TABLE I

REACTION OF AMMONIA-FREE CHLORAMINE WITH 1,1-DIMETHYLHYDRAZINE

Reactants,[a] mmol		Products, mmol		
1,1-Dimethylhydrazine	Chloramine	Ammonium chloride	Triazanium chloride	Tetramethyl-2-tetrazene
30.0 (12.3)	30.0 (0.9)	24.7	4.9	11.2
29.8 (15.2)	30.0 (0.4)	24.9	5.3	8.4
60.2 (44.0)	30.0 (0.0)	23.6	7.4	8.4
30.0 (0.0)	60.2 (12.5)	37.6	11.0	18.8

[a] Figures shown in parentheses indicate mmoles recovered unreacted.

The remainder of the solids was assumed to be ammonium chloride (found 18.2 mmol). The liquid reaction phase was distilled at the lowest temperature possible. The remaining yellow oil was placed on the vacuum line and the remaining ether removed at low pressure. The yellow oil was redissolved in an aliquot portion of dry ether, and its gas chromatogram was taken. Three peaks were observed, in the ratio 86:12:2. The addition of pure tetramethyl-2-tetrazene or pure 1,1-dimethylhydrazine selectively increased the largest or next to largest peaks, respectively; the compound responsible for the smallest peak remained uncharacterized. The experimental results are shown in Table II.

TABLE II

REACTION OF CHLORAMINE–AMMONIA MIXTURES WITH 1,1-DIMETHYLHYDRAZINE (ALL QUANTITIES SHOWN ARE EXPRESSED AS MILLIMOLES)

1,1-Dimethylhydrazine	2,2-Dimethyltriazanium chloride	Ammonium chloride	Tetramethyl-2-tetrazene
33.3	14.0	13.2	1.7
33.3	16.0	16.9	1.2
33.3	16.2	17.0	1.5
33.3	14.7	18.0	1.2

Results and Discussion

It is clear that the ability of chloramine to abstract hydrogen atoms and effect oxidative coupling is demonstrable, not only for relatively acidic hydrogen species[2,3,9] but also may be extended to the generally less acidic class of compounds containing N–H bonds. It is also quite evident that all of the ammonium chloride observed in the reaction of chloramine with 1,1-dimethylhydrazine does not come from decomposition of chloramine on 2,2-dimethyltriazanium chloride or solid ammonium chloride as previously surmised[1] and that the presence of ammonia with chloramine increases the yield of 2,2-dimethyltriazanium chloride and ammonium chloride, while lowering the production of tetramethyl-2-tetrazene.

The mechanism of the attack on 1,1-dimethylhydrazine by chloramine is uncertain, though previous work[1] suggests either an attachment on the $(CH_3)_2N-$ moiety to form 2,2-dimethyltriazanium chloride or a direct abstraction of hydrogen atoms[9] to form either $(CH_3)_2NNH-$ or[10,11] $(CH_3)_2NN<$ as reactive intermediates

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow [(CH_3)_2N(NH_2)_2]Cl \quad (1)$$

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow (CH_3)_2NNH- + NH_3^+ + Cl^- \quad (2)$$

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow (CH_3)_2NN< + NH_4Cl \quad (3)$$

The dimethylazamine fragments in eq 3 could then combine to give tetramethyl-2-tetrazene,[10] or the free radicals formed in eq 2 might combine to yield 1,1,4,4-tetramethyltetrazane, which could be further dehydrogenated[10] by chloramine to give tetramethyl-2-tetrazene. The NH_3^+ species shown in eq 2 may then either react with the radicals formed in (2) to yield the dimethylazamine radical, $(CH_3)_2NN<$, or react with another 1,1-dimethylhydrazine molecule to yield another $(CH_3)_2NNH-$ radical. The presence of a high concentration of ammonia with either of the reactive intermediates in eq 2 or 3 could allow them to revert to 1,1-dimethylhydrazine as follows

$$NH_3 + (CH_3)_2NN< \longrightarrow 0.5N_2H_2 + (CH_3)_2NNH_2 \quad (4)$$

$$NH_3 + (CH_3)_2NNH- \longrightarrow -NH_2 + (CH_3)_2NNH_2 \quad (5)$$

The N_2H_2 formed in eq 4 may then decompose to ammonium azide,[12] nitrogen and hydrazine,[13] or nitrogen and ammonia.[14] Thus, as has been found, the presence of ammonia during the chloramination of 1,1-dimethylhydrazine results in higher yields of 2,2-dimethyltriazanium chloride and lower yields of tetramethyl-2-tetrazene.[15]

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[9] L. A. Paquette and W. C. Farley, *J. Org. Chem.*, **32**, 2718 (1967).

[10] C. G. Overberger and L. P. Herin, *ibid.*, **27**, 417 (1962).

[11] W. R. McBride and E. M. Bens, *J. Am. Chem. Soc.*, **81**, 5546 (1959).

[12] F. O. Rice and M. Freamo, *ibid.*, **73**, 5529 (1951).

[13] C. V. King, *ibid.*, **62**, 379 (1940).

[14] M. van Thiel and G. C. Pimentel, *J. Chem. Phys.*, **32**, 133 (1960).

[15] NOTE ADDED IN PROOF.—An alternative explanation may be based on the observation made by us as this paper was in proof that chloramine reacts with tetramethyl-2-tetrazene in the presence of ammonia to give dimethyltriazanium chloride. In the absence of ammonia no dimethyltriazanium chloride is obtained. This reaction is under intensive investigation and will be the subject of an early communication.

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Oxidation of the (3)-1,7-Dicarba-*nido*-dodecahydroundecaborate(−1) Ion. A New Preparation of 1,3-Dicarba-*nido*-nonaborane(13)

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The selective degradation of (3)-1,7-dicarba-*nido*-dodecahydroundecaborate(−1) ion, (3)-1,7-$B_9C_2H_{12}^-$, with chromic acid produced 1,3-dicarba-*nido*-nonaborane(13), 1,3-$B_7C_2H_{13}$, in 76% yield. Previously, 1,3-$B_7C_2H_{13}$ was prepared[1] through the oxidation of 1,8-$B_9C_2H_{11}$. The oxidation of the (3)-1,7-$B_9C_2H_{12}^-$ ion may proceed through a six-electron redox reaction as shown in eq 1. The structures of the (3)-1,7-$B_9C_2H_{12}^-$

$$(3)\text{-}1,7\text{-}B_9C_2H_{12}^- + 6H_2O \longrightarrow B_7C_2H_{13} + 2B(OH)_3 + 5H^+ + 6e^- \quad (1)$$

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[1] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 869 (1968).

ion[2] and $1,3\text{-}B_7C_2H_{13}$ are shown in Figure 1. It can be clearly seen that the $1,3\text{-}B_7C_2H_{13}$ structural framework is obtained if the two boron atoms removed during the oxidation are boron atoms 4 and 8.

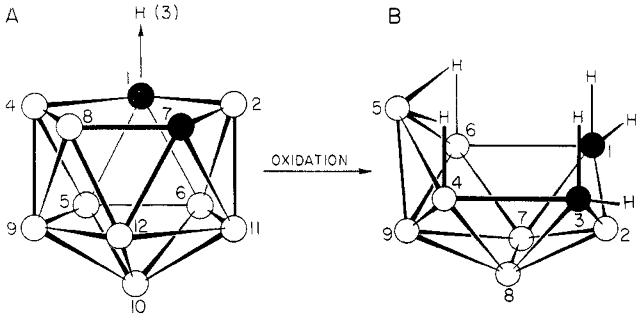

Figure 1.—(A) Structure of the $(3)\text{-}1,7\text{-}B_9C_2H_{12}^-$ ion. (B) Structure of $1,3\text{-}B_7C_2H_{13}$: ○, BH; ●, carbon.

Recently, Papetti, *et al.*,[3] developed a hot flow-tube method for accomplishing the rearrangement of $1,2\text{-}B_{10}C_2H_{12}$ to $1,7\text{-}B_{10}C_2H_{12}$. The ethanolic potassium hydroxide degradation[2] of $1,7\text{-}B_{10}C_2H_{12}$ to yield $(3)\text{-}1,7\text{-}B_9C_2H_{12}^-$ was reexamined, and it was found that the $(3)\text{-}1,7\text{-}B_9C_2H_{12}^-$ ion could be prepared in 89% yield by heating an ethanolic potassium hydroxide solution of $1,7\text{-}B_{10}C_2H_{12}$ for 40 hr at the reflux temperature. The oxidation of the $(3)\text{-}1,7\text{-}B_9C_2H_{12}^-$ ion is now the preferred method of preparing $1,3\text{-}B_7C_2H_{13}$ in this laboratory.

Experimental Section

1,7-Dicarba-*closo*-dodecaborane(12) was prepared by the method of Papetti, *et al.*[3] Methylene chloride was solvent grade and all other reagents were reagent grade and were used without further purification.

All reactions were conducted under a nitrogen atmosphere and subsequent product work-up of the $1,3\text{-}B_7C_2H_{13}$ required a nitrogen atmosphere.

Preparation of Potassium (3)-1,7-Dicarba-*nido*-dodecahydroundecaborate(−1).—Into a 1-l. flask flushed with nitrogen was placed 50 g (0.89 mol) of potassium hydroxide dissolved in 500 ml of absolute ethanol. To this solution was added 50.0 g (0.345 mol) of $1,7\text{-}B_{10}C_2H_{12}$ and the resulting solution was heated under nitrogen for 40 hr at the reflux temperature. After cooling, sufficient water (*ca.* 600 ml) was added to precipitate the unreacted carborane which was extracted from the aqueous ethanolic solution with four 150-ml portions of *n*-hexane. The *n*-hexane solution was dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness yielding 12.0 g (0.083 mol) of $1,7\text{-}B_{10}C_2H_{12}$. The aqueous ethanolic phase was evaporated to dryness and the residual solid was dissolved in 150 ml of methanol. To this methanol solution was added 90 g of powdered Dry Ice followed by 500 ml of ether with stirring. The precipitated K_2CO_3 was separated by filtration and thoroughly washed with ether; the solution was evaporated to an oil, to which an additional 500 ml of ether was added, and the remaining K_2CO_3 was separated by filtration. The ether solution was evaporated to a low volume and the product was transferred to a Dean–Stark distillation apparatus. The residual ether, alcohol, and water were distilled using toluene as the carrier. The white crystalline product was separated by filtration and dried under high vacuum for several hours yielding 40.0 g (0.232 mol) or 89% of the potassium salt based on the quantity of $1,7\text{-}B_{10}C_2H_{12}$ consumed. The product was identified by its infrared and ^{11}B nmr spectra.

Preparation of 1,3-Dicarba-*nido*-nonaborane(13).—Into a 2-l. three-necked, round-bottom flask equipped with a mechanical stirrer, addition funnel, and N_2 inlet was placed 20.0 g (0.116 mol) of $(3)\text{-}1,7\text{-}KB_9C_2H_{12}$ dissolved in 100 ml of water. To this solution was added 200 ml of methylene chloride and 200 ml of 2 *N* H_2SO_4. The resulting mixture was flushed with nitrogen and maintained at 0°. A dichromate solution consisting of 35 g (0.118 mol) of $Na_2Cr_2O_7 \cdot 2H_2O$ in 500 ml of 2 *N* H_2SO_4 was added dropwise with rapid stirring. The addition time was 2 hr. At once after complete addition, the two phases were separated and the aqueous phase was washed four times with 75-ml portions of methylene chloride. The combined methylene chloride extracts were washed once with water, dried over anhydrous magnesium sulfate, filtered, and evaporated on a mechanical pump to a low volume. The remaining solvent was removed under high vacuum on a sublimation apparatus, and the product was sublimed at 50° to a −80° cold finger. The yield was 10.1 g or 76%, and the product was identified by its infrared and ^{11}B nmr spectra.

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Decarbonylation of Molybdenum Acetyl Complexes

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The reaction of $\pi\text{-}C_5H_5Mo(CO)_3CH_3$ with triphenylphosphine in refluxing tetrahydrofuran or hexane affords mixtures of $\pi\text{-}C_5H_5Mo(CO)_2(P(C_6H_5)_3]COCH_3$ and $\pi\text{-}C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$. The σ-methyl complex appears to arise *via* decarbonylation of the acetyl derivative.[1] Similar investigations in other laboratories,[2-5] carried out with a variety of phosphorus ligands, led to other acetyl complexes of the formula $\pi\text{-}C_5H_5Mo(CO)_2(L)COCH_3$, but the decarbonylation reactions were not observed in these studies. This is apparently due to the relatively mild conditions and/or short reaction times employed; in one instance[5] the decarbonylation was purposely avoided.

We have now investigated the course of the reactions of $\pi\text{-}C_5H_5Mo(CO)_3CH_3$ with the donor ligands $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $P(OCH_3)_3$ *via* proton nmr spectroscopy. We find that the decarbonylation reactions

$$\pi\text{-}C_5H_5Mo(CO)_2(L)COCH_3 \longrightarrow \pi\text{-}C_5H_5Mo(CO)_2(L)CH_3 + CO$$

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