dation (GP-3343) for financial support of the work performed at Michigan State University.

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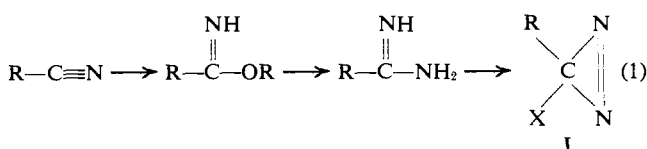American Oil Company, Whiting, Indiana

The Halogenation of Amidines. I. Synthesis of 3-Halo- and Other Negatively Substituted Diazirines[1]

Sir:

Syntheses of diazirine and a variety of its alkyl derivatives have been carried out successfully for several years.[2] However, the only reported 3-halodiazirine derivative is difluorodiazirine.[3]

We have found that halogenation of alkyl- or arylamidines and isoureas in aqueous dimethyl sulfoxide (DMSO) solution affords the corresponding alkyl-, aryl-, or alkoxy-3-halodiazirine (I) in practical yields. The method, which appears to be a general one, makes accessible the substituted 3-halodiazirine from the corresponding nitrile precursor (eq. 1).[4]

$$NH \qquad NH \qquad R \quad N$$

$$R-C\equiv N \longrightarrow R-\overset{\parallel}{C}-OR \longrightarrow R-\overset{\parallel}{C}-NH_2 \longrightarrow \underset{X}{\overset{R}{\diagdown}}\underset{N}{\overset{N}{C}} \quad (1)$$

I

In the chlorination of acetamidine, addition of acetate ion produced a mixture of methylchlorodiazirine and methylacetoxydiazirine. Presumably, other nucleophiles which do not interfere with the halogenation of the amidine should compete with the halide ion to give the corresponding negatively substituted diazirine.

In a typical experiment aqueous sodium hypochlorite solution[5] (300 ml., 0.78 M) containing 60 g. of additional NaCl was dropped rapidly into a stirred 150-ml. DMSO solution of acetamidinium hydrochloride (0.025 mole) and 10 g. of LiCl. The volatile contents were removed continuously by means of a vacuum pump pulling through a train of four U-tube traps at −35, −80, −126 (methylcyclohexane slush bath), and −196°. The temperature of the reaction mixture rose from 25 to 55° during the addition. The product, methylchlorodiazirine, was retained principally in the −126° trap. Yields of 60% are typical. Less volatile diazirines were generally retained in the −80° trap. Methylbromodiazirine was prepared by a similar procedure using freshly prepared NaOBr. For less

(1) Presented before the Division of Organic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.
(2) For a survey of the field see E. Schmitz, Angew. Chem. Intern. Ed. Engl., 3, 333 (1964); Angew. Chem., 76, 197 (1964).
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(4) The amidine salts used in this study were either purchased from Aldrich Chemical Company, Milwaukee, Wis., or prepared according to the method of Pinner as described by A. W. Dox, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 5.
(5) Commercial Clorox.

**Table I.** Diazirines (I) Prepared by Halogenation of Amidines in DMSO

Nitrile precursor	R	X	N=N stretch,[c] cm.$^{-1}$	Ultraviolet, mμ
CH$_3$CN	CH$_3$	Cl	1585	354
CH$_3$CN	CH$_3$	Br	1570	355
CH$_3$CN	CH$_3$	CH$_3$COO	1575	349[d]
(CH$_3$)$_3$CCN	(CH$_3$)$_3$C	Cl	1565	358[d]
c-C$_3$H$_5$CN	c-C$_3$H$_5$	Cl	1565	357[d]
C$_6$H$_5$CN	C$_6$H$_5$	Cl	1560	388[d]
C$_6$H$_5$CN	C$_6$H$_5$	Br	1555	388[d]
p-CH$_3$OC$_6$H$_5$CN	p-CH$_3$OC$_6$H$_5$	Cl	1560	405[d]
CH$_3$OCN[a]	CH$_3$O	Cl	1545	365[d]
CH$_2$=CHCN[b]	CH$_2$=CH	Cl	1560	

[a] The actual starting material for this reaction was O-methylisourea hydrogen sulfate. [b] Preparation of this amidinium salt was not clean. By using the crude mixture a small amount of vinylchlorodiazirine was obtained. [c] Infrared spectra were recorded with a Perkin-Elmer Infracord instrument. [d] Broad peaks, position indicated is shoulder on long wave length side.

volatile diazirines it was convenient to add CCl$_4$ to the DMSO solution before addition of the NaOCl or NaOBr solution at atmospheric pressure. The product was extracted into the CCl$_4$ layer from which it was purified by the appropriate method, usually column chromatography through silica gel.

Product identification was substantiated by physical data such as proton n.m.r., ultraviolet, infrared, and mass spectra; molecular weights were obtained using a mass-spectral effusion method. Table I lists those diazirine derivatives which were prepared along with the infrared absorption frequency of the characteristic diazirine -N=N- stretch[3,6,7] and the wave length of their ultraviolet absorption.[6,8,9] In all cases the proton n.m.r. spectrum was consistent with the proposed structure. Mass spectra of the 3-halodiazirines were generally characterized by fragmentation to produce ions of m/e which result from loss of halide and both halide and a nitrogen molecule. The latter was usually the most intense peak. Satisfactory elemental analyses were obtained on several liquid diazirine products, but explosions in the combustion tube were frequent.

The reaction mechanism probably involves the sequence illustrated in eq. 2. Initial formation of the

$$(2)$$
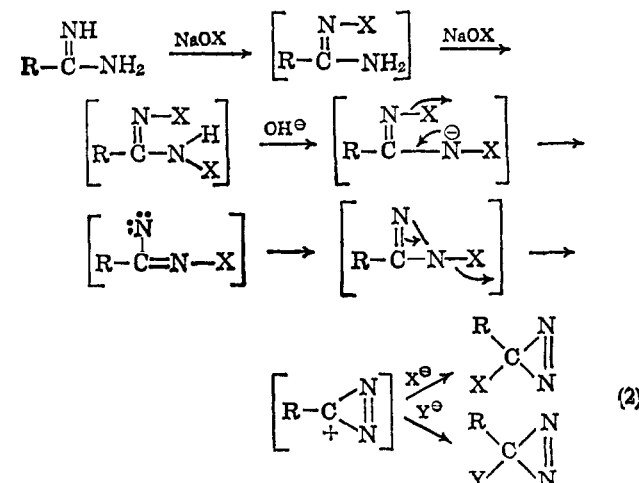
(6) W. H. Graham, J. Am. Chem. Soc., 84, 1063 (1962).
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monohaloamidine is precedented.[10,11] After the second halogenation step the mechanism appears to be closely related to the Neber reaction.[12] The ring closure to the proposed intermediate, N-halodiazirine, might involve the nitrene as pictured or be a direct displacement of halide by the N-halo anion.[13] The same question arises in considering the mechanistic details of the Neber reaction.[14,15] Whether the N-halodiazirine dissociates as shown to the diazirinium ion followed by competitive reaction of the carbonium ion with nucleophiles present or reacts by an S_N2' process with the nucleophiles is a moot question. The former alternative is interesting because the stability of the diazirinium ion would derive from its aromatic character according to Hückel's $4n + 2$ rule.[16] This heterocyclic ion is isoelectronic with the well-characterized cyclopropene-carbonium ion derivatives.[17] The prominence of the fragments of m/e corresponding to the diazirinium ions in the mass spectra suggests that their formation under solvolytic conditions is not unreasonable.

Most of the halodiazirines prepared were comparable in stability to diazirines reported previously.[2] However, methoxychlorodiazirine decomposed spontaneously at room temperature to give 1,4-dimethoxy-1,4-dichloro-2,3-diaza-1,3-butadiene.[18] Phenylchlorodiazirine decomposed at room temperature over a period of several days to give 1,4-diphenyl-1,4-dichloro-2,3-diaza-1,3-butadiene.

The chemistry unique to the 3-halodiazirines remains to be investigated. However, like other diazirines, they appear to decompose thermally to produce carbene intermediates.[19,20] Thus, methylchlorodiazirine yields vinyl chloride and nitrogen upon thermal decomposition; decomposition of phenylchlorodiazirine in refluxing cyclohexene gave a mixture believed to be *exo*- and *endo*-7-chloronorcarane.[21]

This synthesis provides ready access to a large number of diazirine derivatives of potential biological activity.[22] Also the synthesis affords a wide variety of diazirine precursors to carbene intermediates which are not now readily available.

Acknowledgment. This investigation was supported by Army Ordnance Contract DA-01-021 AMC-11536(Z). The author wishes to thank Mr. Kirt Keller for technical

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assistance and Mr. R. D. Strahm, who ran the ultraviolet spectra.

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Trimeric Alkylthiotricarbonyls of Manganese and Rhenium

Sir:

During recent studies of the properties of organotin-sulfur compounds, we have noted two general reactions. Firstly, the sulfur in these compounds can behave simply as a donor atom and replace carbon monoxide in metal carbonyls; secondly, these tin-sulfur compounds react with metal and metalloid halides causing fission of the Sn–S bond, with subsequent formation of a mercapto derivative of the metal or metalloid and an organotin halide as a by-product.[1]

We now wish to report the formation of novel metal carbonyl derivatives from the reaction of organotin-sulfur compounds with metal carbonyl halides—a system in which both substitution and fission reactions could occur.

Bromopentacarbonylmanganese reacts with bis(methylthio)dimethyltin[2] in diethylene glycol dimethyl ether above 70° to give the diamagnetic, trimeric methylthiotricarbonylmanganese, obtained as orange crystals in 69% yield. *Anal.* Calcd. for $C_{12}H_9Mn_3O_9S_3$: C, 25.8; H, 1.6; O, 25.8; S, 17.2; mol. wt., 558. Found: C, 26.0; H, 1.6; O, 26.0; S, 17.2; mol. wt.,[3] 548. Infrared C–O stretching modes are observed at 2021 (vs), 2014(w), and 1950(s) cm.$^{-1}$. Chloropentacarbonylrhenium reacts similarly above 120° to give pale yellow crystals of methylthiotricarbonylrhenium in 59% yield. *Anal.* Calcd. for $C_{12}H_9Re_3O_9S_3$: C, 15.1; H, 1.0; O, 15.1; mol. wt., 952. Found: C, 15.4; H, 1.1; O, 15.2; mol. wt.,[3] 971. In addition to these two compounds a number of alkyl and aryl analogs of both of these compounds have been similarly prepared. In addition to the well-known dimeric alkylthiotetracarbonyls[4] of manganese and rhenium, mention has been made in the patent literature[5] of "hydrocarbylthio-manganese tricarbonyls, existing as trimers and dimers under varying conditions."

The formation of the methylthiotricarbonylmanganese unit and its trimerization in this reaction can be rationalized as follows. Reaction of a bidentate sulfur ligand with bromopentacarbonylmanganese has been previously shown[6] to replace two carbon monoxide groups to produce $LMn(CO)_3Br$. Regarding $(CH_3)_2$-$Sn(SCH_3)_2$ as a bidentate ligand, one would expect $(CH_3)_2Sn(SCH_3)_2Mn(CO)_3Br$ to be formed, but subsequent fission of the Sn–S bond owing to presence of halogen causes the reaction shown. The $Mn(CO)_3SCH_3$

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