Anal. Calcd for $C_7F_8H_6O_2$: C, 30.67; H, 2.21. Found: C, 30.75; H, 2.38.

Registry No.—II ($n = 1$), 13811-24-0; IV, 4259-30-7; $Br(CF_2CF_2)_2CO_2C_2H_5$, 424-35-1; $Br(CF_2CF_2)_3CO_2C_2H_5$, 13811-27-3; $Br(CF_2CF_2)_4CO_2C_2H_5$, 13811-28-4; $CF_3CFBrCF_2CO_2C_2H_5$, 13952-49-3; $BrCF_2CF_2CONH_2$, 13811-29-5; $Br(CF_2CF_2)_2CONH_2$, 13811-30-8; $Br(CF_2CF_2)_3CONH_2$, 13811-31-9; $Br(CF_2CF_2)_4CONH_2$, 13811-32-0; $CF_3CFBrCF_2CONH_2$, 13811-33-1; $BrCF_2CF_2CN$, 421-97-6; $Br(CF_2CF_2)_2CN$, 13811-35-3; $Br(CF_2CF_2)_3CN$, 13811-36-4.

Acknowledgment.—The author wishes to thank Mr. J. C. Lavis for his technical assistance.

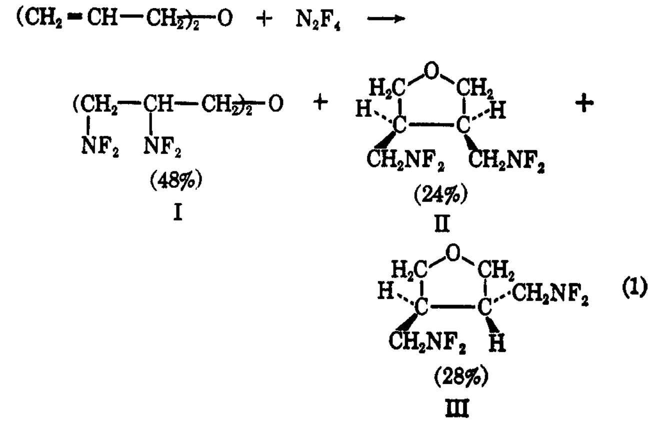
Radical Reactions of Tetrafluorohydrazine. Diallyl Ether[1]

SAMUEL F. REED, JR.

Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama 35807

Received February 10, 1967

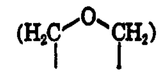
Studies on the radical reactions of tetrafluorohydrazine have now included the reaction with diallyl ether. The expected addition reaction[2] would yield di[2,3-bis(difluoramino)propyl] ether (I); however, it followed, in part, an unexpected course yielding two isomeric cyclic bis(difluoramino)-substituted compounds II and III (eq 1). The ratio of bis- to tetrakis(difluoramino) derivatives was approximately 1:1 under our reaction conditions.



On examination of the crude product fraction by gas chromatography, three components were noted to be present in a ratio of 2:1:1 based on peak areas. Attempts to effect separation of the products by distillation were not successful in yielding the pure components, and small quantities of the three products were separated by gas chromatography for purposes of characterization.

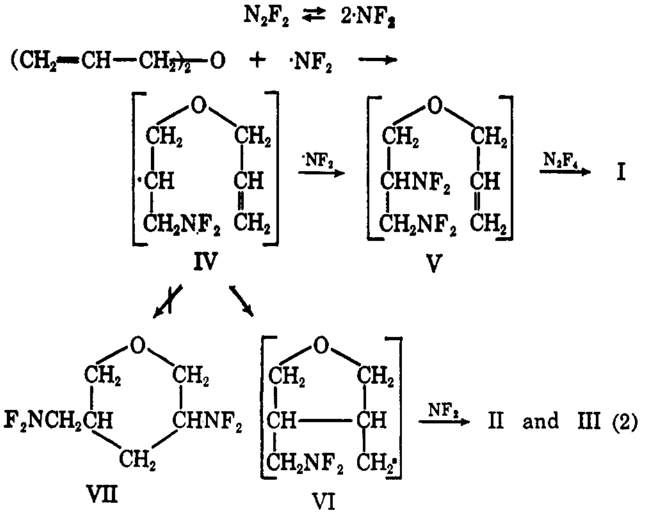
The F^{19} nmr spectrum of I showed a triplet centered at ϕ −56.8 (J = ~27 cps) and a multiplet centered at −42.0 representing the $-CH_2NF_2$ and $>CHNF_2$ groups, respectively. The proton resonance included superimposed triplets at τ 6.07 (J = 27 cps) due to the $-CH_2NF_2$ and $>CHNF_2$ protons. The methylene protons adjacent to the oxygen atom coincided with the center of the above triplet. These data are indicative of a compound with the structure of I.

Products II and III were identified as the indicated *cis, trans* isomers by elemental analysis and the following data. The F^{19} nmr spectra showed only triplets typical of primary alkyl difluoramines centered at ϕ −55.8 (J = 26 cps) and ϕ −56.5 (J = 27 cps) for II and III, respectively, indicating the presence of $-CH_2NF_2$ groups. The resonance signals in the pmr spectrum of II occurred as a triplet of multiplets centered at τ 6.42 ($-CH_2NF_2$), a multiplet centered at 6.04


$(H_2C{-}O{-}CH_2)$

and also a multiplet centered at 7.58 ($>CH{-}CH<$). Peak areas of methylene to methine protons was 4:1. The proton nmr spectrum of III showed a very complicated multiplet centered at τ 6.22 assigned as the signal arising from ring methylenes as well as part of the triplet from the $-CH_2NF_2$ groups. Also present was a multiplet centered at τ 7.23 attributed to the ring methine protons.

Tetrafluorohydrazine is known[2,3] to undergo a number of radical reactions with various substrates. In this instance the reaction mechanism is considered to involve the sequence given in eq 2. After initial disassociation of tetrafluorohydrazine, the difluoramino radical attacks at the terminal carbon atom of one of the carbon–carbon double bonds of diallyl ether to give the intermediate (IV), a 3-oxa-5-hexen-1-yl radical, which may react in either of two ways to give the 2,3-bis(difluoraminopropyl) allyl ether (V), or by an intramolecular attack of the radical on the remaining carbon–carbon double bond to give the cyclic intermediate (VI). In either instance the intermediates, V and VI, react further to yield the observed products, since V will ultimately give I by its further reaction with tetrafluorohydrazine, and VI, by reacting with a difluoramino radical, may give products II and III depending upon its configuration during cyclization.



---

[1] This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama under Contract Number DA-01-021 ORD-11909 (Z).

[2] A. L. Logothetis, U. S. Patents 3,196,167, (July 1965) and 3,215,709, (Nov 1965); H. Certontain, *J. Chem. Soc.*, 6602 (1965); A. J. Dijkstra, Ph.D. Thesis, "Kinetic Study of the Addition of Tetrafluorohydrazine to Olefins," University of Leiden, 1965; and R. C. Petry and J. P. Freeman, unpublished work.

[3] J. P. Freeman, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 128.

There was no evidence to support the alternate course of cyclization resulting in the formation of a six-membered ring compound (VII) containing primary and secondary difluoramino groups.

The observed cyclization has an analogy to the mechanism proposed for the formation of certain intermediates and cyclic structures in the intra–intermolecular polymerization of various diallyl compounds;[4] however, only six membered ring structures have been reported in these instances. Julia[5] has reported the cyclization of appropriately substituted 5-hexen-1-yl radicals to both five- and six-membered rings, while others[6,7] found that similar radicals gave predominately five-membered ring compounds. Brace[8] has reported that the azobisisobutyronitrile-initiated reaction of perfluoroalkyl iodides with heptadiene and diallyl ether yielded only the cyclopentane derivatives as cyclic products, and proposed a mechanism as presented above for their formation. This latter work likely represents the first example of the cyclization of 1,6-dienes *via* radical attack to give simple cyclic products, and hence, the presently reported work is another case of a similar type reaction.

Other 1,6-dienes investigated were N,N-diallyl acetamide and acrylic anhydride. A bis(difluoramino) derivative of N,N-diallyl acetamide was obtained which was believed to be a cyclic five-membered ring product; however, the compound was not purified sufficiently for conclusive structural determination. The reaction with acrylic anhydride resulted in its polymerization and no attempt was made toward the structural characterization of this polymeric material.

Experimental Section

Tetrafluorohydrazine–Diallyl Ether Reaction.—To a thick-walled glass container (Fischer-Porter Aerosol tube) of 100-cc capacity was introduced a mixture of 5.0 g (0.51 mole) of diallyl ether in 30 ml of carbon tetrachloride. The Aerosol tube was connected to a high-pressure manifold and the entire system was flushed three times with dry nitrogen. The system was degassed and then precharged with tetrafluorohydrazine until no further pressure drop was observed (200 psi). The system was heated by an externally placed oil bath to a temperature of 80° and this temperature was maintained over a period of 3 hr. During this time the N_2F_4 pressure was maintained between 420 and 160 psi by frequently recharging as necessary. Heating was continued until no further pressure drop was observed. After cooling, the mixture was degassed by first venting the excess N_2F_4 and flushing several times with dry nitrogen. The reaction mixture was transferred to a RB flask and the solvent removed at reduced pressure on a rotary evaporator to give 12.4 g of liquid residue. Examination of the residue by gas chromatography indicated a mixture of three components in the ratio 2:1:1 based on gc retention times and peak areas. Distillation of the mixture through an 18-in. Holtzman column gave two fractions, bp 60–65° (4 mm) and 76–78° (4 mm), but was ineffective in giving complete separation of the three components. A small quantity of each was separated by gc.[9] Each product was characterized by its nmr spectra and elemental analysis.

Anal. Calcd for $C_6H_{10}F_8N_4O$: C, 23.53; H, 3.27; F, 49.67; N, 18.30. Found (I): C, 23.71; H, 3.17; F, 49.88; N, 18.62. Calcd for $C_6H_{10}F_4N_2O$: C, 35.64; H, 4.95; F, 37.62; N, 13.86. Found (II): C, 35.76; H, 4.82; F, 37.70; N, 14.25. Found (III): C, 35.78; H, 5.08; F, 37.41; N, 14.17.

Registry No.—I, 13673-71-7; II, 13673-72-8; III, 13673-73-9; tetrafluorohydrazine, 10036-47-4; diallyl ether, 557-40-4.

Acknowledgment.—The encouragement and support of Dr. R. C. Petry, the technical support of Mr. Hollis H. Hill, and the interpretation of the nmr spectra by Dr. F. A. Johnson and Mrs. Carolyn Haney are gratefully acknowledged.

---

[4] C. S. Marvel, *J. Polymer Sci.*, **68**, 101 (1960).

[5] M. Julia, J. M. Suram, and L. Katg, *Compt. Rend*, **251**, 1030 (1960); M. Julia and F. LeGoffic, *ibid.*, **255**, 714 (1962); M. Julia, *Rec. Chem. Progr.*, **25**, 3 (1964).

[6] R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

[7] C. Walling and M. J. Pearson, *ibid.*, **86**, 2262 (1964).

[8] N. O. Brace, *J. Am. Chem. Soc.*, **86**, 524 (1964); N. O. Brace, *J. Org. Chem.*, **31**, 2879 (1966).

[9] A 0.25 in. × 5 ft column packed with Dinonyl Phthalate on Chromosorb was employed in an Aerograph Instrument, Model-A-100-C at 100°. Helium served as the carrier gas and a thermal conductivity cell served as the detector.

A Photochemical Cycloaddition of Thiobenzophenone to α-Phellandrene

YOSHIMORI OMOTE, MICHIKAZU YOSHIOKA, KAZUTOSHI YAMADA, AND NOBORU SUGIYAMA

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo, Japan

Received March 3, 1967

An extensive study of the ultraviolet irradiation of thiobenzophenone in alcoholic solvents was reported by Oster and co-workers.[1] The photolytic products from thiobenzophenone were benzhydryl mercaptan, dibenzhydryl disulfide, and tribenzhydryl tetrasulfide, whereas that from benzophenone was dibenzopinacol.[2]

Although the photochemical cycloaddition of carbonyl compounds to carbon–carbon double bonds to form oxetanes is well known,[3–10] very few studies on the photoreaction of thioketones with olefinic compounds have been found in the literature. Dobashi and co-workers[11] observed the formation of 3,3,4,4-tetraphenyl-2,5-dithiabicyclo[4,4,0]decane or 3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo[4,4,0]decane by the photoaddition of thiobenzophenone to cyclohexene or 2,3-dihydropyran, respectively. Kaiser and Wulfers[12] have also reported the novel photolytic reaction of the mixture of thiobenzophenone and ethylene derivatives to form 1,1-diphenylethylene derivatives. A four-membered ring containing a sulfur atom (thietane) was postulated as a possible intermediate for this photolytic reaction.

When an equimolar mixture of thiobenzophenone and α-phellandrene was irradiated with a Pyrex, filtered, ultraviolet light, we observed the gradual de-

---

[1] G. Oster, L. Citarel, and M. Goodman, *J. Am. Chem. Soc.*, **84**, 703 (1962).

[2] J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

[3] E. Paterno and G. Chioffii, *Gazz. Chim. Ital.*, **39**, 341 (1909).

[4] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

[5] R. Srinivasan, *ibid.*, **82**, 775 (1960).

[6] J. F. Harris, Jr., and D. D. Coffman, *ibid.*, **84**, 1553 (1962).

[7] D. R. Arnold, R. C. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425, (1964).

[8] N. C. Yang, M. Nussin, M. J. Jorgenson, and S. Murov, *ibid.*, 3657, (1964).

[9] N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

[10] J. Saltiel, R. M. Coates, and W. G. Dauben, *J. Am. Chem. Soc.*, **88**, 2745 (1966).

[11] G. Dobashi, M. Fukuyama, M. Yamanouchi, and T. Koizumi, 19th Annual Meeting of the Chemical Society of Japan, Mar 31, 1966.

[12] E. T. Kaiser and T. F. Wulfers, *J. Am. Chem. Soc.*, **86**, 1897 (1964).