Reaction of Tetrahydrolinalyl Hypochlorite with Tributylphosphine in Methanol.—In an experiment similar to that described above, tributylphosphine in methanol at −78° reacted with tetrahydrolinalyl hypochlorite to give as the only pentane-soluble product, tetrahydrolinalool.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenylphosphine in Methanol.—To a solution of 10.8 g. (0.042 mole) of triphenylphosphine in a mixture of 100 ml. of methanol and 100 ml. of methylene chloride at −78° was added 8.1 g. (0.042 mole) of tetrahydrolinalyl hypochlorite at such a rate that the temperature did not exceed −75°.

A 25-ml. aliquot of the reaction mixture was added to 200 ml. of water. The aqueous solution was extracted with two 25-ml. portions of pentane. The combined pentane extracts were washed with several portions of water, dried over anhydrous magnesium sulfate and evaporated to give a semi-solid residue. The residue was triturated with 20 ml. of pentane and filtered. The solid was recrystallized from hexane; m.p. 156–158°. There was no depression of melting point on admixture with an authentic sample. The infrared spectrum was identical to that of triphenylphosphine oxide.

The pentane filtrate was evaporated and the residue was analyzed by g.l.c. The only material found by this technique was tetrahydrolinaloöl. The infrared spectrum of the oil also indicated tetrahydrolinaloöl as the major constituent.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenylphosphine in 1-Butanol.—To a solution of 16.5 g. (0.063 mole) of triphenylphosphine dissolved in a mixture of 100 ml. of 1-butanol and 100 ml. of methylene chloride at −78° was added 12.1 g. (0.063 mole) of tetrahydrolinalyl hypochlorite in 50 ml. of pentane at such a rate that the temperature did not exceed −75°. The reaction mixture was allowed to warm to room temperature and 200 ml. of pentane was added. The resulting solution was extracted with 25-ml. portions of water until the extract no longer gave an acid test with litmus paper.

Titration of 10-ml. aliquots with sodium hydroxide solution showed that 78% (based on hypochlorite used) of titratable material was present. Addition of sodium hydroxide solution to the remaining aqueous solution precipitated triphenylphosphine oxide, which after recrystallization from hexane had m.p. 156–158°, no depression of melting point with an authentic sample.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenyl Phosphite under Irradiation.—The reaction conditions were essentially the same as employed before except that during the addition of the hypochlorite a mercury lamp was allowed to shine on the reaction flask. Isolation by chromatography afforded 2.05 g. of liquid *vs. ca.* 7 g. for a similar run without irradiation. The 2.05 g. contained *ca.* 20% tetrahydrolinalyl chloride and 80% olefins by g.l.c. analysis.

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, LIVERMORE, CALIF.]

A Preparation of Primary Perfluoroalkylamines[1]

BY RICHARD K. PEARSON[2] AND RICHARD D. DRESDNER

RECEIVED JANUARY 27, 1962

Thermal reactions of N_2F_4 and NF_3 with R_FSF_5 and $R_FSF_4R_F'$ were found to give R_FNF_2 and $R_F'NF_2$ (R_F and R_F' are perfluoroalkyl groups).

Introduction

It has been demonstrated[3] that perfluoroalkylsulfur pentafluoride compounds, R_FSF_5, cleave thermally to yield SF_4, $R_F{-}R_F$, R_FF and SF_6. These products are explainable in terms of formation of radicals shown in the equation

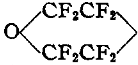
$$C_2F_5 \mid SF_4 \mid F \xrightarrow{\Delta} C_2F_5\cdot + SF_4 + \cdot F \qquad (1)$$

The possible recombinations of these species yield the observed products. It did not seem improbable to presuppose that, if these radicals could be produced under conditions which also yield the $\cdot NF_2$ free radical, a synthesis of R_FNF_2 might be effected. The source of $\cdot NF_2$ might be either NF_3 or N_2F_4. The synthesis of N_2F_4 from reaction of NF_3 with Hg suggests that $\cdot NF_2$ radicals can form from NF_3.[4] Recent work by Johnson and Colburn[5] has shown that N_2F_4 under even moderately elevated temperatures is an excellent source of $\cdot NF_2$ radicals. Our present work shows that the synthesis of R_FNF_2 compounds can be brought about by passing either NF_3 or N_2F_4 through a hot tube reactor with R_FSF_5. It also demonstrates that $R_FSF_4R_F'$ compounds cleave at elevated temperatures in the presence of $\cdot NF_2$ radicals to give excellent yields of R_FNF_2 and $R_F'NF_2$.

Experimental

Materials.—The NF_3 used in this work was obtained from electrochemical action on pyridine[6] in anhydrous HF. The only impurity was CF_4 to the extent of 5 mole %.

The N_2F_4 used in the large scale experiments contained 1 mole % amounts of CF_4 and C_2F_6 according to infrared analysis. The N_2F_4 used in the small scale experiments was purified by chromatography using a 10-ft. column of 13-X Molecular Sieves (30–60 mesh) activated overnight in vacuum at 320°. No impurities could be detected by infrared analysis at several hundred mm. pressure in a 5-cm. infrared cell.

The compounds $C_2F_5SF_5$ (b.p. 11.3°),[7] $(C_2F_5)_2SF_4$ (b.p. 70–70.5°),[7] $C_2F_5SF_4CF_3$ (b.p. 47.1°),[8] $C_6F_{11}SF_5$ (b.p. 110–111°)[9] and  $O(CF_2CF_2)_2SF_4$ (b.p. 80.3°)[10] were prepared by electrochemical action in HF solutions of, respectively, $(C_2H_5)_2S$ (both $C_2F_5SF_5$ and $(C_2F_5)_2SF_4$), $CH_3SC_2H_4SCH_3$, $(C_6H_5)_2S$ and thioxane. Besides initial purification by distillation, the materials used were repurified by preparative scale chromatography using a 30-ft. column of Octoil-S (a vacuum pump fluid supplied by Consolidated Vacuum Corporation) on 42–60 mesh firebrick.

The CH_3SF_5 was prepared from electrochemical action in HF of dimethyl disulfide, CH_3SSCH_3. The 26–27° boiling fraction (mol. wt. 180) was chromatographed using a 10-ft. column of Octoil-S on 42-60 mesh firebrick followed by a 10-ft. column of hexadecane on firebrick. Its infrared and mass spectra, and molecular weight by vapor density (144.4 observed, 142.1 calculated), were all consistent with its expected structure. The F^{19} n.m.r. spectrum excluded the presence of any C–F bonds and confirmed the presence of the SF_5 group.

---

[1] Presented at the 140th Meeting of the American Chemical Society, Chicago, Sept. 3–8, 1961; see Abstracts of Papers, p. 15N.

[2] University of Florida, Gainesville, Fla.

[3] R. D. Dresdner, *J. Am. Chem. Soc.*, **77**, 6633 (1955).

[4] C. B. Colburn and A. Kennedy, *ibid.*, **80**, 5004 (1958); R. D. Dresdner, F. N. Thermac and J. A. Young, *J. Inorg. Nucl. Chem.*, **14**, 299 (1960).

[5] F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

[6] J. H. Simons, *et al.*, *J. Electrochem. Soc.*, **95**, 47 (1949).

[7] R. D. Dresdner, *J. Am. Chem. Soc.*, **79**, 69 (1957); F. W. Hoffmann, *et al.*, *ibid.*, **79**, 3424 (1957).

[8] R. D. Dresdner and J. A. Young, *ibid.*, **81**, 574 (1959).

[9] R. D. Dresdner, T. M. Reed III, T. E. Taylor and J. A. Young, *J. Org. Chem.*, **25**, 1464 (1960).

[10] F. W. Hoffmann, *et al.*, *J. Am. Chem. Soc.*, **79**, 3424 (1957).

The $C_6H_5SF_5$ was supplied by William A. Sheppard of E. I. du Pont de Nemours & Co., Wilmington, Del. This material was found by chromatography to contain less than 0.5% impurity.

Apparatus and Procedure.—Two types of reactors were used in these experiments. In the small scale experiments, where approximately 10 gaseous cc. of each reactant was employed, a short reactor (7 cm. × 1 cm.) was used and was operated at relatively low pressures (less than 10 mm.). It is referred to as the "low pressure reactor." The large scale experiments were carried out in a larger reactor (referred to as the "high pressure reactor") at pressures near atmospheric and at temperatures generally 100 to 200° lower than in the "low pressure reactor."

"High Pressure Reactor."—The reactor used at atmospheric pressure was a nickel tube 43 cm. long by 1.8 cm. in diameter, packed with $^1/_8$ inch NaF pellets. To our knowledge these pellets do not exert any catalytic effect, and are used to control mixing of the reactants, contact time and uniformity of heating in the reaction zone. This reactor tube was heated using a 30-cm. tube furnace. A thermocouple at the outer surface of the tube was used to measure and control the reaction temperature. To carry out an experiment, NF_3 or N_2F_4 was passed from a pressurized container through a bubbler containing a given amount of R_FSF_5 maintained at some fixed temperature compatible with the mixture desired. The gas flow was noted on a ball flow meter placed in front of the R_FSF_5 bubbler and previously calibrated with the gas used. The mixture of gases was then passed into the packed nickel tube at the desired temperature. The reaction pressure noted on the system manometer was maintained close to one atmosphere by setting the rate of gas flow and controlling the rate of product taken off through a leak stopcock into an evacuated trap cooled with liquid nitrogen. A crude measure of the non-condensable gases was made by estimating the volume of the system involving the product collection trap and noting the pressure increase with time during the course of the reaction.

In the cases where NF_3 was used, all the products were allowed to evaporate aliquot-wise into a 2-liter volume from which a sample was taken for infrared analysis. The proper absorption lines were then evaluated and the partial pressure of each component recorded. The total composition was then calculated in mole %. In the case of N_2F_4, this was done for all the materials obtained from the reaction except the pure fraction of $C_2F_5NF_2$ (mol. wt. 171, b.p. −34.8 to −33.8°).[11] The various spectra of the so-called pure $C_2F_5NF_2$ showed at least one minor peak at 9.72 μ which did not remove on hydrolysis (not SiF_4).

Table I shows the quantities of products determined in the "high pressure reactor" experiments. From the material balances obtained, the results are no better than 3% in error and no worse than 6%.

TABLE I

PRODUCT DISTRIBUTION IN ATMOSPHERIC PRESSURE EXPERIMENTS

Expt. (see Table III)	Charged, mmoles		Recovered, mmoles					
	NF_3 +	$C_2F_5SF_5$ →	$C_2F_5NF_2$ +	SF_4 +	SF_6 +	C_2F_6 +	CF_4 +	C_4F_{10}
1-H	38	41	7.6(18%)	32	8.9	30	8.2	1.7
2-H	89	41	10.5(30%)	25	10.3	24	5.1	0.0
	N_2F_4 +	$C_2F_5SF_5$ →	$C_2F_5NF_2$ +	SF_4 +	SF_6 +	C_2F_6 +	CF_4 +	NF_3
3-H	154	118	75(70%)	83	20	23	24	15

The yields of perfluoroethylamine are based on the amount of $C_2F_5SF_5$ consumed in each experiment assuming further that it is possible to make one mole of amine from each mole of unrecovered sulfur compound under optimum conditions. However, if the mechanism requires that C_2F_5 radical is needed to abstract a fluorine atom from NF_3, the reported yields in the NF_3 experiments are technically doubled.

"Low Pressure Reactor."—This reactor was a nickel tube 1 cm. in diameter packed with $^1/_8$ inch NaF pellets for a distance of 7 cm. The reaction temperature was measured by a thermocouple at the outside surface of the tube, with a layer of asbestos cloth between thermocouple and surface of the nickel tube. The furnace consisted of a double winding of Chromel wire located several layers of asbestos cloth above the thermocouple. The furnace, as well as the NaF pellet packing, was 7 cm. long.

Flow of gaseous materials through the reactor could be controlled by cracking a stopcock in front of the reactor and also a stopcock at the exit end with −196° traps and a high vacuum beyond the exit stopcock. Pressure could be observed on a manometer at the exit end of the reactor. Adjustment of the two stopcocks had to be made from time to time during a run in order to maintain a reasonably constant pressure while the gaseous mixture was fed through the reactor. Rough values of residence times were calculated as displacement time for the feed gases at the reaction temperature.

A Typical Experiment in the "Low Pressure Reactor."—Tetrafluorohydrazine (9.4 gaseous cc. at S.T.P.) was measured by P-V-T relationships in a calibrated vacuum system and mixed with 7.0 cc. of perfluoroethylsulfur pentafluoride. This mixture was passed through the hot tube under conditions shown in Table III, expt. 6-L. A preliminary separation of reaction products was made by passing them through U-traps held at −112, −140 and −196° in high vacuum. The −112° fraction contained 2.6 cc. of pure unreacted $C_2F_5SF_5$ as was shown by its infrared spectrum. The −140° fraction (5.24 cc.) was chromatographed using a 30-ft. column of Octoil-S (30%) suspended on GC-22, 42–60 mesh firebrick. Three components were separated: 2.1 cc. of $C_2F_5NF_2$ (observed mol. wt. 170 by vapor density, calcd. 171), 2.3 cc. of SF_4 (the column caused hydrolysis, OSF_4 to give an equivalent quantity of SOF_2) and 0.61 cc. of $C_2F_5SF_5$. The quantity of each of these fractions was measured by P-V-T. Infrared and mass spectra of each pure fraction were obtained to aid in identifying each component. A mass spectrum was taken of the −196° fraction (11.8 cc.) and the following quantities of material were found to be present: 6.2 cc. of N_2F_4, 0.83 cc. of $SOF_2(SF_4)$, 2.0 cc. of CF_4, 0.98 cc. of SiF_4, 1.15 cc. of C_2F_6 and 0.64 cc. of SF_6.

A summary is given in Table II of the distribution of products from this experiment. Neither NF_3 nor N_2 was detected in this experiment; they may have formed in the reaction but, because their vapor pressures at −196° are not negligible, they could have been removed from the reaction mixture on pumping. Indeed, non-condensable gas was observed to pass through the −196° traps during the run and was detected on a thermocouple vacuum gauge. Nitrogen trifluoride was observed as a product in other experiments.

TABLE II

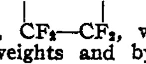
PRODUCT DISTRIBUTION FROM A LOW PRESSURE EXPERIMENT

(Expt. 6-L, Table III)

Product	Charged, cc.	Recovd., cc.	Consumed, cc.
$C_2F_5SF_5$	7.0	3.2	3.8
N_2F_4	9.4	6.2	3.1
$C_2F_5NF_2$		2.1	
$SOF_2(SF_4)$		3.1	
SF_6		0.64	
CF_4		2.0	
C_2F_6		1.15	
SiF_4		.98	

In Table III, experiments 4-L through 6-L and 8-L through 14-L were carried out in a manner similar to that described above. Only minor changes (such as in fractionation temperatures and chromatographic columns) were made in different experiments where it was necessary to accommodate reactants and products of higher or lower volatility.

Identification of CF_3NF_2, $C_2F_5NF_2$, $C_6F_{11}NF_2$ and c-C_4F_8O,



$$\begin{array}{l} CF_2CF_2{-}O \\ \;\;| \qquad\quad\;\; | \\ CF_2{-}{-}CF_2 \end{array}$$

was made by vapor density molecular weights and by their infrared and mass spectra after isolation and purification by gas chromatography. The molecular weights and infrared absorption maxima with relative intensities are: $C_2F_5NF_2$ (obsd. mol. wt. 171, calcd. 171),

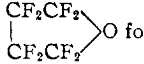
---

[11] G. E. Coates, J. Harris and T. Sutcliffe, *J. Chem. Soc.*, 2762 (1951); J. A. Cuculo and L. A. Bigelow, *J. Am. Chem. Soc.*, **74**, 710 (1952).

TABLE III

PREPARATION OF PERFLUOROALKYL AMINES

Expt.[a]	Mole ratio NF/SF	SF compd.	NF compd.	% SF consumed	% yield[d] $(R_F)NF_2$	T, °C.	Residence time, sec.	Pressure, mm.
1-H	0.9	$C_2F_5SF_5$	NF_3	All	18	512	69	760
2-H	2.2	$C_2F_5SF_5$	NF_3	86	30	520	43	760
3-H	1.3	$C_2F_5SF_5$	N_2F_4	91	70	517	89	760
4-L	1.3	$C_2F_2SF_5$	N_2F_4	71	77	710	6.3	1
5-L	1.0	$C_2F_5SF_5$	N_2F_4	76	69	720	1.8	1
6-L	1.3	$C_2F_5SF_5$	N_2F_4	54	55	770	4.5	1.4
7-S[b]	1.0	$C_2F_5SF_5$	N_2F_4	0	0	153	1800	440
8-L	1.2	$(C_2F_5)_2SF_4$	N_2F_4	85	60	720	11.5	1
9-L	1.5	$(C_2F_5)_2SF_4$	N_2F_4	57	93	660	9.8	1
10-L	1.2	$C_2F_5SF_4CF_3$	N_2F_4	45	C_2F_5–78, CF_3–73	710	11	3
11-L	1.1	$C_2F_5SF_4CF_3$	N_2F_4	45	C_2F_5–92, CF_3–96	730	11	9
12-L	1.5	$C_6H_{11}SF_5$	N_2F_4	93	16	740	11	7
			N_2F_4	57	0[c]	705	6.6	5
13-L	1.4		N_2F_4	94	0[c]	745	6.8	8
14-L	9.5		N_2F_4	100	0[c]	515	35	760
15-H	1.0							
16-H	10.0		N_2F_4	57	0[c]	520	50	760

[a] H refers to experiments carried out in the "high pressure reactor" while L refers to the relatively small scale experiments using the "low pressure reactor." [b] This reaction was carried out in a sealed Pyrex tube. [c]  formed and there was no evidence for $F_2NCF_2CF_2OCF_2CF_2NF_2$. [d] Yields of R_FNF_2 are based on the perfluoroalkyl sulfur compound assuming that, under optimum conditions, it is possible to make one mole of amine from each mole of unrecovered R_F(or R_F') from R_FSF_5 or $R_FSF_4R_F'$.

infrared maxima (μ) at 7.30w, 8.00vs, 8.40s, 9.13m, 10.26m, 10.66m, 12.36vw, 13.36w, 13.45w, 13.55w.; CF_3NF_2 (obsd. mol. wt. 119, calcd. 121), infrared maxima (μ) at 7.82vs, 8.10vs, 8.20s, 9.80s, 9.87s, 9.93s, 10.60s, 11.75vw, 11.81vw, 13.78m, 13.92m, 14.07m., $C_6F_{11}NF_2$ (mol. wt. by mass spectr. 333, calcd. 333), infrared maxima (μ) at 7.37w, 7.60s, 7.72s, 7.40s, 8.21s, 8.40m, 9.56m, 10.06m, 10.25m, 10.62m, 11.40m, 13.03m, 13.72w., c-C_4F_8O (obsd. mol. wt. 210, calcd. 216), infrared spectrum identical to that reported for this compound.[12]

The F^{19} n.m.r. spectrum of $C_2F_5NF_2$ served to verify its identity further. This spectrum permitted identification of CF_3, CF_2 and NF_2 groups from chemical shift and spin coupling parameters. Chemical shifts were +6.25, +44.3 and −91.2 p.p.m., respectively, relative to trifluoroacetic acid. Spin coupling to the NF_2 group results in a triplet splitting of 9 c.p.s. in the CF_3 resonance. A small coupling of approximately 1 c.p.s. was observed between CF_3 and CF_2 groups.

Results and Discussion

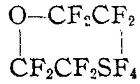
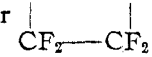
Table III summarizes conditions and yields of R_FNF_2 in the experiments carried out. Several conclusions based on these data are discussed in the following paragraphs.

Perhaps the first significant observation one makes is that yields of R_FNF_2 are much better using N_2F_4 rather than NF_3 as the source of $\cdot NF_2$ radicals. This is not surprising in view of the equilibrium recently reported by Colburn[5]

$$N_2F_4 \rightleftarrows 2\cdot NF_2$$

The equilibrium constant reported by Colburn for this reaction gives a value of about 97% dissociation of N_2F_4 at 100° at 10^{-2} mm. and 1.5% dissociation at 760 mm. at this temperature. Under the conditions of our experiments (over 500°), one would expect substantial dissociation into $\cdot NF_2$ radicals. That this radical is thermally stable toward disproportionation in the absence of oxidizable species is demonstrated by our work.

A second observation one makes is that very nearly quantitative yields of R_FNF_2 can be obtained when $R_FSF_4R_F'$ compounds are used. This might be expected since the F· from the SF_5 group is not available to combine with $R_F\cdot$ or $R_F'\cdot$ radicals. Therefore the use of $(R_F)_2SF_4$ compounds as the source of R_F groups, rather than R_FSF_5 or $R_FSF_4R_F'$, would give the best yields of R_FNF_2 with fewer side reaction products.

When the thioxane compound  undergoes pyrolysis the principal products formed are the cyclic ether  and SF_4.[13] This oxide formed regardless of the presence of $\cdot NF_2$ radical even when 900% excess N_2F_4 was used. Apparently the tendency of the di-radical $\cdot CF_2$-CF_2-O-$CF_2CF_2\cdot$ toward ring closure is very much stronger than its reactivity toward radical combination with $\cdot NF_2$.

Experiment 12-L in which N,N-difluoroamino-perfluorocyclohexane was prepared demonstrates that relatively complex perfluoroalkyl-N,N-difluoroamines can be prepared by this reaction. Yields might be expected to be low with larger and more complex R_F groups due to the larger number of possible thermal cleavage fragments. The low (16%) yield of N,N-difluoroaminoperfluorocyclohexane obtained can at least in part be explained on this basis since several other unidentified species were observed in chromatograms of the reaction mixture along with the expected perfluorocyclohexane. This experiment does not represent

---

(12) "Fluorine Chemistry," Vol. II, ed. J. H. Simons, Academic Press, Inc., New York, N. Y., 1954, p. 479.

(13) R. D. Dresdner and J. A. Young, *J. Org. Chem.*, **24**, 566 (1959).

the optimum yields obtainable since a complete study of reaction variables was not made. One might, however, expect to get better yields using a larger excess of N_2F_4.

A reasonable mechanism for the reaction of N_2F_4 with RSF_5 and R_2SF_4 which accounts for the observed products and stoichiometry involves initial thermal cleavage of the sulfur compound to yield radicals and SF_4.

$$R \mid SF_4 \mid F \longrightarrow R\cdot + SF_4 + F\cdot$$

$$R \mid SF_4 \mid R \longrightarrow 2R\cdot + SF_4$$

Recombination of these radicals with $\cdot NF_2$ (from thermal equilibrium with N_2F_4) and with each other yield the observed products. Where NF_3 is used as the source of $\cdot NF_2$ groups, a step in which a fluorine abstraction from NF_3 by R· seem likely

$$R\cdot + NF_3 \longrightarrow RF + \cdot NF_2$$

This would account for the lower yields of RNF_2 (based on the sulfur compound) and larger amounts of RF observed.

It might be mentioned that attempts were made to extend this reaction to the preparation of hydrocarbon difluoroamine compounds but without success. The compound CH_3NF_2 has been reported by Frazer[14] as resulting from ultraviolet-initiated reaction of CH_3I with N_2F_4. Since the mechanism of this reaction undoubtedly involves a methyl free radical, it seemed likely that CH_3SF_5 might pyrolyze in an atmosphere of $\cdot NF_2$ radicals to give $CH_3\cdot$ and by radical combination yield CH_3NF_2. This compound might not be stable enough, however, to survive the temperatures necessary to thermally crack the CH_3SF_5. One might therefore expect to get either little or no CH_3NF_2: but one might reasonably expect to get HCN which is its dehydrohalogenated product. The failure to obtain evidence of CH_3NF_2 formation would suggest that CH_3SF_5 does not yield methyl radical on cracking. The CH_3F which results from pyrolysis of CH_3SF_5 could possibly form *via* an intramolecular attack of an adjacent fluorine atom. Like CH_3SF_5, the phenyl derivative $C_6H_5SF_5$ underwent thermal cracking in the presence of N_2F_4 to yield only fluorobenzenes with no evidence of formation of $C_6H_5NF_2$.

This work was done under the auspices of the U.S. Atomic Energy Commission. The authors wish to thank James A. Happe of the Lawrence Radiation Laboratory for his help in n.m.r. spectroscopy.

[14] J. W. Frazer, *J. Inorg. Nucl. Chem.*, **11**, 166 (1959).

[CONTRIBUTION NO. 755 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Thiacyanocarbons. I. Tetracyano-1,4-dithiin, Tetracyanothiophene and Tricyano-1,4-dithiino[c]isothiazole[1]

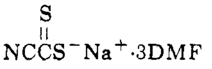
BY HOWARD E. SIMMONS, ROBERT D. VEST, DALE C. BLOMSTROM, JOHN R. ROLAND AND THEODORE L. CAIRNS

RECEIVED MARCH 24, 1962

Disodium dimercaptomaleonitrile has been found to be a versatile intermediate for the synthesis of thiacyanocarbons, molecules which contain only carbon, nitrogen and sulfur and a plurality of cyano groups. Oxidation of this salt has given tetracyano-1,4-dithiin, which can be further converted to tetracyanothiophene by heat. Reaction of tetracyano-1,4-dithiin with sulfur in the presence of nucleophiles gave tricyano-1,4-dithiino[c]isothiazole by a novel insertion mechanism. The physical and chemical properties of these compounds are reported preliminarily.

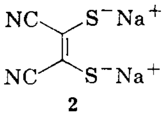
Introduction

Recently, Bähr and Schleitzer[2] have described the reaction of sodium cyanide and carbon disulfide in dimethylformamide to give a crystalline solvate of sodium cyanodithioformate 1 and further the unusually facile dimerization of 1 with loss of sulfur to form disodium dimercaptomaleonitrile(2).

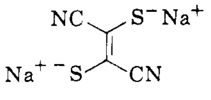


$$NC\overset{\overset{\displaystyle S}{\|}}{C}S^-Na^+\cdot 3DMF$$

1



2



3

We have studied the chemistry of salts 1 and 2, and this series of papers[3] presents some of our results. The successful synthesis of disodium dimercaptofumaronitrile (3)[2a] has allowed a study of the stereochemistry and stability of the isomers 2 and 3. In papers III[3b] and IV[3c] the mechanism of the oxidation of salts 1, 2 and 3 to give tetracyano-1,4-dithiin (4) is presented in detail.

The present paper describes the synthesis and properties of tetracyano-1,4-dithiin (4), tetracyanothiophene (7) and tricyano-1,4-dithiino[c]-isothiazole (6), all of which are readily available from salt 1 or 2. It has become evident that several new sulfur-containing heterocyclic compounds related to the cyanocarbons[4a,b] are accessible from

---

[1] In this and subsequent papers in this series bold face arabic numerals are employed to name chemical structures, as suggested by L. F. Fieser and M. Fieser, "Style Guide for Chemists," Reinhold Publishing Corp., New York, N. Y., 1960, p. 66.

[2] G. Bähr and G. Schleitzer, *Ber.*, **88**, 1771 (1955); **90**, 438 (1957); G. Bähr, *Angew. Chem.*, **68**, 525 (1956).

[3] (a) II, H. E. Simmons, D. C. Blomstrom and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962); (b) III, H. E. Simmons, D. C. Blomstrom and R. D. Vest, *ibid.*, **84**, 4772 (1962); (c) IV, H. E. Simmons, D. C. Blomstrom and R. D. Vest, *ibid.*, **84**, 4782 (1962).

[4] (a) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick and W. J. Middleton, *ibid.*, **79**, 2340 (1957). (b) See series beginning T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middle-