Thus, decomposition of the sodium salt of I gave MCP containing d_0, d_1, and, unexpectedly, d_2 species (23, 55, and 22%, respectively). The occurrence of d_0 and d_1 products clearly shows that MCP is formed by competitive processes and the presence of d_2 products shows that hydrogen–deuterium exchange is also involved in these reactions.[9] Thus, in ethylene glycol-d_2 the extent of concomitant carbenic (<27%) and cationic (>73%) participation leading to MCP was estimated by comparing the deuterium contents of the MCP and 1-butene. However, the extent of carbenic and cationic pathways leading to all hydrocarbon products was approximately 0.035 and 0.96, respectively.

Similar results were obtained when 2,2-dimethylpropanal tosylhydrazone (II) anion was decomposed in that the formation of 1,1-dimethylcyclopropane decreased and 2-methyl-1-butene increased[7] with increasing solvent protonicity (Table I). Since the neopentyl cation or diazonium ion affords dimethylcyclopropane to only a minor extent (<1%) while it is a major product (>95%) from *t*-butylcarbene the extent of concomitant carbenic and cationic modes of decomposition occurring in various solvents can be directly determined by product analysis.[10] Thus, for example, in diethyl Carbitol, the carbenoid fraction is 0.98, in hexanol 0.89, in ethyl Cellosolve 0.50, and in ethylene glycol 0.02.[11]

(9) A small portion of the d_0 product comes from protonation with protium in the solvent, protium formed in neutralization of the tosylhydrazone, and protium generated *via* the processes outlined in Scheme I.

(10) The carbenoid fraction is the amount of dimethylcyclopropane plus that portion of 2-methyl-2-butene arising *via* the carbenoid route. The latter is estimated (by difference) from the cationic ratio (2-methyl-1-butene/2-methyl-2-butene, ~1.1–1.25) which was obtained by solvolysis of neopentyl tosylate or diazotization of neopentylamine at conditions comparable to the tosylhydrazone decomposition reaction conditions. For results of thermolysis of diazoneohexane in various solvents see W. Kirmse and K. Horn, *Chem. Ber.*, **100**, 2698 (1967).

(11) (a) Diazoalkanes derived from I and II respond similarly to protonicity in the solvents studied; with more highly hindered diazo compounds the ability of a given protic solvent to effect cationic decomposition is considerably lessened. Lowering the reaction temperature or the amount of base in a proton–donor solvent enhances decomposition of a tosylhydrazone by a cationic route. (b) Cationic decomposition of a diazo compound generated *in situ* may be frequently effected in aprotic solvents by using insufficient base to neutralize the parent tosylhydrazone. The protonicity of such systems is controlled by the stoichiometric ratio of the base and the tosylhydrazone.

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Reexamination of the Reactions of Triethyl- and Trimethylboron with Sodium and Potassium in Liquid Ammonia

Sir:

Smith and Kraus[1] reported that trimethylboron is quantitatively reduced by sodium in liquid ammonia according to the equation

$$(CH_3)_3B + NH_3 + Na \longrightarrow (CH_3)_3BNH_2Na + 0.5H_2 \qquad (1)$$

These investigators suggested that the metal replaces a hydrogen in the coordination compound $(CH_3)_3BNH_3$. Later, Holliday and Thompson[2] mixed trimethylboron with potassium metal in liquid ammonia and obtained the salt $(CH_3)_3BNH_2K$ and approximately 0.5 mole of hydrogen gas per g-atom of potassium metal upon complete decolorization of the solution.

The object of the present study was to suggest a mechanism for the reaction

$$R_3B + NH_3 + M \longrightarrow R_3BNH_2M + 0.5H_2 \qquad (2)$$

where R = methyl or ethyl and M = sodium or potassium. The reactions of trimethyl- and triethylboron with sodium and potassium in liquid ammonia were studied conductometrically in a closed system. Either a high-precision ac bridge, similar to that described elsewhere,[3] or a Wayne Kerr Universal bridge B221A was used in conductance measurements. The conductance measurements were made in a Pyrex vessel which had pinpoint tungsten or platinum electrodes sealed into a side arm and a calibrated bulb for volume determination. Triethylboron (K and K Laboratories, Inc.) was first degassed by two high-vacuum distillations and then distilled onto a sodium mirror. Next it was distilled off the sodium into a tared tube containing a break-seal. Trimethylboron was prepared following the procedure described by Brown.[4] Trimethylboron was also distilled off a sodium mirror and stored in glass ampoules on the high-vacuum line. The freezing points of both triethyl- and trimethylboron agreed with reported values.[5] Using the ideal gas law, a molecular weight of 58 was obtained for trimethylboron. Ammonia (Matheson) was purified by a method described elsewhere.[6]

A run consisted of distilling sodium or potassium metal from another side arm into the reaction vessel which had been previously evacuated to pressures of less than 5×10^{-6} torr after flaming. The ammonia was then distilled into the reaction vessel. In the case of triethylboron studies, the reaction vessel was removed from the high-vacuum line, transferred to a refrigerated bath at −34°, and allowed to come to thermal equilibrium. The initial resistance of the solution was measured, and then the break-seal containing the triethylboron was broken with a glass-encased magnet. The resistance was subsequently followed with time. When trimethylboron was used, the frozen metal–ammonia solution with trimethylboron condensed on its surface was transferred directly to the bath, thawed, agitated, and allowed to reach thermal equilibrium. The resistance was then followed as a function of time. In all runs the concentration of alkali metal was less than that of the alkylboron so that the end of the reaction could be determined visually by the disappearance of the blue color. Finally, the metal concentrations were determined by addition of ammonium bromide to the metal solution which resulted in the reaction

$$NH_4^+ + M \longrightarrow NH_3 + M^+ + 0.5H_2 \qquad (3)$$

The total hydrogen evolved was pumped into the gas buret, and its volume and pressure were measured.

The results of this study are summarized in Table I.

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(1) J. E. Smith and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 2751 (1951).

(2) A. K. Holliday and N. R. Thompson, *J. Chem. Soc.*, 2695 (1960).

(3) G. E. Smith, Ph.D. Thesis, Michigan State University, 1963.

(4) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

(5) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 50.

(6) D. F. Burow and J. J. Lagowski in "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 125.

Table I. Results of Trialkylboron Studies

Run no.	Metal	Concentration, *M*		Contact time, days	% metal reacted/24 hr
		Initial metal	Initial trialkylboron		
85A	K	3.0×10^{-3}	5.2×10^{-2a}	7	5.8
74A	Na	9.0×10^{-3}	7.3×10^{-2a}	19	5.3
47A	Na	1.6×10^{-2c}	1.6×10^{-1b}	25	3.2
9D	K	4.3×10^{-2d}	1.5×10^{-1b}	7	3.4
7A	Na	2.1×10^{-2c}	7.8×10^{-2b}	31	. . .[e]
91A	Na	3.6×10^{-2d}	4.2×10^{-2b}	8	0.9

[a] Trimethylboron. [b] Triethylboron. [c] Estimated from conductance. [d] Determined from hydrogen evolution. [e] Not estimated but solution was not faded.

Using conductance data reported by Kraus[7] and Smith,[3] concentration *vs.* time data were calculated. In all of the studies, metal concentration *vs.* time plots yielded straight lines indicating zero-order kinetics.

It can be seen in Table I that a minimum of 0.85% to a maximum of 5.8% of metal reacted per day in any run. Only in run 74A did the solution completely decolorize, indicating complete reaction of the metal, after 19 days. In all other runs the solutions remained blue for the contact times listed in Table I, at the conclusion of which the runs were terminated. An attempt was made following run 91A to recover the unreacted triethylboron as follows. After 8 days, the run was discontinued and the ammonia was distilled out of the reaction vessel through an acetone–Dry Ice trap and condensed in a liquid nitrogen trap. The triethylboron which remained in the reaction vessel and acetone–Dry Ice trap was next distilled into a tared vial which was sealed off and reweighed. (An interesting observation was made during this distillation. The mixture of unreacted triethylboron and sodium took on a red color while warming upon melting of the sodium. The red color faded after several minutes. A red flash was observed in another run when the reaction vessel was heated with a flame, and again the red color faded only slowly. It seems that the red color may be due to a sodium complex, but its nature was not investigated.) From a 0.199-g sample of triethylboron, 0.171 g was recovered after a single distillation. The recovery of 86% of the starting compound after 8 days indicates that little, if any, reaction had occurred according to eq 2.

To compare our results with those of Smith and Kraus[1] and Holliday and Thompson,[2] we might first point out that Smith and Kraus also reported that trimethylboron reacts with sodium amide in liquid ammonia according to the equation

$$(CH_3)_3BNH_3 + NaNH_2 \longrightarrow (CH_3)_3BNH_2Na + NH_3 \quad (4)$$

In the experiment reported by Holliday and Thompson,[2] a large excess of potassium was used and the amount of hydrogen obtained was in agreement with eq 5,

$$M + NH_3 \longrightarrow MNH_2 + 0.5H_2 \quad (5)$$

in which M is an alkali metal. On the other hand, in studying reaction 1, Smith and Kraus[1] used equivalent amounts of sodium and trimethylboron. Under these conditions, the hydrogen obtained will be in agreement with both eq 1 and 5. Furthermore, it has been shown that carefully prepared alkali metal–ammonia solutions are stable for up to several months[6] and decompose only slowly according to eq 5 which is autocatalytic,[8] while an unstable alkali metal–ammonia solution rapidly produces amide ions.[8,9]

In our experiments, excess amounts of trimethylboron or triethylboron failed in all cases but one to bleach metal-ammonia solutions even after long contact periods, and concentration *vs.* time data could be best fitted to zero-order kinetics. We conclude, therefore, that the mechanism for reaction 2 is eq 5 and 4, the rate depending on the stability of the solution to reaction 5, and that the ammonia coordination compounds of both trimethyl- and triethylboron are not reduced by sodium and potassium in liquid ammonia.

Acknowledgment. This work was supported by the National Science Foundation. The authors thank Mr. Norder for his cooperation.

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(7) C. A. Kraus, *J. Am. Chem. Soc.*, **43**, 749 (1921).

(8) R. E. Cuthrell and J. J. Lagowski, *J. Phys. Chem.*, 71, 1928 (1967).

(9) W. L. Jolly and C. J. Hallada in "Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965, p 37.

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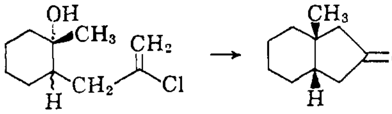
Intermediates for 16-Keto and A-Nor Steroids and Derivatives

Sir:

In our initial studies of cycloalkanone formation by intramolecular cyclization of β-chloroallyl groups with electrophilic centers, we succeeded in obtaining *cis*-8-methyl-2-hydrindanone.[1] This fact suggested that 2-(β-chloroallyl)-1-tetralones could provide tricyclic ketones of potential utility in total synthesis of natural products such as 16-keto steroids and A-nor steroids containing *cis*-ring fusions in the hydrindanone portion of the molecule. Using 5- or 6-methoxy-1-tetralones (to allow further elaboration of cyclohexenones obtainable by Birch reduction) and introducing angular methyl groups (potentially C_{18} and C_{19}) by enolate alkylation (route a) or Grignard addition (route b), the following possibilities present themselves. We now wish to report that such synthetic sequences can be carried out in good over-all yield[2] beginning with commercially available 1-tetralones[3] when proper conditions are chosen for the crucial final cyclization.[4]



Monoalkylation of tetralones I and II was accomplished efficiently by using methylmagnesium carbonate[5] and 2,3-dichloropropene in dimethylformamide to

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(1) P. T. Lansbury and E. J. Nienhouse, *J. Am. Chem. Soc.*, **88**, 4290 (1966).

(2) All compounds gave satisfactory elemental analyses and consistent spectral properties (infrared, ultraviolet, and nmr).

(3) The routes described herein are considerably better than those conceivable beginning with 2-tetralones, which are also more costly.

(4) Reaction of VI and VII with acid can lead to simple dehydration (from VI) and/or hydrolysis of the β-chloroallyl group to an *uncyclized* acetone derivative. It appears that such compounds can be partially converted to tricyclic ketones VIII and IX, which may be the thermodynamic products (P. T. Lansbury and F. R. Hilfiker, unpublished observations).

(5) M. Stiles, *J. Am. Chem. Soc.*, **81**, 2598 (1959).