zation of this sample from ethanol gave pure V, m.p. 246.5–247, identical with an authentic sample by infrared analysis and mixture melting point.

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Reactions of Dichloramine. I. A Convenient Method of Preparation of Diazirine

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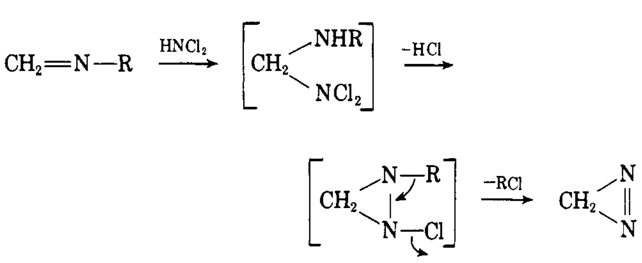
The preparation of diazirine by the reaction of difluoramine and *t*-octylazomethine,[1] although an efficient method[2] of preparing diazirine, suffers the disadvantage of the lack of general availability of difluoramine and the hazards associated with its use.[3]

Dichloramine,[4] although highly reactive,[5] is easily prepared in solution from ordinary laboratory reagents. Like difluoramine, dichloramine reacted readily with *t*-octylazomethine[6,7] to produce diazirine in moderate yield. The best yield of diazirine was obtained when 5% NaOCl solution[8] was dropped slowly into a mixture containing an aqueous sodium formate–formic acid buffer, ammonium chloride, and *t*-octylazomethine maintained at 5–12°. Dibutyl ether was sometimes used as solvent with somewhat better results. The volatile contents were removed under vacuum through a train of four traps at −35, −80, −142, and −196°. The diazirine was retained principally in the −142° trap and was generally contaminated by CO_2 to the extent of 15% or less. Yields of 25–33% were typical. Other procedures, involving preparation of dichloramine prior to addition of the imines, gave poorer yields, probably because of the instability of the dichloramine solutions.

The mechanism of the reaction is believed to involve the *in situ* formation of dichloramine in the buffered aqueous phase, extraction of dichloramine into the organic phase,[4] addition to the imine, internal ring closure by displacement of chloride from nitrogen, and loss of the elements of *t*-octyl chloride from the unstable N-chlorodiaziridine. The addition–ring closure mechanism is preferred to one involving formation of chloronitrene because of the evidence for a similar mechanism in the addition of hydroxylamine–O-sulfonic acid to the imine double bond.[9]



R = *t*-octyl

This method of preparation of diazirine has advantages over the recently discovered method using methylenediammonium salts[2b] because of the ease of preparation and handling of *t*-octylazomethine and the adaptability of the method to the preparation of substituted diazirines for which the diammonium salt precursors cannot be prepared.[10]

Experimental

Diazirine.—A 1-l. three-neck flask, fitted with a 500-ml. pressure-equalizing dropping funnel, magnetic stirring bar, and thermometer was connected to a train of four U-tube traps which were cooled to temperatures of −35, −80, −142 (methylcyclopentane slush bath), and −196°. To the flask was added 150 ml. of a formate buffer solution[11] (1 *N* in formic acid and 1 *N* in sodium formate), 150 ml. of a 4 *N* NH_4Cl solution (0.6 mole NH_3), and 150 ml. of dibutyl ether, and the contents were cooled to 5°. Immediately prior to beginning the addition of NaOCl, 7.05 g. (0.05 mole) of *t*-octylazomethine was added[12] to the reaction flask. The flask was opened to a vacuum pump through the four cold traps and 300 ml. of 0.4 *N* NaOCl was added over a period of 6 min. Vigorous gas evolution was observed during the addition and for several minutes afterwards. The traps were isolated from the reactor after 5 min. and a vacuum was applied to the traps for another 10 min. The bulk of the diazirine (308 cc., STP, 27.5%) was retained in the −142° trap with a smaller amount (12 cc., STP, 1%) being trapped in the −196° trap. The purity of the diazirine in the −142° trap was 85–90%; CO_2 was the chief contaminant along with traces of methyl formate and cyanogen chloride. The −196° trap contained chiefly CO_2 along with lesser amounts of diazirine and traces of ethane. Analyses of the gas mixtures were by mass and infrared spectra. The yield data for several runs at various ratios of *t*-octylazomethine–sodium hypochlorite is summarized in Table I. The theoretical yield of dichloramine is based upon the assumption that 2 moles of sodium hypochlorite produce 1 mole of dichloramine. *Caution: Diazirine is explosive and should be prepared only with proper safety precautions.*

TABLE I

DIAZIRINE YIELDS

	Moles		
NaOCl	*t*-Octylazomethine	Diazirine	Yield, %
0.12	0.025	0.0078	31.2
0.12	0.05	0.0143	28.5
0.12	0.075	0.0157	26.2
0.12	0.10	0.0154	25.7
0.12	0.20	0.0082	13.6
0.075	0.060	0.011	29.6

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[1] W. H. Graham, *J. Am. Chem. Soc.*, **84**, 1063 (1962).

[2] For other methods of preparation of diazirine, see (a) E. Schmitz and R. Ohme, *Tetrahedron Letters*, 612 (1961); (b) R. Ohme and E. Schmitz, *Chem. Ber.*, **97**, 297 (1964).

[3] W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963), and references cited therein.

[4] R. M. Chapin, *J. Am. Chem. Soc.*, **51**, 2112 (1929).

[5] R. E. Corbett, W. S. Metcalf, and F. G. Soper, *J. Chem. Soc.*, 1927 (1953).

[6] M. D. Hurwitz, U. S. Patent 2,582,128 (1952).

[7] W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

[8] Commercial "Clorox."

[9] For evidence, see the excellent review article by E. Schmitz, *Angew. Chem., Intern. Ed. Engl.*, **3**, 333 (1964).

[10] Methyldiazirine has been prepared by a modification of this procedure using acetaldehyde-*t*-octylimine. The yield and purity of product were less favorable, however.

[11] Both 90% and 98–100% grades of formic acid contain appreciable amounts of methyl formate which will contaminate the product if not removed prior to reaction by a suitable degassing procedure.

[12] The *t*-octylazomethine was not added earlier in order to minimize any side reaction such as hydrolysis.