the presence of nitric oxide this reaction can be diverted and the corresponding β-difluoramino-N′-fluorodiimide N-oxides (I) are obtained in good yields. In addition, small amounts of the olefin $N_2F_4$ adduct (II) and the β-fluoro-N′-fluorodiimide N-oxides (III) were also isolated in most instances. The olefins investigated and the characterization data on their products are shown in Table I.



I





II III

The products from the reactions have been isolated primarily by separation of the mixtures by gas chromatography, although in several instances distillation at reduced pressure has been successful. In several reactions the bis(difluoramino) adducts were not isolated but their presence was established by their retention times on gas chromatography compared with the pure adduct prepared from $N_2F_4$. Major efforts in characterization of products have involved those obtained from the simple olefin.

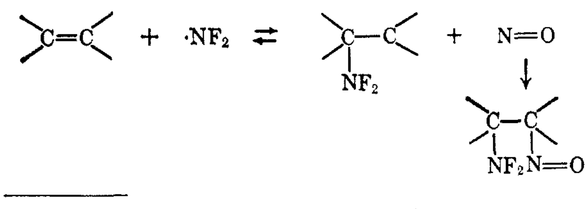
The characterization of the N′-fluorodiimide N-oxides was based in large part on comparison of their properties with the simpler homologs prepared earlier by the reaction of tetrafluorohydrazine with aliphatic and aromatic nitroso compounds.[4] In several instances sufficient quantities of the products were available for elemental analysis. The infrared spectra of difluoramino-N′-fluorodiimide N-oxides are characterized by strong absorption bands at 6.6–6.8 μ which are characteristic of azoxy compounds and at 10.7–11.2 μ due likely to N–F stretching vibrations.

$F^{19}$ nmr spectral data (Table I) are reported for the $-N(\rightarrow O){=}NF$, $-NF_2$, and C–F groups in terms of $\phi$ values. The $F^{19}$ spectra for the N-fluoroazoxy groups showed singlets in the range of $\phi$ −43.00 to −53.67 which is consistent with that reported by Stevens and Freeman[4] (−37.60 to −53.15). In addition, the $F^{19}$ nmr spectra data for the $-NF_2$ and C–F groups are consistent with the structural assignments.

The total yield of products varied from 37 to 76% based on the quantity of tetrafluorohydrazine or nitric oxide consumed in the reactions. Gas chromatography data obtained by measurement of peak areas have shown the following relative product distribution: difluoramino-N′-fluorodiimide N-oxides, 60–90%; fluoro-N′-fluorodiimide N-oxides, 20–35%; bis(difluoramines), 5–10%. These three classes of products account for at least 95% of the total products. The difluoramino-N′-fluorodiimide N-oxides from methyl methacrylate, methacrylonitrile, and 2-methyl-2-butene were separated by distillation in yields of 45, 48, and 34%, respectively.

The production of the β-difluoramino and β-fluoro-N′-fluorodiimide N-oxides when the reaction of olefins and tetrafluorohydrazine in carried out in the presence of nitric oxide is completely consistent with the mechanisms previously suggested for the $N_2F_4$–olefin reaction[2] and the $N_2F_4$ nitroso compound reaction.[4,5] Under the conditions of the reaction as conducted in this study, the concentration of nitric oxide is extremely high compared to the difluoramino radical concentration (<0.1% at 30° and 760 mm) and nearly all the intermediate radical is intercepted by nitric oxide. It is probable that most of the bis(difluoramine) is produced toward the end of the reaction when the difluoramino radical concentration is comparatively higher. The initial steps are given in Scheme I. These steps are consistent with the orienta-

SCHEME I



---

[1] This work was conducted under the sponsorship of the Advanced Research Projects Agency under Army Ordnance Contract DA-01-021 ORD-11909.

[2] A. J. Dijkstra, Ph.D. Thesis, University of Leiden, 1965; H. Cerfontain, *J. Chem. Soc.*, 6602 (1965); R. C. Petry and J. P. Freeman, unpublished work.

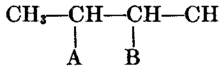
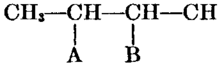
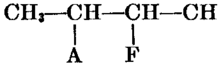
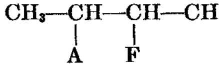
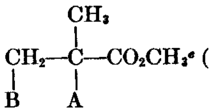
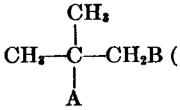
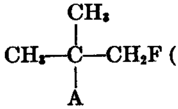
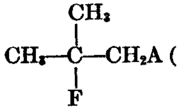
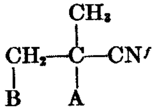
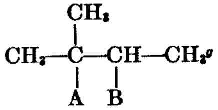
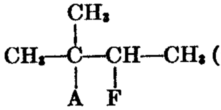
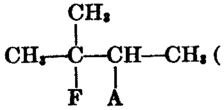
[3] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc., Sect. A*, 582 (1966).

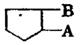
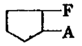
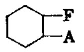
[4] T. E. Stevens and J. P. Freeman, *J. Org. Chem.*, **29**, 2279 (1964).

[5] J. W. Frazer, B. E. Holder, and E. F. Worden, *J. Inorg. Nucl. Chem.*, **24**, 45 (1962).

TABLE I

$\beta$-DIFLUORAMINO-N′-FLUORODIIMIDE N-OXIDES

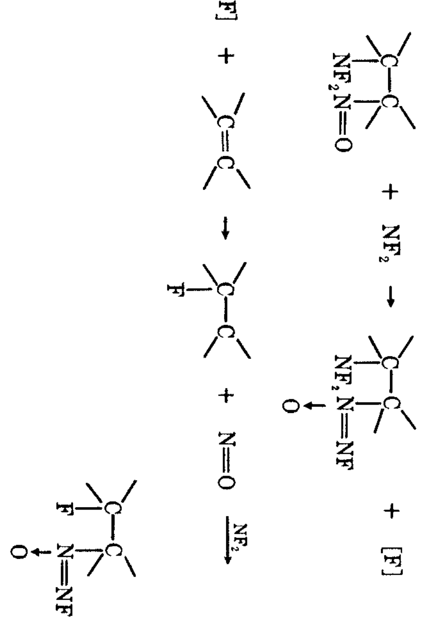
| Olefin | Products, $A = -\overset{O}{\overset{\uparrow}{N}}{=}NF$; $B = -NF_2$ | Infrared data, μ | | $F^{19}$ nmr data, $\phi$ | | | Elemental analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calcd, % | | | | Found, % | | | |
| | | $\overset{O}{\overset{\uparrow}{-N{=}N-}}$ | NF | $\overset{O}{\overset{\uparrow}{-N{=}NF}}$ | $-NF_2$ | C-F | C | H | F | N | C | H | F | N |
| 2-Butene |  $CH_3\text{—}\underset{A}{CH}\text{—}\underset{B}{CH}\text{—}CH_3$ (1) | 6.58 | 10–12 | Singlet<br>−48.75 | AB of ABX<br>A at −30.3; B at −42.6<br>$J_{AB}$ = 595, $J_{AX}$ = 33,<br>$J_{BX}$ = 9 cps | | 28.07 | 4.68 | | 24.56 | 28.99 | 5.14 | | 25.47 |
| |  $CH_3\text{—}\underset{A}{CH}\text{—}\underset{B}{CH}\text{—}CH_3$ (1) | 6.58 | 10–12 | Singlet<br>−47.60 | AB of ABX<br>−34.2 | | 28.07 | 4.68 | | 24.56 | 28.74 | 5.03 | | 23.95 |
| |  $CH_3\text{—}\underset{A}{CH}\text{—}\underset{F}{CH}\text{—}CH_3$ (2) | 6.58 | 10.78 | Singlet<br>−45.42 | | Multiplet<br>+184.65 | 34.78 | 5.80 | | 20.29 | 34.30 | 6.08 | | 20.96 |
| |  $CH_3\text{—}\underset{A}{CH}\text{—}\underset{F}{CH}\text{—}CH_3$ (2) | 6.61 | 10.9 | Singlet<br>−45.61 | | Multiplet<br>+195.6 | 34.78 | 5.80 | | 20.29 | 34.98 | 6.01 | | 20.71 |
| Methyl methacrylate |  $\underset{B}{CH_2}\text{—}\overset{CH_3}{\underset{A}{C}}\text{—}CO_2CH_3{}^{e}$ (3) | 6.68 | 10.7<br>11.08 | Singlet<br>−49.15 | Triplet<br>−58.37 | | 27.91 | 3.72 | 22.33 | 19.33 | 27.97 | 4.11 | 22.40 | 19.01 |
| Isobutylene |  $CH_3\text{—}\overset{CH_3}{\underset{A}{C}}\text{—}CH_2B$ (4) | 6.7 | 10–12 | Singlet<br>−45.15 | $J_{HF}$ = 27 cps | | 28.07 | 4.68 | | 24.56 | 28.31 | 4.81 | | 24.86 |
| |  $CH_3\text{—}\overset{CH_3}{\underset{A}{C}}\text{—}CH_2F$ (5)<br> $CH_3\text{—}\overset{CH_3}{\underset{F}{C}}\text{—}CH_2A$ (6)<br>mixture | 6.65 | 10.9 | Singlet<br>−50.12 | | Multiplet<br>+221.90<br>+224.22 | 34.78 | 5.80 | | 20.29 | 34.56 | 5.96 | | 20.57 |
| Methacrylonitrile |  $\underset{B}{CH_2}\text{—}\overset{CH_3}{\underset{A}{C}}\text{—}CN^{f}$ (7) | 6.66 | 10.75<br>10.9 | Singlet<br>−53.7 | Triplet<br>−56.4 | | 26.37 | 2.75 | 31.32 | 30.77 | 26.08 | 3.11 | 30.50 | 30.43 |
| 2-Methyl-2-butene |  $CH_3\text{—}\overset{CH_3}{\underset{A}{C}}\text{—}\underset{B}{CH}\text{—}CH_3{}^{g}$ (8) | 6.7 | 10–12 | Singlet<br>−42.25 | AB of ABX<br>−38.5 | | 32.43 | 5.41 | 30.81 | 22.70 | 33.12 | 5.69 | 30.10 | 22.22 |
| |  $CH_3\text{—}\overset{CH_3}{\underset{A}{C}}\text{—}\underset{F}{CH}\text{—}CH_3$ (9) | 6.72 | 11.02 | Singlet<br>−43.00 | | Multiplet<br>+181.82 | 39.47 | 6.58 | 25.00 | 18.42 | 40.02 | 7.07 | 25.90 | 19.78 |
| |  $CH_3\text{—}\overset{CH_3}{\underset{F}{C}}\text{—}\underset{A}{CH}\text{—}CH_3$ (10) | 6.6 | 10.87 | Singlet<br>−48.5 | | Multiplet<br>−192 | 39.47 | 6.58 | 25.00 | 18.42 | 39.35 | 6.42 | 24.80 | 19.02 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Pentene | $CH_3CH_2CH_2\underset{\underset{A}{\vert}}{C}H{-}CH_2B$ (11) | 6.59 | 10.12 | Singlet<br>−50.2 | Triplet<br>−53.0 | | 32.43 | 5.41 | 30.81 | 22.70 | 32.51 | 5.65 | 31.06 | 23.10 |
| | $CH_3CH_2CH_2\underset{\underset{A}{\vert}}{C}H{-}CH_2F$ (12) | 6.6 | 10.91 | Singlet<br>−49.7 | | Triplet<br>+224.0 | 39.47 | 6.58 | 25.00 | 18.42 | 39.30 | 6.76 | 24.76 | 19.00 |
| | $CH_3CH_2CH_2\underset{\underset{F}{\vert}}{C}H{-}CH_2A$ (13) | 6.6 | 11.03 | Singlet<br>−48.4 | | Multiplet<br>+222.3 | 39.47 | 6.58 | 25.00 | 18.42 | 39.73 | 6.76 | 25.25 | 18.86 |
| 1-Hexene | $CH_3CH_2CH_2CH_2\underset{\underset{A}{\vert}}{C}H{-}CH_2B$ (14) | 6.58 | 10–12 | Singlet<br>−49.7 | Triplet<br>−53.4 | | 36.18 | 6.03 | 28.64 | 21.11 | 36.60 | 6.11 | 28.55 | 21.45 |
| | $CH_3CH_2CH_2CH_2\underset{\underset{A}{\vert}}{C}H{-}CH_2F$ (15) | 6.65 | 10.80 | Singlet<br>−48.4 | | Triplet<br>+221.2 | 43.37 | 7.23 | 22.89 | 16.87 | 43.62 | 7.05 | 23.11 | 17.20 |
| | $CH_3CH_2CH_2CH_2CHF{-}CH_2A$ (16) | 6.58 | 10.96 | Singlet<br>−50.4 | | Multiplet<br>+186.2 | 43.37 | 7.23 | 22.89 | 16.87 | 43.60 | 7.36 | 23.05 | 17.10 |
| Cyclopentene |  (17) | 6.62 | 10–12 | Singlet<br>−50.7 | AB of ABX<br>−48.1 | | 32.79 | 4.37 | 31.15 | 22.95 | 33.17 | 4.54 | 30.89 | 23.33 |
| |  (18) | 6.62 | 10.95 | Singlet<br>−45.5 | | Multiplet<br>+190.6 | 40.00 | 5.33 | 25.33 | 18.67 | 39.83 | 5.51 | 25.50 | 19.05 |
| Cyclohexene[d] |  (19) | 6.62 | 10.76 | Singlet<br>−47.08 | | Multiplet<br>+177.2<br>+178.45 | 43.90 | 6.10 | 23.17 | 17.07 | 44.18 | 6.51 | 23.34 | 17.01 |

[a] The bisdifluoroamines were obtained in all reactions in addition to those products listed. [b] Infrared spectra were obtained using a Perkin-Elmer Infracord spectrophotometer with a sodium chloride prism. [c] Nmr spectra obtained on a Varian Associates Model V-3000-B high-resolution spectrometer using a 40-Mc radio frequency unit and probe. [d] Only the N-[$\beta$-fluoroalkyl]-N′-fluorodiimide N-oxide could be isolated. [e] Bp 91–93° (0.65 mm), $n^{20}{}_D$ 1.4201. [f] Bp 60° (0.45 mm), $n^{20}{}_D$ 1.4197. [g] Bp 73–74° (12 mm), $n^{20}{}_D$ 1.4196.

tion observed in that the fluorazoxy group is attached to the more highly substituted carbon; *i.e.*, it is derived from the more stable radical. Also, it is known that nitic oxide will not add to olefins but is very efficient at trapping hydrocarbon radicals.[6] The fluoroazoxy compounds arise from further reaction of the nitroso compound and difluoramino radicals.[4] Since a fluorine atom (or its equivalent) is produced in this latter reaction, the origin of the $\beta$-fluoro-N′-fluorodiimide N-oxides is also accounted for (Scheme II). The lack of discrimination in the isobutylene and 2-methyl-2-butene reactions which produce isomeric $\beta$-fluoro-N′-fluorodiimide N-oxides (Table I) is also consistent with a fluorine radical attack. The addition of crushed glass to the reaction vessel decreased the amount of fluorocarbon product. It was previously noted that glass vessels were attacked during the nitroso compound–$N_2F_4$ reaction.[4]

SCHEME II



## Experimental Section

**General Comments.**—The reactions were conducted in an all-glass system in solution at subatmospheric pressures. The most common solvent employed was chloroform, although other solvents have proven satisfactory. Subatmospheric pressures of 700–300 mm have generally been used. The olefin in solvent is introduced into a flask which is connected to a condenser and glass manifold system. The total system is evacuated by several freeze–thaw cycles after which equal parts of tetrafluorohydrazine and nitric oxide are added to the system. The temperature is usually maintained below 30°, although in certain instances reactions have been conducted at temperatures as high as 60°. The experimental data for several reactions are present in Table II.

Experimental conditions were altered for some of the olefins by conducting the reactions at higher pressures of tetrafluorohydrazine–nitric oxide. These reactions were carried out in glass aerosol tubes connected to a high-pressure manifold system. The olefin in solvent was introduced into the aerosol tube, the tube placed on the manifold system, and flushed with nitrogen several times. The system was then charged with tetrafluorohydrazine–nitric oxide (premixed in a 50:50 mole ratio) and the reaction allowed to proceed at a designated temperature (usually ambient temperature) while maintaining the pressure between 80 and 200 psi by frequently recharging the system at necessary intervals. Little, if any, change in product distribution based on a comparison of peak areas from gas chromatography was observed between reactions conducted at subatmospheric or at elevated pressures. A rate enhancement was qualitatively observed. It is important to remember that the same general safety precautions must be observed in these reactions as specified for the olefin–$N_2F_4$ reactions. All of these reactions constitute explosion hazards and must be carried out with this possibility allowed for.

---

[6] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **79**, 2480 (1957).

TABLE II

EXPERIMENTAL DATA ON REACTIONS OF OLEFINS WITH TETRAFLUOROHYDRAZINE–NITRIC OXIDE MIXTURES

| Olefin (mmoles) | $N_2F_4$ added, mmoles | NO added, mmoles | Time, hr | Pressure range, mm | Maximum temp, °C | $N_2F_4$ consumed, mmoles | NO consumed, mmoles |
|---|---|---|---|---|---|---|---|
| 2-Butene (23.7) | 62 | 62 | 69 | 690–500 | 26 | 21 | 36 |
| 2-Methyl-2-butene (143) | 62 | 62 | 19 | 565–350 | 30 | 34 | 41 |
| Isobutylene (23.7) | 30 | 30 | 28 | 630–410 | 30 | 18 | 27 |
| 1-Pentene (100) | 62 | 62 | 22 | 555–485 | 30 | 34 | 24 |
| 1-Hexene (100) | 62 | 62 | 29 | 585–490 | 30 | 24 | 23 |
| Cyclopentene (100) | 62 | 62 | 72 | 520–295 | 30 | 48 | 46 |
| Cyclohexene (100) | 62 | 62 | 42 | 590–410 | 30 | 41 | 44 |
| Methyl methacrylate (100) | 62 | 62 | 21 | 573–285 | 30 | 43 | 23 |
| Methacrylonitrile (117) | 190 | 185 | 144 | 573–400 | 25 | 85 | 82 |

**Reactions of 2-Methyl-2-butene with Tetrafluorohydrazine and Nitric Oxide.**—To a 200-ml round-bottom flask was introduced 30.0 ml of dry chloroform and 10.0 g of 2-methyl-2-butene. The flask was attached to a vacuum manifold and deaerated by several freeze–thaw cycles. Into a separate evacuated flask attached to the manifold was condensed 6.43 g (62 mmoles) of tetrafluorohydrazine and 1.85 g (62 mmoles) of nitric oxide which was then allowed to expand into the reaction flask. The initial pressure was 569 mm. The reaction started within minutes with the formation of a greenish blue coloration and a decrease in pressure. The greenish blue color changed to a light yellow after 2–3 hr. The reaction was continued for a period of 19 hr with stirring (magnetic stirrer) to give a final pressure reading of 350 mm. The excess gas fraction was removed from the reactor and condensed into an expansion bulb and after expansion the mass spectrum of the gases was obtained. The gas fraction was made up of the following: 45.2% $N_2F_4$, 32.9% NO, 5.3% $SiF_4$, 6% $N_2O$, 4.4% $CHCl_3$, 4.6% $N_2$, and 1.6% $N_2F_2$. A total of 3.53 g (34 mmoles) of tetrafluorohydrazine (55%) and 1.24 g (41 mmoles) of nitric oxide (66%) was consumed in this reaction.

After thorough degassing[7] the flask containing the solution was opened to the air, removed from the manifold, and examined by gas chromatography. This product fraction consisted of several components. The major part of the solvent and excess 2-methyl-2-butene were removed on a rotary evaporatior at reduced pressure. The residue (9.63 g) was examined by gas chromatography and found to contain three major, one intermediate, and several minor components. The intermediate component was identified as 2-methyl-2,3-bis(difluoroamino)-butane by comparison of its retention time with that of an authentic sample.[2] The residue was fractionated through an 18-in. semimicro spinning band column to give 2.14 g (22.7%) of a mixture of *meso-* and *dl*-3-(2-methyl-2-fluorobutyl)-N′-fluorodiimide N-oxides, bp 52–59° (13 mm), and 5.21 g (33.8%) of 3-(2-methyl-2-difluoroaminobutyl)-N′-fluorodiimide N-oxide, bp 73–74° (12 mm). Some decomposition of the latter compound was noted to occur during the distillation (see Table I for characterization data). In most cases the products in the crude residue after removal of solvent and excess olefin were separated by gas chromatography using an Aerograph gas chromatographic instrument, Model A-110-C, with a 5-ft dinonyl phthalate column at 50–100°.

**Registry No.**—Tetrafluorohydrazine, 10036-47-2; **1**, 14296-41-4; **2**, 14296-42-5; **3**, 14296-43-6; **4**, 14296-44-7; **5**, 14362-58-4; **6**, 14296-45-8; **7**, 14296-46-9; **8**, 14296-47-0; **9**, 14296-48-1; **10**, 14362-59-5; **11**, 14296-49-2; **12**, 14296-50-5; **13**, 14296-51-6; **14**, 14296-52-7; **15**, 14296-53-8; **16**, 14296-54-9; **17**, 14296-55-0; **18**, 14296-28-7; **19**, 14296-29-8.

**Acknowledgment.**—The interpretation of the $F^{19}$ nmr spectra were carried out by Mrs. Carolyn Haney. The technical support of Mr. J. O. Woods is greatly appreciated.

[7] This step is critical since mixtures of air, hydrocarbons, and $N_2F_4$ are highly explosive.

---

# Derivatives of Thiacyclobutene (Thiete). II.[1] Reactions of 7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-Dioxide[2-4]

DONALD C. DITTMER AND FRANKLIN A. DAVIS

*Department of Chemistry, Bowne Hall, Syracuse University, Syracuse, New York 13210*

*Received August 4, 1967*

7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide (**1**) is isomerized to the endocyclic olefin, 7-thiabicyclo[4.2.0]-1(6)-octene (**2**) by treatment with potassium hydroxide in tetrahydrofuran. Treatment of the exocyclic compound **1** with potassium *t*-butoxide in *t*-butyl alcohol gave principally 2-methylsulfonylcyclohexanone (**3**), a small amount of *endo* sulfone **2**, and isobutylene. Treatment of the *exo* sulfone with potassium ethoxide gave 1-ethoxy-7-thiabicyclo[4.2.0]octane 7,7-dioxide (**7**). *endo* sulfone **2**, but not the *exo* sulfone **1**, could be aromatized to benzothiete sulfone **8**.

The synthesis of the first bicyclic thiete sulfone, 7-thiabicyclo[4.2.0]-1(8)-octane 7,7-dioxide (**1**) has been reported previously[5] and the preparations of several monocyclic thiete sulfones[6,7] and fused aromatic derivatives of thiete sulfone[5b,8] have been described.

---

[1] Part I: D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

[2] This work was aided by National Science Foundation Grants GP 726 and GP 5513.

[3] Reported in part at the 148th National Meeting, American Chemical Society, Chicago, Ill., Sept 1964.

[4] Taken from the Ph.D. Thesis of F. A. Davis, Syracuse University, 1966.

[5] (a) D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **29**, 3131 (1964); (b) L. A. Paquette, *ibid.*, **30**, 629 (1965).

[6] See references given in ref 5a for earlier work.

[7] J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966); G. Opitz and H. Schempp, *Z. Naturforsch.*, **19b**, 78 (1964); G. Opitz and H. Schempp, *Ann.*, **684**, 103 (1965); R. H. Hasek, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **30**, 1495 (1965).

[8] D. C. Dittmer and N. Takashina, *Tetrahedron Letters*, 3809 (1964); L. A. Paquette and T. R. Phillips, *J. Org. Chem.*, **30**, 3883 (1965).