ethyl *trans*-2-methylpent-3-ene-1,3-dicarboxylate, 22528-27-4; dimethyl *cis*-2-*n*-propylhept-3-ene-1,3-dicarboxylate, 22485-83-2; dimethyl *trans*-2-*n*-propylhept-3-ene-1,3-dicarboxylate, 22528-28-5; dimethyl 2-isopropyl-5-methylhex-4-ene-1,3-dicarboxylate, 22482-50-4; *trans*-**5**, 22485-84-3; *cis*-**5**, 22485-85-4; *cis*-4-methyl-5-acetylhept-5-en-2-one, 22485-86-5; dimethyl pent-3-ene-1,3-dicarboxylate, 22482-51-5; dimethyl 1-methylpent-3-ene-1,3-dicarboxylate, 22483-45-0; 1,2-dicarbethoxy-3-carbomethoxypent-3-ene, 22485-87-6; 1,3-dicyanopent-3-ene, 22485-88-7; dimethyl 2,5-dimethylhex-4-ene-1,3-dicarboxylate, 22485-89-8.

Studies of Nitriles. III.[1a] Synthesis of Chlorocyanoacetylene and Cyanoacetylene, and a Novel Malononitrile Synthesis from Chlorocyanoacetylene[1b]

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Pyrolysis of trichloropropionitrile and dichloropropionitrile at 900–1000° under reduced pressure provided a novel synthesis of chlorocyanoacetylene (*ca.* 80%) and cyanoacetylene (40–60%). Chlorocyanoacetylene reacted with ammonia to give malononitrile in high yields.

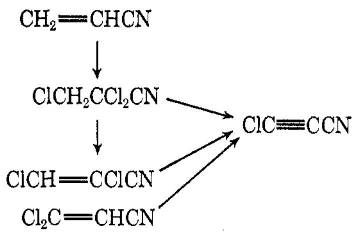
Cyanoacetylene is a compound of considerable interest, because it has two conjugated triple bonds in the molecule and, perhaps, will find wide application in the synthesis of a variety of heterocyclic compounds. It may also be useful as a monomer in the chemistry of polymers. Although cyanoacetylene has been known for many years, its chemical properties remain uninvestigated, largely owing to lack of a convenient synthesis. The most orthodox method for its synthesis has been recorded by Moureu,[2] and involves the dehydration of propiolamide with phosphorus pentoxide. Since propiolamide has to be prepared from acetylene by a series of reactions including carbonylation, esterification, and amidation, this approach is far from being practical. Several workers[3] thereafter somewhat improved Moureu's method but could not alter its lengthy nature.

Recently, several patents claim that cyanoacetylene can be prepared by the dehydration of propargylaldehyde oxime[4] or by some gas-phase reactions of acetylene[5] or acetonitrile[6] with hydrogen cyanide at high temperatures.

Chlorocyanoacetylene was first prepared by Kloster-Jensen[7] by the reaction of chlorine with lithium cyanoacetylide and its melting point (42–42.5°) and ir and uv spectral data were recorded by the same author. Recently, Bjorvatten[8] reported the X-ray crystallographic study of chlorocyanoacetylene with the sample supplied by Kloster-Jensen. However, for lack of a convenient synthesis the investigation of its chemical properties has been hampered for years.

In the preceding paper[1a] we reported that chlorocyanoacetylene was produced by the copyrolysis of carbon tetrachloride and acetonitrile. Further, it was suggested that its formation would be explained by the pyrolytic dehydrochlorination of β,β-dichloroacrylonitrile, which was the main product of the copyrolysis.

The present paper deals with a convenient one-step synthesis of chlorocyanoacetylene from trichloropropio- or dichloroacrylonitriles, and a synthesis of cyanoacetylene from dichloropropio- or chloroacrylonitriles, together with a novel synthesis of malononitrile from chlorocyanoacetylene.



(1)

Chlorocyanoacetylene is a colorless, easily sublimable crystalline compound, the vapor being a strong lachrymator. It can be safely distilled[9] under atmospheric pressure (bp 80–82°) and can be stored for months in a refrigerator or even at room temperature with only slight decomposition. It should be mentioned, however, that chlorocyanoacetylene appears to have rather

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[1] (a) Paper II: N. Hashimoto, Y. Kawano, and K. Morita, *J. Org. Chem.*, **35**, 828 (1970); (b) Part of this work was presented at the symposium on The Chemistry of Heterocyclic Compounds, Osaka, Japan, Oct 1968, and at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, April 1969.

[2] C. H. Moureu, and J. Ch. Bongrand, *Ann. Chem.*, **14**, 53 (1920).

[3] S. Murahashi, T. Takizawa, S. Kurioka, and S. Maekawa, *Nippon Kagaku Zasshi*, **77**, 1689 (1956); *Chem. Abstr.*, **53**, 5163 (1959); Union Carbide Corp., Netherlands Application Patent 296,042 (1965); *Chem. Abstr.*, **63**, 17907 (1965).

[4] J. Happel, C. J. Marsel, and A. A. Reidlinger, U. S. Patent 3,006,948 (1958); *Chem. Abstr.*, **56**, 8574 (1962).

[5] L. J. Krebaum, U. S. Patent 3,079,424 (1963); *Chem. Abstr.*, **59**, 3777 (1963); *J. Org. Chem.*, **31**, 4103 (1966).

[6] L. J. Krebaum, U. S. Patent 3,055,738 (1962); *Chem. Abstr.*, **58**, 2375 (1963).

[7] E. Kloster-Jensen, *Acta Chem. Scand.*, **18**, 1629 (1964).

[8] T. Bjorvatten, *ibid.*, **22**, 410 (1968).

[9] Chlorocyanoacetylene burns in air only moderately with a sooty flame but it may cause a hazardous explosion if it burns in a nearly closed vessel. In a large-scale synthesis, it was found that the pyrolytic dehydrochlorination of trichloropropionitrile was accompanied by a minute but nonnegligible amount of hazadous low boiling materials. These low boiling substances were isolated and identified as $ClC{\equiv}CH$ (trace), $ClC{\equiv}CCl$, and $ClCN$, by mass spectra. The former two compounds are extremely flammable, and it was proved that they were the cause of small explosions met sometimes at the early stage of the investigations, but it was soon discovered, thanks to the excellent work of Ott, *et al.*, that the addition of very small (*ca.* 1%) amount of ethyl ether to the material greatly hampered both ignition and explosion.

TABLE I

PYROLYTIC SYNTHESIS OF CYANOACETYLENES

A. Chlorocyanocetylene

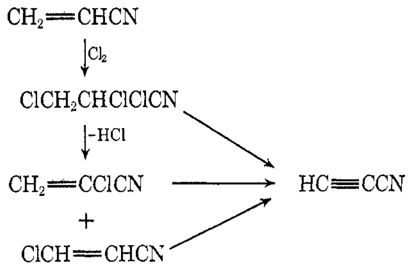
Material		Pyrolysis conditions			Yield of					
		Temp of furnace,[a] °C	Pressure, mm	Reaction time, min	HC≡CCN		ClC≡CCN		ClCH=CClCN	
	Mmol used				mmol	%[b]	mmol	%[b]	mmol	%[b]
$ClCH_2CCl_2CN$	838.6[c]	900	25	385	56.3	6.7	640	78	8.9	1.1
ClCH=CClCN	820.0	900	25	345	36.7	4.5	661	81	17.1	2.1
Cl_2C=CHCN	41.0	900	25	20			16	39		
Cl_2C=CHCN	41.0	980	22	20			29.7	72		

B. Cyanoacetylene

Material		Pyrolysis conditions			Yield, %,[b] of					
		Temp of furnace,[d] °C	Pressure, mm	Reaction time, min		CH_2=	CH_2=	ClCH=CHCN		ClCH=
	Mmol used				HC≡CCN	CHCN	CClCN	*trans*	*cis*	CClCN
$ClCH_2CHClCN$	162.4[e]	900	20	52	23.4	4.2	20.4	10.5	10.5	0.6
$ClCH_2CHClCN$	162.4[e]	1000	20	62	40.3	3.7	9.8	3.9	3.5	
CH_2=CClCN	171.4	1000	18	66	40.3	3.2	21.0			
trans-ClCH=CHCN	114.3	1000	25	60	55.0					

[a] Two furnaces were used in series. The first one (20 cm long) was heated to 700° in all experiments and the second one (15 cm) was heated to the temperatures shown. [b] Based on total material used. [c] Consisted of 795 mmol of α,α,β-trichloropropionitrile and 43.6 mmol of β-chloropropionitrile. [d] Two furnaces (20 and 15 cm) were used in series and heated at the same temperatures shown. [e] Consisted of 154.4 mmol of α,β-dichloropropionitrile and 2.0 mmol of α,α,β-trichloropropionitrile.

low ignition temperature and its contact with air, therefore, must be avoided at elevated temperatures.



(2)

It is known that dichloroacetylene reacts with ammonia to give monochloroacetonitrile,[10] and that some 2-alkynamides give nitriles by the Hofmann rearrangement.[11]

$$ClC{\equiv}CCl \xrightarrow{NH_3} ClCH_2CN \quad (3)$$

$$R{-}C{\equiv}C{-}CONH_2 \longrightarrow RCH_2CN \quad (4)$$

An analogous reaction with chlorocyanoacetylene should lead to production of malononitrile, as depicted by eq 5. In fact, the formation of malononitrile was

$$ClC{\equiv}CCN + NH_3 \longrightarrow NCCH_2CN \quad (5)$$

readily ascertained by preliminary experiments, but the yields of malononitrile varied between wide limits. However, further refinements of the reaction conditions finally led us to an industrially feasible process for the production of malononitrile, of which the detailed experiments will be described elsewhere in the future.

Results and Discussion

Synthesis of Chlorocyanoacetylene. The Pyrolysis of Trichloropropionitrile and Dichloroacrylonitrile.—The pyrolysis was carried out in the same manner as described in the previous paper.[1a] The starting materials were introduced into the reaction tube by the leak method. The reaction conditions and the compositions of the products determined by gas chromatography are sumarized in Table I. These data show that the formation of chlorocyanoacetylene is by far the predominate course of the reaction in the pyrolyses of these chlorinated propio- and acrylonitriles, although the product was accompanied by a small amount of cyanoacetylene, an inevitable by-product.

This is especially true when purified starting materials are used. However, when crude α,α,β-trichloropropionitrile was pyrolyzed, the yield of cyanoacetylene increased along with the amount of the contaminating β-chloropropionitrile, which is formed as a by-product in the synthesis of α,α,β-trichloropropionitrile from acrylonitrile and chlorine. It was interesting to note that practically no appreciable quantity of acrylonitrile, which should result from β-chloropropionitrile under the reaction conditions, was formed. This suggests that the pyrolytic dehydrochlorination proceeds through a radical chain mechanism (eq 6–11) rather

$$ClCH_2CCl_2CN \xrightarrow{-HCl} ClCH{=}CClCN \quad (6)$$

$$ClCH{=}CClCN \longrightarrow Cl\cdot + ClCH{=}\dot{C}CN \quad (7)$$

$$Cl\cdot + ClCH{=}CClCN \longrightarrow Cl\dot{C}{=}CClCN + HCl \quad (8)$$

$$Cl\dot{C}{=}CClCN \longrightarrow ClC{\equiv}CCN + Cl\cdot \quad (9)$$

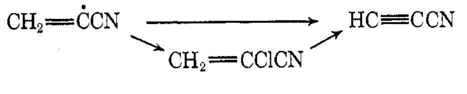
$$ClCH{=}\dot{C}CN \longrightarrow HC{\equiv}CCN + Cl\cdot \quad (10)$$

$$\searrow CCl{\equiv}CCN + H\cdot \quad (11)$$

than a simple elimination mechanism, and that the acrylonitrile is acting as a scavenger of the chlorine atom, which plays an important role in the reaction (eq 12–14). If this is the case, then it is also under-

$$ClCH_2CH_2CN \xrightarrow{-HCl} CH_2{=}CHCN \quad (12)$$

$$CH_2{=}CHCN + \cdot Cl \longrightarrow CH_2{=}\dot{C}CN + HCl \quad (13)$$



(14)

standable that cyanoacetylene is inevitably produced in a small amount even from pure starting materials, though this does not exclude some other possibilities,

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[10] E. Ott, *et al.*, (a) *Chem. Ber.*, **63**, 1941 (1930); (b) *ibid.*, **64**, 1324 (1931); (c) *ibid.*, **75**, 1517 (1942); (d) *ibid.*, **76**, 80 (1943); (e) *ibid.*, **76**, 88 (1943).

[11] I. J. Rinkes, *Rec. Trav. Chim. Pays-Bas*, **39**, 704 (1920).

TABLE II

PYROLYSIS OF α-β-DICHLOROPROPIONITRILE[a]

Run no.	1	2
Feed rate (g/hr)	160	267
Yields on material consumed, %		
Cyanoacetylene	2.7	0.9
α-Chloroacrylonitrile	15.4	21.8
trans-β-Chloroacrylonitrile	10.2	16.1
cis-β-Chloroacrylonitrile	10.3	18.6
β,β-Dichloroacrylonitrile	3.4	1.1

[a] Under 25-mm pressure and at *ca.* 580°.

e.g., wall effect, etc., which may lead to the formation of cyanoacetylene directly from α,β-dichloroacrylonitrile.

Synthesis of Cyanoacetylene.—The apparatus used was the same as described in the previous paper[1a] and the starting materials were prepared by the known methods. The feeding of the starting materials was carried out either by distillation or by the leak method. When the distillation method was adopted, the vapor of α,β-dichloropropionitrile was introduced into a reaction tube under nitrogen, because cyanoacetylene was extremely susceptible to oxidation at high temperatures. The yield of cyanoacetylene was 40–55% (Table I). By-products are acrylonitrile and α,β-dichloroacrylonitrile, as well as monochloroacrylonitriles. Undoubtedly, the first two by-products are derived from β-chloro- and α,α,β-trichloropropionitrile, respectively, which were present in the starting material. Addition of carbon tetrachloride accelerated the pyrolysis of α,β-dichloropropionitrile or monochloroacrylonitriles and suppressed the production of acrylonitrile. Addition of even a small amount of β-chloropropionitrile, which produces acrylonitrile under these conditions, to the starting material led to a sharp decrease of the yield of cyanoacetylene and an increased production of monochloroacrylonitriles.

These results suggest that the dehydrochlorination is of radical nature. However, because the material balance of each experiment was *ca.* 70%, it would not be adequate to discuss the reaction mechanism in more detail. In fact, it was observed that the reaction tube was lined with a thick and tough layer of carbon. Besides, some high-boiling products were formed, which were not analyzed. Furthermore, some cyanoacetylene might have escaped trapping because of its high volatility.

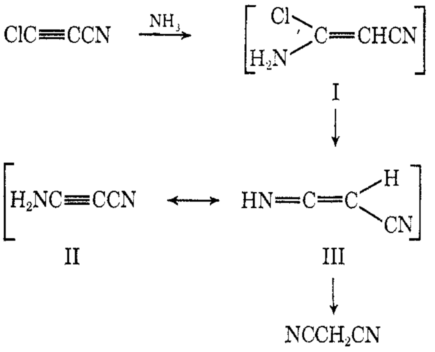
Synthesis of Malonitrile from Chlorocyanoacetylene.—The best results were obtained when a controlled flow of gaseous ammonia was passed through a stirred, dilute (below *ca.* 5%) solution of chlorocyanoacetylene in organic solvents like aromatic hydrocarbons, ethers, esters, acetonitrile, and methylene chloride.

The concentration of the reactants was very critical in this reaction. This seemed largely due to the fact that the malononitrile formed also reacts with chlorocyanoacetylene, especially in the basic medium. In accord with this assumption, the yield of malononitrile was almost zero when the reaction was carried out with the external addition of malononitrile.

When the reaction was carried out in ethyl acetate as solvent at −20°, it seemed that the initial step of the reaction proceeded very smoothly, with simultaneous precipitation of NH_4Cl, but, with rise of the reaction temperature, the reaction mixture resinified rapidly, especially at high concentrations. This may be explained by the presence of a molecular species like II or III, which may polymerize at high temperatures.

The reaction failed in methanol or water giving only a small amount of β-chloro-β-methoxyacrylonitrile in the former solvent.

Though the mechanism of the reaction is not clear, it may be illustrated by the following scheme, which is consistent with the mechanism proposed by Ott, *et al.*, for the formation of monochloroacetonitrile by the reaction of dichloroacetylene with ammonia.



Experimental Section

Materials.—α,α,β-Trichloropropionitrile[12] and α,β-dichloroacrylonitrile[12a] were prepared according to the literature. The purity of trichloropropionitrile was 97%, containing 3% β-chloropropionitrile,[13] and that of α,β-dichloroacrylonitrile was almost 100%. β,β-Dichloroacrylonitrile was obtained by the procedure described in the previous paper.[1a] α,β-Dichloropropionitrile[14] and α-chloroacrylonitrile[14] were prepared according to the literature. The purity of the α,β-dichloropropionitrile was *ca.* 95.7%, contaminated by 1.6% α,α,β-trichloropropionitrile and 2.7% β-chloropropionitrile, as determined by gas chromatography [the column: 1 m, TCP (10%) on Chromosorb W, 60–80 mesh, at 120°]. α-Chloroacrylonitrile was practically pure. β-Chloroacrylonitriles were prepared by a modification of the patent literature[15] (see below).

Pyrolysis of α,β-Dichloropropionitrile under Reduced Pressure. At Low Temperatures.—The reaction was carried out in a quartz tube, 22 mm in diameter and 1 m in length, mounted nearly horizontally and heated to 550–580° in an electric furnace 71 cm in length. The upper end of the reaction tube was connected to a vaporizing flask into which was fed α,β-dichloropropionitrile through a leak from a buret. The lower end of the quartz tube was connected to an aspirator through a trapping system, which involves in succession an air cooled trap, two round-bottomed flasks cooled with Dry Ice–ethanol, a trapping tube, and another trapping tube containing acetone, both being cooled with Dry Ice–ethanol. α,β-Dichloropropionitrile was fed at the rate of *ca.* 160 or 267 g/hr, while evacuating the whole system to *ca.* 25 mm. The condensates were combined and fractionally distilled at first under an atmospheric pressure, then under reduced pressures. Each fraction was purified, if necessary, by repeated distillation. The results of two experiments, which were carried out using low and high feed rates of the material, are given in Table II.

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[12] I. G. Khaskin, and Z. A. Vasil'eva, *Khim. Prom.*, **41**, 577 (1965); *Chem. Abstr.*, **64**, 586 (1966); (b) W. H. Jura, and R. J. Gaul, *J. Amer. Chem. Soc.*, **80**, 5402 (1958); (c) N. B. Lorette, *J. Org. Chem.*, **26**, 2324 (1961); (d) I. G. Khaskin, *et al.*, USSR Patent 198,312 (1962); *Chem. Abstr.*, **68**, 104573 (1968).

[13] J. G. Erickson, U. S. Patent 2,524,011 (1950); *Chem. Abstr.*, **45**, 2016 (1951).

[14] H. Brintzinger, K. Pfannstiel, and H. Koddebusch, *Angew. Chem.*, **60**, 311 (1948); see also ref 12b.

[15] G. C. Morrison and W. O. Fugate, U. S. Patent 3,069,458 (1962); *Chem. Abstr.*, **58**, 13799 (1963).

Chlorocyanoacetylene and Cyanoacetylene.—The pyrolysis apparatus was the same as that used for the copyrolysis of acetonitrile and carbon tetrachloride, with a slight modification.[1a] The whole system was evacuated with an aspirator while the sample was fed by the leak method. The reaction product, most of which condensed as a crystalline mass in the first trapping tube, was dissolved in tetrachloroethylene and analyzed by gas chromatography. The column was SE-30 (10%) or TCP (10%) on Chromosorb W. The temperature of the column was 65°. Typical results are shown in Table I.

Malononitrile. General Procedure.—Four grams of chlorocyanoacetylene was dissolved in a solvent and the solution was placed in a four-necked flask equipped with a thermometer, an inlet tube for ammonia, a reflux condenser, and a mechanical stirrer. With efficient stirring, a stream of gaseous ammonia was introduced directly into this solution. The rate of feeding ammonia was *ca.* 100 ml/min, which corresponded to the rate of consumption of *ca.* 0.2 g of chlorocyanoacetylene/min. When the inside temperature reached 30°, cooling was started in order to maintain this temperature during the reaction period. After ammonia had been introduced into the reaction mixture for 20 min, the precipitated NH_4Cl was filtered off and most of the solvent was evaporated. A small amount of water was added and the solution was extracted with benzene. The combined benzene extract was washed, dried (Na_2SO_4), and evaporated to leave the reaction product, which was almost pure malononitrile, which, in most cases, crystallized when it was cooled to room temperature. The product obtained was further purified by distillation under reduced pressure. The yield of malononitrile was 60–87%.

Identification of β-Chloro-β-methoxyacrylonitrile.—Pure samples of the two isomers were isolated by preparative gas chromatography and their structures were confirmed by the following data, respectively, except the assignment of *cis–trans* isomerism. Sample A had shorter retention time on gas chromatography: mp 33–33.4°; ir (liquid film) 3090, 2225, 1618, 1320, 1120 cm^{-1}; nmr ($CDCl_3$) δ 4.02 (s, 3), 4.67 (s, 1).

Anal. Calcd for C_4H_4ClNO: C, 40.87; H, 3.43; N, 11.92. Found: C, 40.92; H, 3.30; N, 11.64.

Sample B had longer retention time: ir (liquid film) 3075, 2240, 1615, 1230 cm^{-1}; nmr ($CDCl_3$) δ 3.86 (s, 3), 4.73 (s, 1).

Anal. Calcd for C_4H_4ClNO: C, 40.87; H, 3.43; N, 11.92. Found: C, 40.52; H, 3.67.

Reaction of Chlorocyanoacetylene in the Presence of Additional NH_4Cl and Malononitrile.—In a four-necked flask equipped with a stirrer, a thermometer, an ammonia inlet tube, and Teflon Tube for feeding chlorocyanoacetylene, which was sent by means of a stroke pump, malononitrile (4 g), benzene or ethyl acetate (36 g), and powdered NH_4Cl (3.25 g) were placed and stirred mechanically. To this stirred suspension chlorocyanoacetylene was added in a form of 20% solution in the same solvent, at the rate of 0.2 g of chlorocyanoacetylene/min for 20 min. After 5 min, the addition of ammonia (the rate of flow was 100 ml/min) was started and continued for 20 min. Under the reaction conditions, the concentrations of the malononitrile and the chlorocyanoacetylene were kept almost constantly at 10 and 2.5%, respectively. After the reaction had finished, the analysis of the reaction mixture was carried out as described above.

Registry No.—Chlorocyanoacetylene, 2003-31-8; cyanoacetylene, 1070-71-9; malononitrile, 109-77-3.

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Fluorocyclopropanes. I. Preparation and Nuclear Magnetic Resonance Spectra

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Hexafluoropropylene epoxide transfers a difluoromethylene group to olefins in a general and convenient synthesis of fluorinated cyclopropanes. In one case the reaction was shown to be stereospecific. However, loss of stereospecificity can result from thermal isomerization of the fluorinated cyclopropane, which occurs slowly near 200°. The nmr spectra of the fluorinated cyclopropanes show that generally the vicinal coupling constants *cis* J_{HF} (9–17 Hz) and *cis* J_{FF} (5–10 Hz) are greater than *trans* J_{HF} (1–2 Hz) and *trans* J_{FF} (2–5 Hz), respectively.

Fluorinated cyclopropanes have been prepared by the pyrolysis of sodium chlorodifluoroacetate,[2] trifluoromethyl-substituted organometallics,[3–6] ketene,[7] diazomethane,[8] fluorine-substituted diazo compounds,[9–10] difluorodiazirine,[11] and selected chlorofluorocyclopropanes,[12] and base treatment of dichlorofluoromethane[13] and tetrachlorodifluoracetone[14] in the presence of olefins. These procedures suffer from either lack of generality or difficult preparation of the fluorinated starting material. This paper reports a method for the preparation of fluorinated cyclopropanes from hexafluoropropylene oxide which complements the use of sodium chlorodifluoroacetate. Both starting materials are readily available and both give stereospecific addition of CF_2; hexafluoropropylene oxide is useful for reaction with low-boiling olefins while sodium chlorodifluoroacetate is appropriate for reaction with solids and most liquids.

Results and Discussion

Above 170° hexafluoropropylene oxide (1) served as an apparent source of CF_2 which added to thio-

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(10) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 3617 (1966).

(11) R. A. Mitsch, *ibid.*, **87**, 758 (1965); *J. Heterocycl. Chem.*, **1**, 271 (1964).

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