In the study of ethyl bromide 0.65 ml. of ethyl bromide (at ~10°) was added to 90 ml. of 0.0599 *M* potassium isopropoxide in a 100-ml. flask in a 20.0 ± 0.05° bath. At intervals, 10-ml. samples were withdrawn by pipet into an excess of acid and then titrated with base.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMICAL ENGINEERING AND CHEMISTRY, UNIVERSITY OF FLORIDA]

Some Thermal Reactions of Perfluoroalkyl Derivatives of SF_6 with Fluorocarbon Olefins[1]

BY R. D. DRESDNER, T. J. MAO AND J. A. YOUNG

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Thermal reactions between the reactants (A) $(CF_3)_2SF_4$ and $CF_3CF{=}CF_2$ and (B) CF_3SF_5 and $CF_3C{\equiv}CCF_3$ were carried out at atmospheric pressure and slightly above 500° in a flow system. In reaction A the major products by weight were a mixture of C_5F_{12} isomers from which a rather pure sample of neo-C_5F_{12} was isolated. Some of its properties and its infrared assignments are given. In reaction B, the only isolable products were the compounds perfluoro-2,3,4-trimethylhexadiene-2,4 and perfluoro-2,3,4,5-tetramethylhexadiene-2,4. Some of the chemical and physical properties of these new dienes are presented.

Both perfluoroalkyl sulfur pentafluorides and the tetrafluorides have demonstrated the tendency to form what appear to be fluorocarbon free radicals when they are heated up to their respective decomposition temperatures. The pentafluorides also appear to produce F· radicals. In all cases thus far examined, SF_4 is the other main product. For example,[2-4] $R_fSF_4R_f$ and R_fSF_5, where R_f is CF_3, C_2F_5 and C_4F_9, have been shown to form $R_f{-}R_f$ when $(R_f)_2SF_4$ is pyrolyzed and both $R_f{-}R_f$ and $R_f{-}F$ when R_fSF_5 is pyrolyzed. These types of fluorocarbon sulfur compounds also have been demonstrated to add their resulting free radicals across the unsaturation in fluorocarbon olefins such as $CF_3CF{=}CF_2$ and $CF_3N{=}CF_2$.[3,4] At the high temperatures involved, some dimerization of the olefins containing only carbon and fluorine is observed when R_fSF_5 type compounds are involved, and frequently some degree of isomerization of the simpler products has been observed.

Experimental

Materials.—The CF_3SF_5 and $(CF_3)_2SF_4$ were prepared as previously described.[3,5] Perfluoropropylene was prepared according to the procedure of LaZerte.[6] It was freed of the CO_2 contaminant by scrubbing with concentrated NaOH until no precipitate was observed in a $Ba(OH)_2$ test solution. The dried products were fractionated and a center cut, b. −29°, mol. wt. 150, was used. This was checked for purity in a model 152 Perkin-Elmer vapor fractometer at room temperature using a stationary phase of the ethyl ester of Kel-F acid 8114. The purity was ascertained as not being less than 99.5% by weight.

Perfluorobutyne-2 was prepared from 2,3-dichloroperfluorobutene-2 purchased from the Hooker Chemical Co. The dichloride was refluxed with an excess of fine zinc powder in dry isopropyl alcohol as the solvent. The zinc surface was activated by washing with dil. HCl, then with water and dry isopropyl alcohol. The yields were slightly in excess of 60%. The $CF_3C{\equiv}CCF_3$ used has a b.p. of −24° and a mol. wt. of 162.

Reaction of $(CF_3)_2SF_4$ and $CF_3CF{=}CF_2$.—The experimental procedure and the equipment for carrying out similar flow reactions with low boiling materials with almost equal boiling points has been described.[3] In this reaction a slight modification was necessary. In order to mix the gases in almost equimolar quantities before they entered the thermal reactor, the olefin was bubbled through a trap containing the sulfur compound. The trap, 12″ long, had an entry tube that reached to the bottom. The respective diameters of the trap and tube were 20 mm. and 8 mm. The trap was immersed in an ice-water-bath at which temperature the $(CF_3)_2SF_4$ was observed to have a vapor pressure of about 400 mm.

Thirty-two grams of $(CF_3)_2SF_4$ (0.13 mole) and 20 g. of $CF_3CF{=}CF_2$ (0.13 mole) were allowed to react at 518° and essentially atmospheric pressure. The mass flow rate was 0.15 g./min. The estimated contact time in the heated zone not below 490° was in the order of 30 to 40 seconds. Under similar conditions the sulfur compound is known to decompose completely to form C_2F_6 and SF_4.

The products were fractionated in a low temperature column. The head coolant was changed from a Dry Ice-acetone mixture to iced water when solids were observed forming on the head near room temperature. The main isolated fractions were: 1, 11.5 g., b. −40 to −39°, m.w. 107–109, identified as SF_4 (b. −39.2°, mol. wt. 108); 2, 3.0 g., b. −30 to −29°, mol. wt. 150 identified by comparison infrared spectrum as perfluoropropylene; 3, 14.5 g., b. 28.5–29.5°, mol. wt. 287–288, m.p. slush below 10°. Some of this fraction formed a subliming solid on the column head even with ice-water coolant. It dissolved in the reflux and could be removed by using very slight suction on the take-off. This material was analyzed qualitatively for sulfur and none was found in several trials. It was assumed to be a mixture of C_5F_{12} isomers.

There were two other undefined fractions obtained, namely, the overhead from the column, 4 g., which was washed with 20% NaOH and then had a mol. wt. of 138 and showed the low pressure melting characteristics of C_2F_6, and the pot residue which amounted to 3 g. and was found to contain sulfur.

The amount of SF_4 recovered represents 88% of the theoretical amount available from the estimated 30 g. of $(CF_3)_2SF_4$ used up in the reaction.

The C_2F_6 recovered indicates that at least 11.5% of the sulfur compound that reacted was not involved in the formation of the C_5F_{12} isomers.

Fraction 3 was assumed to have a high concentration of the neo-C_5F_{12} from the rather high temperature at which solid material was observed. A smaller sample of a similar mixture was obtained in the prior reaction between CF_3SF_5 and $CF_3CF{=}CF_2$,[3] from which a sufficient amount of purified neo isomer was isolated to confirm its structure by n.m.r. spectrographic analysis.[7]

The larger sample of isomers from the current source was enriched in the neo isomer by slow transfer *in vacuo* below 0°. Finally about 1 g. of white crystals was retained,

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[1] This work was supported by the Chemistry Branch of the Office of Naval Research. Reproduction of all or any part of this paper for purposes of the United States Government is permitted.

[2] W. A. Severson, T. J. Brice and R. I. Coon, 128th Meeting, ACS, Minneapolis, Minn., Sept. 11–16, 1955, Div. Ind. Eng. Chem., Fluorine Chem. Subsec.

[3] R. Dresdner, THIS JOURNAL, **77**, 6633 (1955).

[4] R. Dresdner, *ibid.*, **79**, 69 (1957).

[5] A. F. Clifford, H. K. El-Shamy, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953).

[6] J. D. LaZerte, *et al.*, THIS JOURNAL, **75**, 4525 (1953).

[7] N. Muller, P. C. Lauterbur and G. F. Svatos, *ibid.*, **79**, 1807 (1957).

which had a mol. wt. of 288. The m.p. (76.3–78.2°) determination was reported in a prior communication.[8] The purest sample of neo-C_5F_{12} manifested one other interesting property. On standing in a sealed tube over a period of days it converted to an extremely viscous glass. It could be recrystallized by immersion in a bath cooled to −80°. An infrared spectrum was run on the purest available sample with a Perkin-Elmer double beam instrument and the following relative peak assignments were obtained: 7.72 (vs), 8.37(vw), 10.08(s) and 13.64(w).

Anal. Calcd. for C_5F_{12}: F, 79.12; mol. wt., 288. Found: F, 79.55, 79.17; mol. wt., 288.

Reaction between CF_3SF_5 and $CF_3C{\equiv}CCF_3$.—Preliminary to performing the above reaction, it was established that perfluorobutyne-2 was in no way affected by passage through the reactor at 510° at a rate of 0.13 g./min. However, it was found to attack a stainless steel reaction vessel at temperatures as low as 290° at 19 atm. The reaction was more appreciable at 350° and only 12.5 atm. Since CF_3SF_5 does not decompose below 420° in a closed system of this nature, as expected no favorable reaction was observed between the reactants in the pressurized system. On the other hand, using small quantities of reactants in a flow system in the ratio 2 CF_3SF_5 to 1 $CF_3C{\equiv}CCF_3$ clean products boiling up to 100° were obtained.

In a second larger scale reaction, 117 g. (0.72 mole) of perfluorobutyne-2 was allowed to react with 114 g. (0.58 mole) of perfluoromethyl sulfur pentafluoride in the flow system at 525° at a mass flow rate of 0.30 g. per min. An ice-cooled trap was placed after the reactor to trap liquid products. Some 50 g. of SF_4 and 15 g. of CF_3SF_5 were recovered in the low temperature fractionation. The SF_4 is equivalent to 91 g. of the sulfur compound. No relatively pure compounds were found in the ensuing high temperature fractionation until a head temperature of 90° was reached. All fractions were checked by vapor phase chromatography.

The following fractions were found, purified and identified: A, fraction b. 90–92°, mol. wt. 400–404, 93% one component as determined vapor chromatographically; it contained three minor impurities and amounted to 22 g.; B, fraction b. 92–94°, mol. wt. 407–410, 97% one component, same impurities in lesser amounts, $n^{25}D$ 1.2902, to 20 g.

Fraction B was subjected to infrared analysis and showed two peaks in the C=C region with assignments of 5.80 and 5.90 μ. Attempts to react it with Br_2 or MeOH in a sealed glass vessel at temperatures up to 200° failed. The recovered material showed no change in infrared or $n^{25}D$. Reflux with basic permanganate for several days destroyed 20% of an aliquot. The $n^{25}D$ dropped to 1.2886 and the infrared manifested minor changes but no change in the C=C assignments occurred. Further reflux with fresh basic permanganate over a four-day period destroyed another 20% of the aliquot but the remaining material showed no further change in $n^{25}D$ or infrared. The purified sample was re-examined vapor chromatographically and was found to be 99.5% one component, with the same appearance time as the major component of the crude material. Since the vapor chromatograph does not necessarily separate fluorocarbon isomers, the sample was subjected to n.m.r. analysis.[9] The results showed, on comparison with work on other perfluoromaterials,[7] that no five- or six-membered rings, and no CF_2 groups were permitted. There was positive evidence for CF_3, $CF_3C{=}$ and CF assignments. The resonance peaks were four in number. On the basis of the above data and the analysis, it was assumed that fractions A and B were mainly perfluoro-2,3,4-trimethylhexadiene-2,4.

Anal. Calcd. for C_9F_{16}: F, 73.8; C, 26.2; mol. wt., 412; *MR*D, 43.85. Found: F, 74.2; C, 26.0; mol. wt., 408; d^{25} 1.6998; $n^{25}D$, 1.2886; *MR*D, 43.70; b.p. (micro) 92.2°.

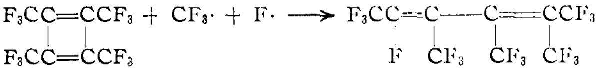
Finally, a fraction boiling between 111.5 and 113.0° amounting to 22 g. was found. It had an $n^{25}D$ of 1.3002 at 25° and an infrared spectrum exceedingly similar to that of the material found in fractions A and B, with the exception that there was only a single C=C assignment at 6.01 μ. This material was 97% pure. It too failed to react with Br_2 or MeOH under the conditions cited above and was subject to oxidation by basic permanganate in much the same manner. The final infrared spectrum again showed minor variations with no change in the C=C assignment. The purified material was again about 99.5% by weight. The terminal $n^{25}D$ at 25° was 1.2994. The n.m.r. results excluded not only 5- and 6-membered rings and CF_2 groups but also CF assignments. The only allowed assignments were in the region for CF_3 or $CF_3C{=}$ configurations. There were only two peaks. On the basis of this information, the infrared spectrum and the analytical results, the major component of this fraction was believed to be perfluoro-2,3,4,5-tetramethylhexadiene-2,4.

Anal. Calcd. for $C_{10}F_{18}$: F, 74.2; C, 25.8; mol. wt., 462; *MR*D, 47.47. Found: F, 74.7; C, 25.9; mol. wt., 457; d^{25} 1.7359; $n^{25}D$ 1.2994; *MR*D, 49.78; b.p. (micro) 111.0.

Discussion of the Results

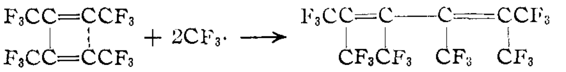
In reaction (A) between $(CF_3)_2SF_4$ and $CF_3CF{=}CF_2$, if it is assumed that the CF_3 groups add across the double bond, no neo isomer should have been formed. Accordingly, a possible reaction path may be that the perfluoropropylene reacts just with one available CF_3 group to form a perfluorobutyl intermediate, $CF_3\dot{C}FCF_2CF_3$. This rearranges to $CF_3\overset{CF_3}{\underset{\cdot}{C}}CF_3$ which then reacts with another CF_3 group to yield the stable perfluoroneopentane. In a similar reaction between CF_3SF_5 and perfluoropropylene[3] some neo isomer was detected, but in an unreported reaction done in this Laboratory between $C_2F_5SF_5$ and perfluoropropylene, although C_5F_{12} material was obtained, no neo isomer was found when the reaction was carried out under essentially the same conditions.

In reaction (B) between CF_3SF_5 and perfluorobutyne-2, there is the same tendency for the olefin to form a dimer in the presence of F· (from SF_5 group) as was evidenced in the reaction between CF_3SF_5 and perfluoropropylene where fluorocarbons containing six and seven carbon atoms were produced. The formation of a tetramer of perfluorobutyne-2 under controlled conditions has recently been reported.[10] If it is assumed that a dimer is formed and subsequently undergoes attack by the CF_3· and/or F· released by the CF_3SF_5, then it is possible to account for the two hexadienes formed. For example



$$\begin{array}{c}F_3CC{=}CCF_3\\ |\quad\ \ |\\ F_3CC{=}CCF_3\end{array} + CF_3\cdot + F\cdot \longrightarrow F_3C\underset{F}{C}{=}\underset{CF_3}{C}-\underset{CF_3}{C}{=}\underset{CF_3}{C}CF_3$$

and



$$\begin{array}{c}F_3CC{=}CCF_3\\ |\quad\ \ |\\ F_3CC{=}CCF_3\end{array} + 2CF_3\cdot \longrightarrow F_3C\underset{CF_3}{C}{=}\underset{CF_3}{C}-\underset{CF_3}{C}{=}\underset{CF_3}{C}CF_3$$

The failure of these unsaturated compounds to add Br_2 or MeOH may be due to steric hindrance.

The values of the C=C infrared assignments can be understood in the light of shifts to higher micron values as the double bond is shifted to higher numbered positions and the carbons containing the double bonds are found to contain side chains.[11] Since the perfluoro-2,3,4-trimethylhexadiene-2,4 has two unequivalent double bonds there are two C=C assignments.

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(8) R. D. Dresdner, THIS JOURNAL, **78**, 876 (1956).

(9) The authors are indebted to Dr. Max T. Rogers of Michigan State University for the n.m.r. results and assistance with their interpretation; CF_3COOH was the standard.

(10) H. C. Brown, *J. Org. Chem.*, **22**, 1256 (1957).

(11) T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearlson, THIS JOURNAL, **75**, 2698 (1953).

The boiling points of the two dienes follow the rather empirical rule that similar homologs boil about 20° apart; however, the "apparent" low boiling points of the two compounds are not too "anomalous," if the C_9F_{16} and $C_{10}F_{18}$ are compared to the fluorocarbons C_7F_{16} (b.p. 82°) and C_8F_{18} (b.p. 102°) and 5° is added for each degree of unsaturation.

Acknowledgments.—The authors wish to thank Dr. Max Rogers of Michigan State University for obtaining n.m.r. spectra on the dienes and assisting in the interpretation of this data. They also wish to thank Dr. T. M. Reed, III, of the University of Florida, for the use of gas chromatographic equipment. Support for this work by the Chemistry Branch of the Office of Naval Research is gratefully acknowledged.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Novel Reductions of N-Nitrosodibenzylamines—A New Reaction[1]

BY C. G. OVERBERGER, JOSEPH G. LOMBARDINO[2] AND RICHARD G. HISKEY

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N-Nitrosodibenzylamines were reduced by sodium hydrosulfite in basic media or by lithium in liquid ammonia to give an unexpected evolution of nitrogen with formation of hydrocarbon products. For example, reaction of sodium hydrosulfite with *cis*-1-nitroso-2,6-diphenylpiperidine gave *cis*-1,2-diphenylcyclopentane and 1,5-diphenyl-1-pentene while *trans*-1-nitroso-2,6-diphenylpiperidine gave a mixture of *cis*- and *trans*-1,2-diphenylcyclopentane and 1,5-diphenyl-1-pentene. Sodium hydrosulfite reduction of N-nitrosodibenzylamine gave high yields of bibenzyl. The products in almost every case were identical to those isolated from mercuric oxide oxidation of the corresponding N-aminodibenzylamine. A mechanism is suggested which has an identical intermediate for these "abnormal" reductions of nitrosamines and for the mercuric oxide oxidation of the corresponding 1,1-disubstituted hydrazines. Other N-nitrosodialkylamines were reduced readily to dialkylhydrazines by sodium hydrosulfite providing a new, convenient method of reducing nitrosamines.

In the course of a study on the oxidation behavior of 1,1-disubstituted hydrazines it was desirable to obtain *trans*-1-amino-2,6-diphenylpiperidine[3] from *trans*-1-nitroso-2,6-diphenylpiperidines. A wide variety of reducing systems were explored[3] including some methods not previously used for reducing a nitrosamine to a hydrazine. Two of these reducing systems gave especially interesting results with *trans*-1-nitroso-2,6-diphenylpiperidine. Both sodium hydrosulfite in basic media and lithium in liquid ammonia yielded only hydrocarbon products when applied to the *trans*-nitrosamine, prompting a more thorough study of the scope of these novel transformations.

Sodium hydrosulfite in strongly basic media has been reported previously to reduce C-nitro and C-nitroso functions to primary amines.[4a,b] This powerful reducing agent has now been applied to a series of nitrosamines and the results are summarized in Table I.

TABLE I

Compound reacted with $Na_2S_2O_4$	Product	Yield, %
N-Nitrosodibenzylamine (I)	Bibenzyl	77
cis-1-Nitroso-2,6-diphenylpiperidine (II)	*cis*-1,2-Diphenylcyclopentane;	56.8
	1,5-diphenyl-1-pentene	21.4
trans-1-Nitroso-2,6-diphenylpiperidine (III)	*trans*-1,2-Diphenylcyclopentane *cis*-1,2-Diphenylcyclopentane	60.4
	1,5-Diphenyl-1-pentene	19
N-Nitrosobenzylphenylamine	1-Phenyl-1-benzylhydrazine	77
N-Nitrosodiphenylamine	Diphenylamine	80
1-Nitroso-2,6-dimethylpiperidine	1-Amino-2,6-dimethylpiperidine	40

From these results, it can be seen that nitrosodibenzylamines eliminate nitrogen, whereas mixed benzylalkyl or dialkyl nitrosoamines are reduced to the corresponding hydrazines. An exception to this rule is N-nitrosodiphenylamine which gave diphenylamine; however, the cleavage of the nitrogen–nitrogen bond in N-nitrosodiphenylamine has previously been reported using other reducing agents.[5] It would appear that the sodium hydrosulfite reduction of dialkyl nitrosamines to the corresponding hydrazines is safer and more convenient than any previously reported methods. The products from the nitrosamines I, II and III were identical to those isolated from the mercuric oxide oxidation of the corresponding 1,1-disubstituted hydrazines[3,6] (Table II) suggesting a common intermediate for both the mercuric oxide oxidation of the hydrazines and for sodium hydrosulfite reduction of nitrosamines (see below).

TABLE II

Hydrazine oxidized with mercuric oxide	Product	Yield, %	Ref.
1,1-Dibenzylhydrazine	Bibenzyl	83	3, 6
cis-1-Amino-2,6-diphenylpiperidine	*cis*-1,2-Diphenylcyclopentane	65	3
	1,5-Diphenyl-1-pentene	25	
trans-1-Amino-2,6-diphenylpiperidine	*cis*- and *trans*-1,2-Liphenylcyclopentane	71	3
	1,5-Diphenyl-1-pentene	14	

The action of lithium in liquid ammonia on a

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[1] This is the 22nd in a series of papers concerned with the preparation and decomposition of azo and diazo compounds. For the previous paper in this series, see C. G. Overberger and J. G. Lombardino, THIS JOURNAL, **80**, 2317 (1958). For a preliminary report of this work see C. G. Overberger, J. G. Lombardino and R. G. Hiskey, *J. Org. Chem.*, **22**, 858 (1957). Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., Sept., 1957 (Abstracts p. 38-P).

[2] From a portion of the Dissertation submitted by Joseph G. Lombardino in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

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