TABLE I

DECOMPOSITION OF TRICHLOROACETIC ACID IN GLYCEROL. SPECIFIC REACTION VELOCITY CONSTANTS AT 110.1°

Time, sec.	Vol. CO_2 at S.T.P., ml.	Completion of reacn., %	Spec. reacn. velocity
180	11.6	29.0	0.00191
240	14.8	37.0	.00192
300	17.8	44.5	.00196
360	20.4	51.2	.00192
420	23.0	57.6	.00204
480	25.3	63.5	.00208
540	27.2	68.2	.00211
600	28.9	72.3	.00213

One run was made at 109.0° on a 50% by weight mixture of glycerol–water yielding a value of *k* of 0.00259 sec.$^{-1}$, or nearly twice the value in the case of the 95% glycerol run, a result consistent with the proposed mechanism.

Decomposition of Trichloroacetic Acid Alone.—The average volume of carbon dioxide at S.T.P. evolved per minute from one mole of trichloroacetic acid at 156.4° was 1.51 ml.; at 159.4°, 2.5 ml.; at 163.8°, 5.03 ml.; and at 166.6°, 8.37 ml. These results yield specific reaction velocity constants in sec.$^{-1}$ of 1.12×10^{-6}, 1.865×10^{-6}, 3.71×10^{-6} and 6.17×10^{-6}, respectively. For the temperature range involved *E* is 60,700 cal.

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Preparation of N-Substituted Hydrazines from Amines and Chloramine

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We have shown in a recent publication[1] that the Raschig hydrazine synthesis may be modified to yield simple monoalkyl hydrazines. The interaction of chloramine with amines has now been shown to constitute a general preparative method as illustrated by the conversion of *n*-hexylamine and cyclohexylamine into the corresponding hydrazines, of allylamine to allylhydrazine, ethanolamine to β-hydroxyethylhydrazine, ethylenediamine to β-aminoethylhydrazine, and morpholine to N-aminomorpholine. Attempts to prepare hydrazinoacetic acid from glycine by this method were unsuccessful.

Experimental

The experimental conditions were similar to those employed previously for the preparation of the simpler monosubstituted aliphatic hydrazines.[1] The cold reaction mixture, consisting of an aqueous chloramine solution prepared from hypochlorite and ammonia containing 0.04 mole of NH_2Cl in 250 ml., 0.25 g. of gelatin and the desired amine (mole ratio NH_2Cl:amine = 1:8), was allowed to warm to room temperature over a period of one hour and then heated on a steam-bath for an additional 10 to 30 minutes to ensure completion of the reaction. An aliquot of the reaction mixture then was analyzed by the iodate procedure to determine the percentage conversion of the amine into the corresponding hydrazine. The N-substituted hydrazines were isolated as salts either by concentration of the reaction mixture for the removal of the excess amine and water, followed by recovery of an aqueous fraction which was converted to the hydrochloride or the sulfate (method A), or by neutralization of the reaction mixture with acetic acid followed by treatment with either benzaldehyde or salicylaldehyde for conversion to the azine, extraction of the latter with ether and treatment of the ether solution with aqueous oxalic acid followed by distillation for the removal of the aldehyde and ether and then subsequent concentration to crystallization, after which the oxalate was purified for analysis (method B).

***n*-Hexylhydrazine Hydrogen Oxalate.**—Method B: from 32.0 g. of *n*-hexylamine; 57% yield. Most of the N-substituted hydrazine was found to separate from solution along with the excess amine as a non-aqueous water-insoluble layer upon cooling. The reaction mixture was neutralized with 200 ml. of glacial acetic acid, filtered, and the filtrate condensed with 8 g. (0.069 mole) of benzaldehyde and extracted with three 75-ml. portions of ether. The ether extracts were added to 7.5 g. of oxalic acid dihydrate dissolved in 100 ml. of water. The suspension was steam distilled to remove benzaldehyde, and *n*-hexylhydrazine hydrogen oxalate was obtained by concentration of the residue. The material was recrystallized from ethanol, m.p. 178°.

Anal. Calcd. for $C_8H_{18}O_4N_2$: C, 46.59; H, 8.80; N, 13.59. Found: C, 46.55; H, 8.91; N, 13.77.

Cyclohexylhydrazine Sulfate.—Method A: from 30.2 g. of cyclohexylamine; 60% yield. The product plus the excess of the amine formed a separate liquid phase. The reaction mixture was fractionated to remove the amine and the aqueous hydrazine fraction treated with an excess of sulfuric acid. Cyclohexylhydrazine hydrogen sulfate was obtained upon evaporation and recrystallized from methanol with the addition of ether, m.p. 117°.

Anal. Calcd. for $C_6H_{16}O_4N_2S$: C, 33.95; H, 7.60; N, 13.20. Found: C, 34.16; H, 7.80; N, 13.16.

Allylhydrazine dihydrochloride: from 18.9 g. of allylamine; 52% yield by analysis. The product was isolated by method A as the dihydrochloride, m.p. 133–35° (lit. 134–140°[2]).

β-Hydroxyethylhydrazine Hydrogen Oxalate.—From 19 g. of ethanolamine; 58% yield. The hydrogen oxalate, m.p. 106°,[3] was isolated from the reaction mixture using method B.

Anal. Calcd. for $C_4H_{10}O_5N_2$: C, 28.92; H, 6.07; N, 16.86. Found: C, 28.62; H, 6.19; N, 16.60.

β-Aminoethylhydrazine Dioxalate.—From 20 g. of ethylenediamine; 75% yield. The dioxalate, m.p. 206°,[3] was isolated from the reaction mixture by method B.

Anal. Calcd. for $C_6H_{13}O_8N_3$: C, 28.24; H, 5.14; N, 16.47. Found: C, 28.25; H, 5.11; N, 16.70.

N-Aminomorpholine: from 28 g. of morpholine. A yellow oil remained behind with the residual material upon distillation. The product was extracted with ether and then fractionated, that portion boiling at 162–165° being converted to the hydrochloride. N-Aminomorpholine hydrochloride was found to melt at 167° (lit. 164°[4]).

Anal. Calcd. for $C_4H_{11}N_2OCl$: C, 34.65; H, 8.00; N, 20.20. Found: C, 35.08; H, 8.03; N, 19.89.

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Reductive Cleavage of Esters and Lactones by Grignard Reagents

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Carboxylate ion displacement studies in the dimesitylmethyl ester series with Grignard reagents

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