to a water bubbler. Helium flowed through the system at a slow rate during the course of the reaction.

A 1.5-ml sample of aniline was mixed with 10 ml of $C_2H_2Cl_4$ in the 35-ml flask and the flask was placed in an ice bath and slowly stirred with a magnetic stirrer. Once the temperature of the solution reached equilibrium with the ice bath, 1.2 ml of F_2NCO_2-*i*-C_3H_7 (1.4 g, 0.01 mole) was added all at once, and the reaction flask was left in the ice bath for 5 min. The ice bath was then removed and the reaction was allowed to proceed at ambient temperature. Mass spectral analysis at various intervals showed that the off gases consisted of HNF_2 contaminated with about 20% CO_2. The reported yields of HNF_2 were determined by bubbling the off gases through acidic iodide traps, a method employed by Haszeldine, *et al.*[17] Based on eq 2, $C_6H_5NHCO_2$-*i*-C_3H_7 was isolated in 80% yield.

Explosive Nature of Difluoramine.—Difluoramine has been known to explode violently when condensed with liquid nitrogen.[14] On rare occasions HNF_2 has been known to explode when condensed with a methylcyclohexane slush bath (−126°) as well.[18] Although no explosions occurred during the course of this study, small quantities and adequate protective precautions are advised.

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Germyl Chemistry. V. Hexamethylphosphoramide as a Solvent for the Preparation and Reaction of Alkali Metal Derivatives of Silane and Germane[1a]

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Previous workers have prepared alkali metal derivatives of SiH_4 and GeH_4 in a variety of solvents. Liquid ammonia has been used in the preparation of $NaGeH_3$ and $KGeH_3$,[2-4] ethylamine in the preparation of $LiGeH_3$,[4] and both liquid ammonia and 1,2-dimethoxyethane in the preparation of $KSiH_3$.[5-7] Each of these solvents, however, suffers from various disadvantages which have prevented the realization of the full potential of these derivatives as intermediates in the synthesis of silyl and germyl compounds. Ammonolysis reactions make the use of liquid ammonia unreliable, while the volatility of the solvent necessitates the use of special apparatus. In addition, the low temperatures which are required often tend to slow down reactions. Ethers are not sufficiently active solvents for alkali metals, and long reaction times are always necessary. Little work has been reported on the use of amines as solvents, but it seems that, even here, solvolysis reactions often complicate the preparations.[4]

We have investigated the use of the aprotic solvent hexamethylphosphoramide, $[(CH_3)_2N]_3PO$ (HMPA), for the preparation and reaction of sodium and potassium derivatives of SiH_4 and GeH_4. This solvent is involatile and moderately inert chemically. It is reported to dissolve alkali metals to concentrations of 1 *M*, giving blue solutions which are stable over a period of a few hours at or below room temperature.[8] It also appears to dissolve certain alkali halides (notably LiCl) to give conducting solutions.[9]

We find that both SiH_4 and GeH_4 react rapidly with solutions of sodium or potassium in HMPA to give a permanent gas (presumed to be hydrogen) and a pale yellow solution. The amount of SiH_4 or GeH_4 taken up corresponds to the reaction

$$\text{Na (or K)} + MH_4\,(M = \text{Si or Ge}) \longrightarrow \text{Na}^+ \text{(or K}^+\text{)} + MH_3^- + 0.5H_2 \quad (1)$$

Potassium was used for most of the reactions, since it dissolved more rapidly than did sodium. When SiH_4 was used, the final solution had a deeper yellow color than when GeH_4 was used. In no case was evidence obtained for reaction of SiH_4 or GeH_4 with 2 equiv of alkali metal, as is observed in the reaction of sodium with GeH_4 in liquid ammonia.[2]

The over-all yield of alkali metal derivative could not be determined directly. The solvent is effectively involatile at room temperature, and the salts remain soluble even on addition of 10 parts of xylene to 1 part of solution. The solutions were therefore treated with alkyl halides to give alkyl derivatives of SiH_4 and GeH_4.

$$RX + MH_3^- \longrightarrow RMH_3 + X^- \quad (2)$$

Alkyl halides used were CH_3I, C_2H_5Br, and CH_3OCH_2Cl. For the chloride and bromide derivatives, a white precipitate formed, presumably the sodium or potassium halide. For the iodide, no precipitate was formed when potassium was used. This implies that KI, at the concentrations employed, is soluble in HMPA. The alkylsilanes and -germanes were isolated by distillation from the reaction vessel and low-temperature vacuum fractionation. The purity and overall yield of the products were determined by gas chromatography. Identification was made by gas chromatographic retention times and infrared data.[10-14] The usual impurities observed were the excess of alkyl halide added, together with SiH_4 or GeH_4 as appropri-

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ate. The mechanism for the formation of SiH_4 or GeH_4 is unknown; no evidence for production of these compounds *before* the addition of alkyl halides was observed.

This work has led to the preparation of CH_3, C_2H_5, and CH_3OCH_2 derivatives of SiH_4 and GeH_4 in good yields, as shown in Table I. An investigation of the relative merits of lithium, sodium, and potassium for the reactions leading to $CH_3OCH_2GeH_3$ showed that the use of lighter alkali metals resulted in lower yields (Li, 9%; Na, 19%; K, 41%). This may, in part, be ascribed to the slower dissolution of sodium and lithium in HMPA, which could lead to more extensive decomposition of the GeH_3^- ion. It is also possible that the stability of the GeH_3^- (and SiH_3^-) ion in solution is dependent upon the nature of the counterion.

TABLE I

ALKYLSILANES AND -GERMANES SYNTHESIZED FROM HMPA SOLUTIONS OF POTASSIUM SILYL AND POTASSIUM GERMYL

Compd	% yield	Retention time,[a] min
CH_3GeH_3	94	3.70[b]
$C_2H_5GeH_3$	65	8.30[b]
$CH_3OCH_2GeH_3$	41	26.40[c]
CH_3SiH_3	90	2.51[b]
$C_2H_5SiH_3$	70	4.75[b]
$CH_3OCH_2SiH_3$	22	13.13[c]

[a] Column temperature, 30°; He flow rate, 100 cc min^{-1}; sample introduced through a commercial gas-sampling valve. [b] Column used was $^1/_4$ in. × 15 ft of 20% squalane on 60–80 Chromosorb W. [c] Column used was $^3/_8$ in. × 20 ft of 20% Carbowax 400 on 60–80 Chromosorb W.

Further work is planned both on spectroscopic studies and preparative reactions involving the solutions of alkali metal derivatives of the group IV hydrides in HMPA.

Experimental Section

All manipulations of volatile compounds were carried out in a Pyrex glass vacuum system of conventional design. Stopcocks were lubricated with Apiezon hydrocarbon greases in preference to fluorocarbon greases which were found to be attacked by alkali metal solutions. Alkali metals were weighed under xylene and pressed into thin plates before reaction. HMPA (Fisher) was dried and stored over 4A molecular sieves. SiH_4 and GeH_4 were prepared by well-known methods.[15,16] Alkyl halides were commercial products, used as received. The vapor-phase chromatography was carried out on a Varian-Wilkins Aerograph A90-P3 gas chromatograph.

Preparative Reactions.—A typical preparation will be described in some detail since variations in technique can result in very low yields. For the other compounds studied, similar procedures were used with suitable adjustment of quantities.

Preparation of CH_3GeH_3.—HMPA (10 ml) was degassed, first at room temperature and then at ~110° (reflux temperature) under ~10^{-4} torr. The reaction vessel was then cooled to about 10°. Potassium (90 mg, 2.30 mmoles) was added and the vessel was rapidly reevacuated. The metal began to dissolve at once to give a blue solution. When the vessel was completely evacuated, GeH_4 (2.76 mmoles) was condensed into a side arm and allowed to expand into the entire vessel. On stirring or shaking, a rapid reaction occurred and the potassium completely dissolved in ~15 min. The solution at this stage was a very pale yellow (an orange or green tint at this stage indicates decomposition of the anion or solvent, respectively). The volatile matter [permanent gas + excess GeH_4 (0.45 mmole)] was removed and CH_3I (2.45 mmoles) was added. This reacted rapidly with the yellow solution with effervescence; no precipitate was formed and the solution became colorless. The volatile products (2.37 mmoles) were removed after 10 min. This material was fractionated under vacuum at −120° to remove excess CH_3I and finally was analyzed by gas chromatography. The product was found to contain 2.16 mmoles of CH_3GeH_3. (An independent sample of CH_3GeH_3 was synthesized from CH_3GeCl_3 and $LiAlH_4$ for the retention time comparison.) The yield of CH_3GeH_3 based on the potassium used (or GeH_4 used) was 94%.

The solutions should be kept below room temperature at all times, especially during dissolution of the alkali metal. Failure to observe this precaution results in attack on the solvent and evolution of volatile matter thought to contain $(CH_3)_2NH$. The characteristic deep blue color of the alkali metal solution is replaced by a dirty brown color in this case.

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The Iodine–Valeronitrile Charge-Transfer Complex

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Various attempts have been made to correlate the stabilities of the complexes formed between iodine and different organic bases with empirical parameters such as the Hammett σ and the Taft σ^* values. Drago, Wenz, and Carlson[1] have shown that ΔH° values for complexes of iodine with N,N-dimethylamides can be correlated with σ^* values. However, these investigators noted that deviations were encountered when the equilibrium formation constants were compared with σ^* values. Arzamanova and Gur'yanova,[2] in an investigation of the complexes of iodine with amines, ethers, and sulfides, have found a relationship between the heats of formation and the dipole moments of the intermolecular bonds. Person, Golton, and Popov[3] have determined the equilibrium constants and ΔH° and ΔS° values for some of the complexes formed between the Lewis acids ICl, IBr, and I_2 and the bases acetonitrile and mono- and dichloro-substituted acetonitriles.

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