REACTIONS OF ORGANIC AND ORGANOMETALLIC COMPOUNDS WITH SOLUTIONS OF METALS IN LIQUID AMMONIA[1]

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[1] This is the second of two papers concerned with reactions of solutions of metals in liquid ammonia; the first paper was confined to a discussion of reactions of inorganic substances (410). The objectives as well as the organization of the two papers are substantially the same.

I. INTRODUCTION

By comparison with the available information concerning the reactions of inorganic substances, that relating to reactions of organic and organometallic compounds with solutions of metals in ammonia is certainly far more extensive. At the same time, most of the latter information is of a qualitative character. This situation arises in part because of the inherently greater complexity of the reactions involved, but also because most of the reactions have been carried out with the sole objective of producing a particular end-product. Relatively less attention has been directed toward problems such as reaction mechanisms and the identification of intermediates, the identification of by-products, the dependence of yield upon process variables, etc. It is indeed unfortunate that in the course of studies conducted solely for purposes of synthesis, much additional valuable information has failed to accrue because relatively simple and well-known techniques were not utilized to full advantage.

As a medium for the study of the reduction of organic and organometallic compounds, liquid ammonia offers almost limitless possibilities and certain distinct advantages (20). In its solvent capacity for organic substances, ammonia is similar to the lower alcohols (56, 118) and is in fact a far better solvent for organic than for inorganic materials. Although solutions of the alkali and alkaline earth metals have been used most commonly, one is by no means limited to these reducing systems. Reductions effected by hydrogen liberated *in situ* by the interaction of alkali metal and a source of active hydrogen such as alcohol, ammonium ion, etc. exhibit considerable selectivity and promise to be of broad applicability. Also, the potentialities of liquid ammonia solutions of intermetallic compounds as reducing agents represent an almost totally unexplored area. Much remains to be learned about the role of diluents such as toluene, ether, and amines (95, 392, 420, 444). These diluents or cosolvents not only alter solubility relationships and rates of reaction but in some cases appear also to exert directive influences upon the course of reactions.

For convenience, the reactions of solutions of metals with organic and organometallic compounds may be classified roughly as follows:

A. Displacement of an equilibrium involving an organic compound, the solvent, and an ammonium salt

Reactions of this type have been discussed elsewhere (410). Whenever a substance is ammonolyzed to form even a small amount of an ammonium salt,

$$RX + 2NH_3 \rightleftharpoons RNH_2 + (NH_4)^+X^-$$

the resulting equilibrium may be displaced completely to the right by removing the ammonium ion through reaction with a metal solution:

$$(NH)_4^+ + e^- \rightarrow NH_3 + \tfrac{1}{2}H_2$$

B. Displacement of hydrogen

Many of the reactions of organic compounds with solutions of metals are simply those of displacement (by a metal) of active hydrogen, with resultant formation of salts,

$$RH + e^- \rightarrow R^- + \tfrac{1}{2}H_2$$

which may undergo ammonolysis, particlarly at elevated temperatures:

$$R^- + NH_3 \rightarrow RH + NH_2^-$$

The hydrogen is not always liberated in molecular form, however, and some or all of it may serve to reduce a portion of the original compound. Among compounds that exhibit this behavior are (410) acetylene, monosubstituted acetylenes, acid amides, esters of carboxylic acids, indole, carbazole, and possibly unsaturated alcohols. In view of the fact that there are thus two reducing agents present in such solutions, the ammoniated electron and *nascent*[2] hydrogen, it becomes desirable to conduct experiments that will distinguish between the reactions due to the two reductants and determine if and when hydrogen may be expected to reduce (hydrogenate) a compound that is not reduced by the metal (electrons). While these questions have been answered only in part, they have assumed greater importance because it has been shown that many compounds which do not contain active hydrogen are reduced by hydrogen generated *in situ* to a greater extent than by the metal solution alone. This situation has been clearly demonstrated by Wooster (435, 437), and substantiated by Smith and coworkers (136), Fernelius and coworkers (55, 108, 110, 113), and Watt and coworkers (226, 227, 412).

Because *nascent* hydrogen has not always been recognized as a possible reducing agent in liquid ammonia solutions of metals, it is frequently not possible to state when reading the literature whether the reduction products were obtained by an electron reduction or by a hydrogen reduction. The possibility that hydrogen reductions *may* have played an important role in much of the published work is inherent in the techniques used by many investigators. Whenever a reaction of a solution of a metal is carried out in an open vessel, more or less moisture condenses from the atmosphere and reacts to liberate hydrogen. Further, it has become customary practice, even when working in a closed system, to add an excess of metal and later destroy this excess by treatment with water, alcohol, or an ammonium salt. If for a particular reaction hydrogen is a more effective reducing agent than the electron, one may desire either the inter-

[2] Use here of the term *nascent* is intended to imply only the presence of hydrogen that exhibits reactions not characteristic of molecular hydrogen under the same experimental conditions.

mediate product (electron reduction) or the more highly reduced product (hydrogen reduction) and hence would modify the procedure accordingly. While many useful preparations may be conducted in open vessels, it is strongly recommended that, before carrying out a large-scale reaction in an open vessel, the *stoichiometry* of the reaction be established on a small scale in a closed system and that the large-scale operation be governed by the findings of the closed-system study. The latter type of study furnishes the following information:

(*1*) *Ratio of gram-atoms of metal to moles of compound in initial reaction:* When the products of reaction are not strongly colored this ratio can be obtained very accurately by determining, for a given weight of compound, the weight of sodium required *just* to impart a permanent blue color to the solution.

(*2*) *Ratio of gram-atoms of hydrogen liberated to moles of compound in the initial reaction:* In case the compound contains no active hydrogen, no hydrogen is liberated. If the hydrogen liberated *does not* reduce the compound, then the above ratio indicates the number of replaceable hydrogens.

(*3*) *Ratio of gram-atoms of hydrogen absorbed to moles of compound in secondary reaction:* Here an excess of alkali metal is added to the reaction mixture and treated with an ammonium salt (or other substance to liberate hydrogen), or the order of addition may be reversed, and the amount of hydrogen absorbed taken as the *difference* between the amount of gaseous hydrogen calculated on the basis of metal added and the amount actually obtained.

(*4*) *Ratio of gram-atoms of metal to moles of a metal salt of the compound:* By first treating a compound containing active hydrogen with an alkali metal and then treating the resulting metal *salt* with alkali metal, one has evidence to show whether the reducing agent in the initial reaction is hydrogen or the electron (108).

(*5*) *Effect of an excess of alkali metal on the initial reaction:* The problem here is to destroy the excess of metal *without generating hydrogen.* Although the excess metal might be extracted by added mercury or converted to insoluble sodium sulfide by adding sulfur, the resulting materials are still reducing in character and might cause complications. Excess alkali metal may be removed by adding sodium nitrate (ammonium nitrate is satisfactory if *not* added in excess) to form M_2NO_2 and then destroying this compound by adding ammonium bromide (55); the resulting products are not reducing agents. Still another possibility involves the addition of sodium bromate and elimination of sodium, for example, in accordance with the reaction (111),

$$NaBrO_3 + 6Na + 3NH_3 \rightarrow NaBr + 3NaOH + 3NaNH_2$$

but the utility of this method is likely to be limited in many instances because of the insolubility of the resulting sodium hydroxide.

(*6*) *Whether or not there is any ammonia vapor-distillation of the reactants or products:* This is an important factor in only a few cases.

While information of the type outlined above is extremely useful in interpreting reactions of solutions of metals, it does not furnish answers to all of the questions that arise. For example, no one has yet devised an apparatus suitable for obtaining similar information for reactions at temperatures above the normal

boiling point of ammonia. Where the reactants have been placed in bombs or autoclaves and allowed to stand for some time, it is reasonable to suppose that the hydrogen liberated in the reaction

$$Na + NH_3 \rightarrow NaNH_2 + \tfrac{1}{2}H_2$$

is at least partially responsible for the reduction observed. The rate of amide formation is usually slow in organic reductions at −33.5°C. but becomes appreciably rapid at higher temperatures, especially because it is autocatalytic.

A hydrogenation system which is very similar to that of solutions of metals in liquid ammonia is the solid calcium hexammoniate, $Ca(NH_3)_6$. Upon decomposition it liberates hydrogen,

$$Ca(NH_3)_6 \rightarrow Ca(NH_2)_2 + 4NH_3 + H_2$$

which effects hydrogenations of very much the same type as those effected by hydrogen liberated in ammonia (54, 100, 213, 214, 215, 216, 221). Although this reducing system has not been investigated thoroughly, it may well possess certain advantages over solutions, since it can be used readily at room temperature and does not necessitate *liquid* ammonia.

C. Metal addition

There are several cases in which the electron apparently adds directly to a molecule or ion. Such a reaction is encountered in the electrolysis of tetrasubstituted ammonium salts:

$$R_4N^+ + e^- \rightarrow R_4N$$

For solutions of metals, these reactions are usually of two types.

(*1*) *Addition to multiple bonds:* Addition of electrons to a double bond, for example, would be expected to result in the formation of a doubly charged anion,

$$R_{n-1}A{=}AR_{n-1} + 2e^- \rightarrow [R_{n-1}A{-}AR_{n-1}]^{--}$$

where n is the valence of element A. Ions of this general type may be stable under the experimental conditions involved or they may be partially or completely ammonolyzed. Such reactions are known for C=C (phenyl-substituted ethylenes, higher benzenoid hydrocarbons, etc.), C≡C, C=O, C=N, C≡N, N=O, N=N, Ge=Ge, and Sn—Sn. Here again the information available is meager, since all of the possibilities have not been fully studied. In a few instances only one electron adds at a double bond and this leads to either a dimerization of the primary reduction product,

$$2CH_3CH{=}NC_2H_5 \rightarrow 2CH_3\underset{|}{C}HNHC_2H_5 \rightarrow CH_3CH(NHC_2H_5)CH(NHC_2H_5)CH_3$$

or the formation of a compound containing an element in an unusual oxidation state:

$$(C_6H_5)_2CO \rightarrow [(C_6H_5)_2CO]^- \quad \text{(metal ketyl)}$$

(2) *Addition to free groups:* Most of the free radicals thus far studied react with electrons to form ions. For example, R_3C, R_3Si, R_3Ge, and R_3Sn form singly charged anions and R_2Ge and R_2Sn form doubly charged anions. In the latter cases, a single equivalent of an alkali metal produces the anions $[R_2Ge—GeR_2]^{--}$ and $[R_2Sn—SnR_2]^{--}$. Investigations by Selwood and coworkers (312, 335, 362) clearly demonstrate that compounds of the empirical formulas given are not free groups but hexasubstituted metalloethanes. Reactions of these materials in liquid ammonia may be interpreted equally well with either formulation.

D. Bond rupture

In numerous instances the reducing action of a metal solution involves the rupture of a bond between two atoms and the combination of an electron with each of the resulting fragments, thus:

$$R_{n-1}A—A'R'_{n'-1} + 2e^- \rightarrow [R_{n-1}A]^- + [R'_{n'-1}A']^-$$

where n is the valence of element A. Some ions (e.g., methide and ethide) formed in this manner are not stable under the experimental conditions and are ammonolyzed:

$$CH_3^- + NH_3 \rightarrow CH_4 + NH_2^-$$

Instances of such bond rupture are known for the following: C—C, Si—Si (?), Ge—Ge, Sn—Sn, Pb—Pb, C—Si (?), C—Ge, C—Sn, C—Pb, Si—Ge, Si—Sn, C—O, Ge—O, Sn—O, C—N, C—Bi, Sn—N, S—S, N—N, C—S, C—Hg, and C—X (where X is a halogen). Undoubtedly further investigations will disclose more types.

E. Removal of halogen

The reactions of solutions of metals with halogen compounds are essentially bond ruptures but for convenience may better be considered separately. According to the general equation given above one would expect the following reaction to take place with organic halides:

$$RX + 2e^- \rightarrow R^- + X^-$$

In cases where the organic radical R is capable of existence as a free group, the following reaction takes place,

$$RX + e^- \rightarrow R + X^-$$

and further action may convert the free group into an ion:

$$R + e^- \rightarrow R^-$$

Thus there are likely to be present during the reduction of a halogen compound both negative organic ions and free groups in addition to the reactants and halide ions. Frequently the ions are unstable and ammonolyze, thus introducing amide ion into the system. Organic halogen compounds are usually reactive toward the amide ion to form either unsaturated hydrocarbons or amines. The

latter and certain of the former react with metals to form salts and these in turn may react with the original halogen compound. The more reactive of the free groups may react either with the solvent or with themselves (Wurtz–Fittig synthesis). Accordingly, it is easy to see that reduction of this type of organic compound may become exceedingly complex and it is fortunate that this does not happen often. It is nevertheless essential to examine all possibilities in order to learn just what is taking place during the course of the reaction. There are two known cases in which a hydrocarbon radical isomerizes in the formation of an ion.

F. Removal of other elements

There are only a few examples of the removal of oxygen from organic combination by solutions of metals in ammonia; these include nitrobenzene, nitronaphthalene, nitrofluorene, and azoxybenzene. Removal of oxygen results in the formation of sodium oxide, which is ammonolyzed to an equimolar mixture of sodium hydroxide and sodium amide (410). The reduction of sulfur in organic combination to sulfide has been studied somewhat more extensively and is discussed in detail elsewhere (see Section XIII).

G. Catalysis by solutions of metals

Catalytic effects have been observed in only a few cases (e.g., the interaction of triethylsilane and ethylamine, and the polymerization of styrene) and do not appear to be a factor of major importance in the study of reactions of solutions of metals with organic materials.

II. HYDROCARBONS

Although studies of reactions of hydrocarbons with solutions of metals have been limited to a relatively small number of compounds, the reactions that have been observed fall within the scope of the types of reaction outlined above. As will be shown later, these studies have brought to light numerous reactions that are useful in processes of synthesis.

A. Saturated hydrocarbons

There is no evidence for any reaction between a saturated hydrocarbon and a solution of a metal, nor is there any reason on the basis of known reactions in liquid ammonia to anticipate any such reaction. It is commonly possible, however, to take advantage of this lack of reactivity and use solutions of metals in ammonia to remove reducible impurities from saturated hydrocarbons.

B. Phenyl-substituted saturated hydrocarbons

Diphenylmethane reacts slowly and incompletely with a liquid ammonia solution of sodium at room temperature to afford some of the sodium salt (277), which is known to undergo oxidation in accordance with the equation (434):

$$2(C_6H_5)_2CHNa + O_2 \rightarrow Na_2O_2 + (C_6H_5)_2CHCH(C_6H_5)_2$$

Diphenylmethane gives a blue color with calcium and the product yields a small quantity of an unsaturated hydrocarbon (191).

Sodium or potassium in ammonia at −33.5°C. directly displaces hydrogen from triphenylmethane (233, 246, 253, 260),

$$(C_6H_5)_3CH + Na \rightarrow (C_6H_5)_3CNa + \tfrac{1}{2}H_2$$

although the reactions occur slowly and the pure alkali salts may be obtained more readily by using the alkali amides (14, 434). Barium reacts with triphenylmethane to give only traces of the barium salt (140).

p-Benzohydryltetraphenylmethane, $(C_6H_5)_2CHC_6H_4C(C_6H_5)_3$, is stable in the presence of sodium in ammonia (364). Wooster and Mitchell (440) have studied the action of potassium in liquid ammonia at −33.5°C. upon phenyl-substituted methanes and ethanes. They observed no reaction with $C_6H_5CH_3$, $(C_6H_5)_4C$, $C_6H_5CH_2CH_3$, and $C_6H_5CH_2CH_2C_6H_5$; slight reaction with $(C_6H_5)_3CCH_3$ and $(C_6H_5)_3CCH_2C_6H_5$; and formation of intense red or orange-yellow alkali salts with $(C_6H_5)_2CH_2$, $(C_6H_5)_3CH$, $(C_6H_5)_2CHCH_2C_6H_5$, and $(C_6H_5)_2CHCH(C_6H_5)_2$. Under similar conditions potassium ruptures a carbon–carbon bond in $(C_6H_5)_3CC(C_6H_5)_3$; the free radical reacts further to form alkali triphenylmethide (246).

The alkali metal salts of hydrocarbons react readily with alkyl and aryl halides and are thus useful reagents in synthesis.

C. Ethylenic hydrocarbons

The simple ethylenic hydrocarbons are not reactive toward solutions of metals in liquid ammonia, e.g., amylene (276), 1-heptene, *cis*-5-decene, *trans*-5-decene (53), and cyclohexene (448). Butadiene and sodium in liquid ammonia give butene and octadiene (191). The interaction of isoprene and sodium in ammonia at −33.5°C. provides a 60 per cent yield of 2-methyl-2-butene, together with high-molecular-weight hydrocarbons. The 2-methyl-2-butene is not further reduced by an excess of sodium in ammonia (300). Alloöcimene, $(CH_3)_2C{=}CHCH{=}CHC(CH_3){=}CHCH_3$, added to sodium in liquid ammonia yields 2,6-dimethyl-3,5-octadiene (102).

D. Phenyl-substituted ethylenic hydrocarbons

The reduction of a number of phenyl-substituted olefins with solutions of metals in ammonia has been studied. The results summarized in table 1, unless otherwise noted, correspond to reactions conducted at −33.5°C. Wooster and Ryan (444) have examined carefully the results of work on the reduction of phenyl-substituted ethylenic hydrocarbons, simple ethylenic hydrocarbons, and phenyl-substituted saturated hydrocarbons. They have pointed out that the following types of reactions are involved: (*1*) displacement of hydrogen, (*2*) addition to a double bond, (*3*) polymerization, (*4*) dimerization, (*5*) cleavage of carbon–carbon bonds, and (*6*) addition to but one of two double bonds in a molecule. In the case of derivatives of saturated hydrocarbons, reaction takes place to any considerable extent when, and only when, the compound contains the benzohydryl group, $(C_6H_5)_2CH$—. Many of the organoalkali compounds that

TABLE 1

Reactions of phenyl-substituted ethylenic hydrocarbons with solutions of metals in liquid ammonia

(R = C_6H_5; M = Na or K)

COMPOUND	METAL	PRODUCTS REPORTED[a]	NOTES	REFERENCES
$RCH{=}CH_2$	Na	RC_2H_5 (50%), styrene polymers, $NaNH_2$	1.34, 1.38 equivalents of sodium; slow reaction	(274, 277, 444)
$R_2C{=}CH_2$	Na	R_2CHCH_3 (I) (67%); $R_2CHCH_2CH_2$-CHR_2 (II) (17%)	Color discharged with NH_4Cl	(140)
	Ca	I (45%)		(140)
		I (45%), II (14%)	Excess calcium	(140)
		I (20%), II (14%)		(140)
	Ba	I (70%), II (35%)		(140)
$RCH{=}CHR$	Na, K	RCH_2CH_2R, MNH_2	Persistent intermediate red color	(444, 448)
	Na		−78°C.	(357)
	Na		Room temperature; ammonolysis immediate	(276)
$R_2C{=}CH_2$	Na	R_2CNaCH_3, $NaNH_2$, $R_2CNaCH_2CH_2$-$CNaR_2$ (10–30%)		(444)
	Na	R_2CNaCH_3, a little 1,1,4,4-tetraphenylbutane	Low temperature; toluene diluent	(448)
$R_2C{=}CHR$	Na, K	R_2CMCH_2R, MNH_2		(440, 443, 444)
	Ca	R_2CHCH_2R (40%)		(140)
	Sr	(61%)		(140)
	Ba	(48%)		(140)
$R_2C{=}CR_2$	Na	$R_2CNaCNaR_2$ and R_2CHNa or R_2CNa_2 (?)	When in excess, 3.65 equivalents of sodium react	(440, 444)
$R_2C{=}CHCH_3$	Na, K	$R_2CMCH_2CH_3$, MNH_2	Reacts readily	(443, 444)
$H_2C{=}CRCR{=}CH_2$	Na	2,3-Diphenylbutane (55%); an oil; some $C_{32}H_{34}$	Ether diluent	(3)
$R_2C{=}CHCH_2R$	Na	$R_2CNaCH_2CH_2R$	Low temperature	(448)
$R_2C{=}CHCHR_2$	Na	$R_2CNaCH_2CHR_2$, $NaNH_2$		(444)

TABLE 1—*Concluded*

COMPOUND	METAL	PRODUCTS REPORTED[a]	NOTES	REFERENCES
$R_2C{=}C{=}CR_2$.....	Na, K	$R_2CMCH_2CMR_2$, MNH_2	3.76, 4.3 equivalents of sodium react readily	(444)
$RCH_2CH_2CH{=}CH_2$.....	Na	$RCH_2CH_2CH_2CH_3$		(23)
$RCH{=}CHCH{=}CHR$....	Na	Hydrocarbon mixture		(191)

[a] In this, and in most of the tabulations included in this paper, either primary reduction products or the final products actually isolated are listed. In many cases the initial resultant of the action of a solution of a metal represents an intermediate formed for purposes of synthesis and it may be further subjected to hydrolysis, oxidation, reaction with other added substances, etc. From the published literature it is not always possible to deduce the identity of the primary reduction products.

might logically be considered as intermediates in the reactions represented in table 1 are not found because they undergo ammonolysis (*vide supra*). In general, the alkali metal atoms are replaced by hydrogen except when they are present in the grouping $(C_6H_5)_2CM$— (where M is an alkali metal). When the organoalkali compounds are stable in liquid ammonia they are useful for purposes of synthesis.

E. Acetylenic hydrocarbons

More than fifty years ago Moissan (310, 311) demonstrated that the addition of acetylene to liquid ammonia solutions of lithium, sodium, potassium, rubidium, cesium, and calcium results in the formation of the corresponding metal acetylides, e.g., $NaC{\equiv}CH$ and $Ca(C{\equiv}CH)_2$. At the same time, some of the acetylene is reduced to ethylene. Magnesium is attacked by ammonia solutions of acetylene to form ammoniated magnesium acetylides (89), $Mg(C{\equiv}CH)_2 \cdot 7NH_3$ (2° to −60°C.) and $Mg(C{\equiv}CH)_2 \cdot 5NH_3$ (above 2°C.). Because the alkali and alkaline earth metal acetylides have found such widespread application in synthesis, considerable attention has been given to the development of optimum conditions for their preparation. The list has been extended to include the strontium and barium salts, and acetylide formation has been effected at temperatures ranging from −80°C. to room temperature. The concomitant reduction of acetylene has been avoided by substitution of amide for metal (330, 331) and by adding the metal to ammonia solutions of acetylene at a rate such that no substantial excess of sodium is present during a major portion of the reaction time (407). Although advantage has been claimed for the use of calcium acetylide (318) in certain specific applications, the predominant practice entails the use of sodium acetylide prepared by passing acetylene gas into solutions of sodium in liquid ammonia at its normal boiling temperature.

The reduction of monoalkylacetylenes has been studied by a number of different workers (53, 273) and with particular care by Henne and Greenlee

(177). They have shown that propyne, for example, is one-third hydrogenated to the corresponding olefin and two-thirds metalated:

$$2CH_3C{\equiv}CH + 2Na \rightarrow 2CH_3C{\equiv}CNa + 2[H]$$
$$CH_3C{\equiv}CH + 2[H] \rightarrow CH_3CH{=}CH_2$$

Addition of sodium followed by an ammonium salt leads to complete reduction and high yields of the corresponding olefin. When ammonium chloride is used, some hydrogen is evolved and reduction does not go to completion; both of these disadvantages are overcome by use of the relatively insoluble ammonium sulfate. This leads to the conclusion that hydrogen from the acetylene molecule is more effective as a reductant than that from the ammonium ion and that the function of the latter is the regeneration of the acetylene from its sodium salt.

The action of liquid ammonia solutions of sodium upon dialkylacetylenes (52, 79, 177, 409) provides high yields of (exclusively) the *trans* form of the corresponding olefins. That these reactions yield only the *trans* isomers is believed to involve the formation of ionic intermediates (150).

$$RC{\equiv}CR + e^- \rightarrow R\bar{C}{=}\overset{|}{C}R$$

$$R\bar{C}{=}\overset{|}{C}R + e^- \rightarrow R\bar{C}{=}\bar{C}R$$

in which the *trans* isomers are produced by electrostatic repulsion leading to a configuration which is maintained during subsequent hydroysis or ammonolysis. Di-*tert*-butylacetylene is not reduced by sodium in ammonia to the olefin (180). This may be due to the relative insolubility of the substituted acetylene, although reduction to the olefin failed also when ether was used as a cosolvent.

Diacetylenes (177) are reduced by sodium or by sodium and ammonium sulfate to the corresponding *trans-trans* dienes. Thus, 2,7-nonadiyne and sodium give a 72 per cent yield of 2,7-nonadiene without evolution of hydrogen, while 1,6-heptadiyne with sodium and ammonium sulfate gives a 61 per cent yield of 1,6-heptadiene.

Sodium in ammonia converts phenylacetylene to the sodium salt and ethylbenzene (274, 279).

$$3C_6H_5C{\equiv}CH + 4Na + 2NH_3 \rightarrow 2C_6H_5C{\equiv}CNa + C_6H_5C_2H_5 + 2NaNH_2$$

Similar reactions probably occur in the case of compounds such as 3-phenyl-5-hexen-1-yne (288).

With regard to the use of the alkali and alkaline earth metal salts of acetylene and substituted acetylenes in the synthesis of organic compounds containing the ethynyl group, it is not feasible here to enumerate all of the cases that have been studied. Sodium acetylide in particular has been used widely in the preparation of mono- and di-alkylacetylenes and related compounds (28, 30, 31, 49, 53, 79, 85, 174, 179, 188, 195, 223, 229, 268, 272, 273, 282, 296, 297, 327, 328, 329, 387, 390, 391, 409, 434), using, for example, alkyl halides, sulfates, or esters as

the alkylation agents. Condensation of acetylides with aldehydes, ketones, and the like has been used extensively in the preparation of acetylenic carbinols (1, 13, 36, 51, 53, 91, 135, 164, 165, 167, 168, 171, 178, 184, 198, 199, 208, 228, 264, 265, 266, 287, 290, 337, 348, 386, 387). Acetylenic acids have been formed by carbonation of alkali acetylides with carbon dioxide either in liquid ammonia or in inert hydrocarbon solvents (201, 291, 449). These and other applications (35, 145, 163, 166, 169, 170, 172, 173, 181, 182, 183, 194, 197, 210, 211, 269, 301, 302, 336, 347) serve to illustrate the scope of application of these reagents. Sodium acetylide exhibits but little reactivity toward acetals (231), and sodium and potassium acetylides fail to metalate 1-heptyne to any appreciable extent (141), while both amyl- and phenyl-acetylene are partially metalated.

F. Aromatic hydrocarbons

The benzene nucleus is not attacked by ammonia solutions of metals (276, 357, 440). Benzene, toluene, xylene, etc. may be used advantageously as co-solvents for the reactions between metal solutions and many organic compounds (437, 448) or for introducing solutions of solids into ammonia (446). The reaction between sodium and 2,5-dihydrotoluene (23) results in 1-methylcyclohexene (50 per cent) and 3-methylcyclohexene (10 per cent).

The reduction of biphenyl to tetrahydrobiphenyl was first reported by Lebeau and Picon (276), who employed solutions of sodium. By means of either sodium or calcium at $-75°$ to $-70°$C., Hückel and Bretschneider (191) reduced biphenyl to the 3,4-dihydro derivative and showed that further action of sodium at $-75°$C. affords the 3,4,5,6-tetrahydro compound. Terphenyl with sodium in ammonia gives a 3,4-dihydro derivative and a compound that is isomeric with terphenyl and does not contain a reactive double bond (191). 3,4-Dihydroterphenyl is not hydrogenated further by sodium in liquid ammonia; it decomposes at 350°C. into terphenyl and hydrogen (192).

Naphthalene is reduced by sodium and potassium solutions to tetrahydronaphthalene, with the concomitant formation of alkali amide (275, 357, 446). When this reaction is carried out at low temperatures ($-33°$C. or lower) a bright red solution results. This color may be regarded as due to a relatively unstable intermediate organoalkali compound. Wooster and Smith (446) have examined the reaction in detail and have shown that the intermediate is the 1,2,3,4-tetrasodium addition product, but that even at $-33°$C. this compound is three-fourths ammonolyzed. Addition of sodium in ammonia at $-75°$ to $-65°$C. to naphthalene in ether produces a green color which changes to orange-red and finally to red (191). Upon treatment with methanol, Δ^2-dihydronaphthalene is obtained. At higher temperatures there results a mixture of the Δ^2- and Δ^1-isomers, while at the boiling point of ammonia some of the Δ^1-compound is formed (in one experiment it was nearly pure). Δ^2-Dihydronaphthalene and sodium in ether and ammonia at $-60°$C. give the Δ^1-isomer; at $-50°$C. Δ^1-dihydronaphthalene is reduced by sodium to tetralin. Similar results are reported for reactions in which calcium was employed (191). Treatment of naphthalene with sodium and isobutyl chloride in liquid ammonia forms 1,2,3,4-tetrahydro-1,4-diisobutylnaphthalene and a little tetralin (193).

Other hydrocarbons that are reduced in a manner presumably similar to that of naphthalene include the following (products noted in parentheses): anthracene (275, 303) (9,10-dihydroanthracene), 9,10-diphenylanthracene (191, 196) (9,10-dialkali salts, and finally some starting material recovered), phenanthrene (191, 276) (1,2,3,4-tetrahydrophenanthrene), acenaphthene (276) (tetrahydroacenaphthene), and dimethylfluorene (277) (tetrahydrodimethylfluorene). Both fluorene (276, 277, 423) and indene (276, 277) react with ammonia solutions of sodium to form sodium salts by substitution, accompanied by some hydrogenation. An ammonia solution of fluorene reacts with magnesium (89). Fernelius and Cappel (106) have shown that the action of sodium and ammonium bromides upon naphthalene, biphenyl, acenaphthene, and phenanthrene results in no more extensive hydrogenation than is accomplished through use of sodium alone. Under the same conditions, however, fluorene is apparently more extensively hydrogenated. The reaction between anthracene and sodium and ammonium bromide yields 1,2,3,4-tetrahydroanthracene and other products (108).

TABLE 2

Reactions of aromatic compounds with solutions of metals in liquid ammonia

(All reactions employing sodium *and* methanol or ethanol)

COMPOUND	PRODUCTS[a]	REFERENCES
Benzene	1,4-Dihydrobenzene (83%)	(435)
Toluene	Dihydrotoluene (83%)	(435)
	2,5-Dihydrotoluene	(23)
Xylene (mixture)	Dihydroxylenes (87%)	(435)
m-Xylene	2,5-Dihydro-*m*-xylene	(17)
p-Xylene	(?2,5-Dihydro-*p*-xylene	(17)
4,5-Dihydro-*m*-xylene	1,3-Dimethylcyclohexene	(23)
p-Cymene	γ-Terpinene	(17)
1,4-Dihydronaphthalene	Tetrahydronaphthalene (not tetralin)	(435)
Tetralin	Hexahydronaphthalene (91%)	(435)
	1,2,3,4,5,8-Hexahydronaphthalene	(17)

[a] See footnote to table 1.

That hydrogen liberated in an ammonia solution might effect more extensive reduction than the electron was first clearly recognized by Wooster and Godfrey (437). They found that the theoretical amount of hydrogen was not obtained when a mixture of ammonia, toluene, and sodium was treated with water, and in addition obtained a product having the characteristics of a cyclic olefin. Further investigations by Wooster (435) served to demonstrate the generality of this type of reaction, which may be effected by the use of protolytic agents other than water, e.g., alcohols, acid amides, primary arylamines, alkyl mercaptans, and aliphatic aldehydes. In general, benzenoid compounds are reduced to the corresponding dihydro derivatives, and Birch (17, 20) has shown that further treatment of these products with solutions of metals provides the tetrahydro compounds. More recently, similar studies have been reported; the results accumulated thus far are given in table 2.

The following compounds do not react with solutions of metals in liquid ammonia: terpinene, terpinolene, carvene, α-pinene, menthene (276), 1,3-dimethylcyclohexene, 2,4-dimethylcylohexene, D-limonene, D-sylvestrene, methylgeraniolene, and 4-methylcyclohexene (23).

III. HALOGEN COMPOUNDS

There are included under this heading only those compounds in which halogen is the only substituent. Compounds that contain other functional groups in addition to halogen are considered elsewhere in this paper under appropriate headings.

A. The liquid ammonia–sodium method for the determination of halogens in organic compounds

With but few exceptions, elements of the halogen family are removed quantitatively from all types of organic combinations by solutions of metals in liquid ammonia. This fact constitutes the basis for one of the most convenient and rapid methods for the determination of organic halogen (73, 80, 92, 93, 299, 392), including that present in polyhalogenated compounds (305). Those interested in the analytical determination of halogens usually have not concerned themselves with the fate of the remainder of the organic molecule. In some cases tars are formed, and polyhalogen compounds are very likely to yield some cyanide, e.g., chloroform, bromoform (but not iodoform), carbon tetrachloride, chloral and bromal hydrates, ethylidene chloride, tetrachloroethylene, and acetylene tetrachloride. Although the quantity of cyanide thus formed is variable, it can be removed readily prior to determining the halogen. The liquid ammonia–sodium method is not quantitative for cyanide in nitriles.

This method has been applied to the analysis of a variety of organic halogen compounds sufficient to demonstrate its generality of application (4, 84, 114, 176, 185, 218). In addition, there are several cases in which the reactivity of organic halogen compounds has been utilized to advantage in purification processes. Even very small quantities of such compounds present as impurities in products not reduced by sodium in ammonia are effectively removed by treatment with this reagent (41, 176, 317, 447).

B. Alkyl halides

The monohalogen substitution products of the paraffin hydrocarbons react with solutions of metals in liquid ammonia to form hydrocarbons, both saturated and unsaturated, sodium halogenides, and sodium amide (table 3). In table 3 the reactions marked (1) proceed as shown by the equation,

$$2RX + 2Na + NH_3 \rightarrow RH + RNH_2 + 2NaX \qquad (1)$$

while those marked (2) proceed thus:

$$RX + 2Na + NH_3 \rightarrow RH + NaNH_2 + NaX \qquad (2)$$

It appears that metal amide is produced in practically all of these reactions, perhaps as shown by equation 2, and it reacts either to ammonolyze the alkyl halide,

$$RX + NaNH_2 \rightarrow RNH_2 + NaX$$

or to effect dehydrohalogenation:

$$C_3H_7Cl + NaNH_2 \rightarrow C_3H_6 + NaCl + NH_3$$

Sodium amide has been shown to enter into both types of reaction (14).

TABLE 3

Reactions of alkyl halides with solutions of sodium in liquid ammonia

HALIDE	PRODUCTS[a]		REFERENCES
CH_3Cl	CH_4		(263)
	CH_4, CH_3NH_2, NaCl	(1)	(60, 271)
CH_3I	CH_4, CH_3NH_2, NaI		(71)
C_2H_5Br	C_2H_6, $NaNH_2$, NaBr	(2)	(433)
C_2H_5I	C_2H_6		(270)
	C_2H_6, $C_2H_5NH_2$, NaI	(1)	(271)
	C_2H_6 (75%), C_2H_4 (4%), $C_2H_5NH_2$ (21%), $NaNH_2$		(71)
n-C_3H_7Cl	C_3H_8, C_3H_6 (trace), $NaNH_2$		(71)
n-C_3H_7I	C_3H_8		(270)
	C_3H_8, $C_3H_7NH_2$, NaI	(1)	(261, 271)
	C_3H_8 (71%), C_3H_6 (7%), $C_3H_7NH_2$ (21%), $NaNH_2$		(71)
n-C_4H_9Cl	C_4H_{10}, $NaNH_2$, NaCl		(47)
iso-C_4H_9Cl	C_4H_{10}, C_4H_8 (trace), $NaNH_2$		(71)
iso-C_4H_9I	C_4H_{10} (70%), C_4H_8 (15%), $C_4H_9NH_2$ (15%), $NaNH_2$		(71)
iso-$C_5H_{11}Cl$	C_5H_{12}, C_5H_{10} (trace), $NaNH_2$		(71)
iso-$C_5H_{11}I$	C_5H_{12}, C_5H_{10} (trace), $NaNH_2$		(71)
tert-$C_5H_{11}I$	*sec*-C_5H_{12} (and explosion)		(261)
$C_2H_5CHI(CH_2)_2CH_3$	C_6H_{14}, C_6H_{12} (trace), $NaNH_2$		(71)
$CH_3(CH_2)_5CHICH_3$	C_8H_{18}, $NaNH_2$		(71)

[a] See footnote to table 1.

The reaction of methyl iodide is complicated by the fact that it reacts readily with liquid ammonia to form tetramethylammonium iodide:

$$4CH_3I + 4NH_3 \rightarrow (CH_3)_4NI + 3NH_4I$$

Sodium reacts readily with the ammonium iodide so formed (71).

Magnesium reacts with ethyl iodide as follows (261):

$$2C_2H_5I + Mg + NH_3 \rightarrow C_2H_6 + C_2H_5NH_2 + MgI_2$$

In any event, studies employing low-molecular-weight alkyl halides in ammonia should take into account complications arising by virtue of rapid interaction of the alkyl halide and the solvent (414).

C. *Phenyl-substituted alkyl halides*

Information relative to reactions of phenyl-substituted alkyl halides is assembled in table 4. The reaction of β,β,β-triphenylethyl chloride is of particular interest, in that it involves a rearrangement of the hydrocarbon nucleus. The similar rearrangement of γ,γ,γ-triphenylpropyl iodide is accompanied by a spontaneous cleavage of a carbon–carbon bond.

TABLE 4

Reactions of phenyl-substituted alkyl halides with solutions of metals in liquid ammonia ($R = C_6H_5$—)

HALIDE	METAL	PRODUCTS[a]	REFERENCES
RCH_2Cl	Na	RCH_3, RCH_2CH_2R, and a solid hydrocarbon	(95, 261)
RCH_2Br	Na	RCH_2CH_2R	(440)
	K	RCH_2CH_2R	(440)
R_2CHCl	Na	R_2CHCHR_2 (66%), R_2CH_2 (28%)	(95, 96)
R_3CCl	Na	R_3CNa	(246, 438, 445)
	K	R_3CK	(246)
	Ca	Unstable red-brown compound	(246)
$RCHCl_2$	Na	RCH_2CH_2R (7%), RCH_2NH_2 (38%)	(95)
R_2CCl_2	Na	$R_2C{=}CR_2$ (90%)	(95, 96)
$RCCl_3$	Na	RCH_2CH_2R (5%), nitrogenous substance	(95)
RCH_2CH_2Br	Na	RC_2H_5 (38%), $RCH{=}CH_2$ (1.3%)	(95)
R_3CCH_2Cl	Na	R_2CNaCH_2R	(441, 443)
$R_3CCH_2CH_2I$	Na	R_3CNa, C_2H_4	(442)
$R(CH_2)_3Br$	Na	RC_3H_7 (28%), $R(CH_2)_3NH_2$ (18%)	(95)
$R(CH_2)_4Br$	Na	RC_4H_9 (43%), $R(CH_2)_4NH_2$ (17%), other hydrocarbons and amines	(95)
$RC(CH_3)_2CH_2Cl$	Na	$RC(CH_3)_3$	(423)

[a] See footnote to table 1.

D. *Unsaturated halides*

Upon reaction with sodium in liquid ammonia, acetylene dibromide yields sodium acetylide and variable quantities of acetylene. These products may be accounted for qualitatively if the following reactions are assumed to occur in varying proportions (261):

$$CHBr{=}CHBr + 2Na \rightarrow CH{\equiv}CH + 2NaBr$$
$$CH{\equiv}CH + Na \rightarrow CH{\equiv}CNa + \tfrac{1}{2}H_2$$
$$CHBr{=}CHBr + 3Na \rightarrow CH{\equiv}CNa + 2NaBr + \tfrac{1}{2}H_2$$

The results of Bachman's studies of reactions of bromoölefins (9) with sodium in liquid ammonia are summarized in table 5. The monobromoölefins give principally the corresponding acetylenes and olefins in a ratio A/O which increases with increase in the length of the hydrocarbon chain. Under similar conditions the dibromoölefins also yield acetylenes and olefins, but high-molecular-weight

polymers are formed at the same time and make up a considerable portion of the products. The ratio A/O is larger for the dibromoölefins than for the corresponding monobromo compounds and also increases with increase in the length of the hydrocarbon chain. Small amounts of saturated hydrocarbons arise in all cases, owing to reduction of the olefins and acetylenes by the hydrogen formed in the reaction.

Vaughn (389) has examined the reactions of a number of halogenated olefins with sodium in liquid ammonia; the results are shown in table 6. The resultant acetylenes were in no case entirely free from hydrogenation products; hence these reactions are not suitable for the preparation of pure acetylenes.

TABLE 5

Reactions of bromoölefins with solutions of sodium in liquid ammonia

HALIDE	MOLES USED		MOLES OBTAINED		ACETYLENE / OLEFIN
	Olefin	Sodium	Acetylene	Olefin	
1-Bromo-1-propene	0.167	0.202	0.006	0.818	0.012
1-Bromo-1-octene	0.167	0.221	0.034	0.075	0.45
1,1-Dibromo-1-propene	0.167	0.389	0.050	0.070	0.81
1,1-Dibromo-1-octene	0.167	0.374	0.052	0.029	1.80

TABLE 6

Reactions of halogenated olefins with solutions of sodium in liquid ammonia

HALIDE	SODIUM	PRINCIPAL PRODUCT IDENTIFIED	YIELD
	moles		*per cent*
β-Bromostyrene	2	Phenylacetylene	96
α-Chlorostyrene	2	Phenylethane	15
p-Methyl-α-chlorostyrene	2	Tolylacetylene	63
Stilbene dibromide	15	Bibenzyl	73
Styrene dibromide	3	Phenylacetylene	66
2-Bromo-1-decene	2	1-Decene	56

Certain condensation products of allyl or substituted allyl halides are covered by a patent issued to Kharasch (217). These are formed, for example, by condensing allyl chloride with itself or its derivatives by treatment with liquid ammonia solutions of alkali or alkaline earth metals.

E. Paraffin polyhalides

The reactions of various paraffin polyhalides with liquid ammonia solutions of sodium are summarized in table 7. It is evident that several of these reactions must be somewhat complex; those marked (1) follow essentially the course:

$$C_nH_{2n}X_2 + 2Na \rightarrow C_nH_{2n} + 2NaX$$

F. Aryl halides

The action of liquid ammonia solutions of metals upon aryl halides has been the subject of only very limited investigations. The principal products of the reaction between sodium and chlorobenzene or iodobenzene in liquid ammonia

TABLE 7

Reactions of paraffin polyhalides with solutions of sodium in liquid ammonia

HALIDE	PRODUCTS[a]	REFERENCES
CH_2Cl_2	CH_4 (55%), $NaNH_2$, NaCl	(63, 72)
$CHCl_3$	CH_4, $NaNH_2$, NaCl, small amounts of C_2H_4, C_2H_2, and NaCN	(60)
CHI_3	CH_4, NaI, some C_2H_4, C_2H_2, NaCN, H_2, and N_2	(60)
CCl_4	CH_4, NaCl, NaCN, small amount of N_2	(60, 80)
CH_2ClCH_2Cl	C_2H_4, NaCl (1)	(63, 72, 261)
CH_3CHCl_2	C_2H_6 (51%), C_2H_4 (5%), $NaNH_2$	(63, 72)
C_2Cl_6	NaCN (not confirmed)	(80, 92)
$CH_3CH_2CHCl_2$	C_3H_8, some C_3H_6	(63)
$CH_3CCl_2CH_3$	C_3H_8 (64%), C_3H_6 (14%), $NaNH_2$, NaCl	(63, 72)
$CH_3CHBrCH_2Br$	C_3H_6, NaBr (1)	(63, 72)
$(CH_3)_2CBrCH_2Br$	C_4H_8, NaBr (1)	(72, 80)
$C(CH_2Br)_4$	$C(CH_2NH_2)_4$ (small amounts)	(149)

[a] See footnote to table 1.

are benzene, diphenylamine, triphenylamine, and sodium halide (420). The following equations suggest the course of the principal reactions:

$$6C_6H_5Cl + 6Na + NH_3 \rightarrow 3C_6H_6 + (C_6H_5)_3N + 6NaCl \quad (1)$$
$$4C_6H_5Cl + 4Na + NH_3 \rightarrow 2C_6H_6 + (C_6H_5)_2NH + 4NaCl \quad (2)$$

A small quantity of aniline is formed in accordance with the equation:

$$2C_6H_5Cl + 2Na + NH_3 \rightarrow C_6H_6 + C_6H_5NH_2 + 2NaCl \quad (3)$$

When petroleum ether is used as a diluent, tertiary amine is the main product. *p-sec*-Butylchlorobenzene reacts with sodium to give a 50 per cent yield of *sec*-butylbenzene and a 10 per cent yield of *p-sec*-butylaniline (185). The *o*- and *p*-chlorotoluenes appear to react according to equation 3, and the action of magnesium upon iodobenzene follows the same course (261). *o*-Bromoxylene reacts slowly with sodium solution to form *o*-xylene and a nitrogen-containing residue (95). *o*-Dichlorobenzene and sodium react as follows (261):

$$2C_6H_4Cl_2 + 4Na + 2NH_3 \rightarrow C_6H_6 + C_6H_4(NH_2)_2 + 4NaCl$$

α-Iodonaphthalene is reduced to naphthalene by the action of sodium in ammonia (146). Indene bromohydrin reacts with sodium to provide a 75 per cent yield of 2-indanol (383).

IV. ALCOHOLS AND PHENOLS

The alcohols react readily with solutions of alkali metals in ammonia with evolution of hydrogen and the formation of alkoxides (61, 260). Secondary and tertiary alcohols react more slowly than primary alcohols and form more soluble alkoxides (61). In many cases it appears that the alcohols do not react completely with sodium or potassium, but instead form compounds of the type $RONa \cdot ROH$ (61, 422). The alkoxides of the alkaline earth metals may be prepared similarly by reaction between solutions of these metals and alcohols (66).

Salts of the di- and poly-hydric alcohols are formed in the same manner as salts of the monohydric alcohols. With but few exceptions only one of the hydrogen atoms is displaced by the metal (62, 69, 74).

The preparation of salts of unsaturated alcohols is usually accompanied by reduction at the primary alcohol grouping or the double bond (64, 65, 74):

$$2CH_2{=}CHCH_2OH + 2Na \rightarrow CH_2{=}CHCH_2ONa + CH_2{=}CHCH_3 + NaOH$$

Phenols react with solutions of the alkali metals in the same manner as the aliphatic alcohols. The naphthols, on the other hand, are in part reduced to the tetrahydronaphthols, so that the preparation of the pure naphthoxides requires the use of an alkali amide rather than the metal solution.

Salts of alcohols, phenols, and naphthols prepared by reaction with solutions of the alkali and alkaline earth metals in liquid ammonia are listed in table 8. Salts of this type have been treated with alkyl halides or other alkylation agents to produce a variety of ethers (69, 260, 393, 422). Similar treatment of the alkoxides with soluble salts of lead and thallium provides the corresponding heavy metal alkoxides (67, 69, 74).

Sodium in liquid ammonia replaces only one of the hydrogen atoms of pinacol, but reacts extensively with acetophenone pinacol, first to replace one hydrogen and then to cleave a carbon–carbon bond (439).

$$\begin{array}{l} C_6H_5(CH_3)COH \\ \quad\quad | \\ C_6H_5(CH_3)COH \end{array} + Na \rightarrow \begin{array}{l} C_6H_5(CH_3)CONa \\ \quad\quad | \\ C_6H_5(CH_3)COH \end{array} + \tfrac{1}{2}H_2$$

$$\begin{array}{l} C_6H_5(CH_3)CONa \\ \quad\quad | \\ C_6H_5(CH_3)COH \end{array} + 2Na + NH_3 \rightarrow 2C_6H_5(CH_3)CHONa + NaNH_2$$

The monosodium salt of cardanol has been used in reaction with ethylene chlorohydrin to produce cardanoxyethanol. Calcium reacts with the latter to form calcium cardanoxyethoxide (295). Efforts to separate geraniol from citronellol by selective reduction of the former with sodium in ammonia have been unsuccessful, probably because of incomplete reduction of the geraniol (98, 99). Campbell and Eby (53) have shown that certain acetylenic carbinols may be reduced to the corresponding olefins by means of sodium in liquid ammonia without cleavage into ketones. Thus, dimethylethynylcarbinol yields 2-methyl-3-buten-2-ol, while dimethylhexynylcarbinol provides *trans*-2-methyl-3-octen-2-ol.

TABLE 8

Reactions of alcohols, phenols, and naphthols with solutions of metals in liquid ammonia
(M = Li, Na, or K; M' = Ca, Sr, or Ba)

COMPOUND	SALT FORMED	REFERENCES
Monohydric saturated alcohols		
Methyl alcohol	CH_3OM	(74)
	$(CH_3O)_2M'$	(67, 74)
Ethyl alcohol	C_2H_5OM	(74, 260, 422)
	$(C_2H_5O)_2M'$	(67, 74)
n-Propyl alcohol	C_3H_7ONa	(393)
n-Butyl alcohol	C_4H_9ONa	(229, 260, 393)
	C_4H_9OK	(422)
Isobutyl alcohol	C_4H_9OM	(74)
	$(C_4H_9O)_2Ca$	(67)
tert-Butyl alcohol	C_4H_9ONa	(51)
n-Amyl alcohol	$C_5H_{11}ONa$	(229, 393)
	$(C_5H_{11}O)_2Ca$	(67)
Isoamyl alcohol	$C_5H_{11}OM$	(74)
	$(C_5H_{11}O)_2Ca$	(74)
Menthol	$C_{10}H_{19}ONa$	(62)
Borneol	$C_{10}H_{17}ONa$	(62)
Monohydric substituted alcohols		
Benzyl alcohol	$C_6H_5CH_2OK$	(422)
3-Phenyl-1-propanol	$C_6H_5(CH_2)_2CH_2ONa$	(64)
Dihydric and polyhydric saturated alcohols		
Ethylene glycol	CH_2OHCH_2OM[a]	(62, 69, 74, 360, 422)
	$(CH_2O)_2Ca$	(69, 74)
Glycerol	Monosodium salt	(62, 359, 360)
Erythritol	Dilithium salt	(74)
	Monosodium salt	(62, 74)
	Calcium salt 1:1	(74)
Pentaerythritol	Di-, tri-, and tetra-sodium salts	(148)
Mannitol	Dilithium salt	(74)
	Monosodium and monopotassium salts	(62, 74, 359)
Unsaturated alcohols		
Allyl alcohol	$CH_2{=}CHCH_2ONa$[b]	(64, 74)
Citronellol	Monosodium salt	(64)
Geraniol	Monosodium salt[c]	(74)
Linaloöl	Sodium salt[c]	(74)
Cinnamic alcohol	$C_6H_5CH{=}CHCH_2ONa$[d]	(65, 74)

TABLE 8—*Concluded*

COMPOUND	SALT FORMED	REFERENCES
Phenols		
Phenol	C_6H_5ONa	(229, 244, 260, 422)
2,4,6-Tri-*tert*-butylphenol	Monosodium salt[e]	(377)
Resorcinol	$C_6H_4(OH)ONa$[f]	(422)
	$C_6H_4(ONa)_2$[f]	(422)
Naphthols		
α-Naphthol	$C_{10}H_7ONa$[g]	(422)
	$C_{10}H_{11}ONa$ (*ar*)	(422)
β-Naphthol	$C_{10}H_{11}ONa$ (*ar*, *ac*)	(422)

[a] Insoluble; stable in presence of excess sodium. The di-M salts may be formed by heating the solid mono-M salts.

[b] Also C_3H_6 (50 mole per cent of C_3H_5OH), no hydrogen, no reduction of C=C, NaOH.

[c] Also $C_{10}H_{18}$, NaOH.

[d] Also some $C_6H_5(CH_2)_2CH_2ONa$, $C_6H_5CH{=}CHCH_3$, and $C_6H_5(CH_2)_2CH_3$.

[e] Salt formation by this hindered phenol is difficult or impossible by other methods.

[f] The monosodium salt is very soluble, but none of the disodium salts of the dihydroxybenzenes is appreciably soluble (235).

[g] Birch (17) has shown that the action of sodium in ammonia upon sodium α-naphthoxide results in traces of 5,8-dihydro-α-naphthol. Similarly, sodium β-naphthoxide yields traces of (?5,8)-dihydro-β-naphthol and β-tetralone.

It was pointed out previously that the hydrogen generated during the formation of salts of alcohols, phenols, and the like may participate in reduction reactions leading to products that may be the same as, or different from, those resulting from the action of the metal alone. This possibility may be enhanced and in some cases the reducing action may be restricted to that of hydrogen by providing an excess of a lower alcohol (prior to or concurrently with the addition of metal) that will react preferentially with the added metal. A number of reactions effected under these conditions have been examined by Birch and others; the results are summarized in table 9.

V. ETHERS AND OXIDES

The addition of sodium to a liquid ammonia solution of ethylene oxide results in a very vigorous reaction, the products of which have not been identified (445). Under similar conditions, indene oxide is reduced to 2-indanol (383).

The simple aliphatic ethers are not reactive toward solutions of metals in ammonia (190, 260); in fact, such ethers have been used to advantage as cosolvents in reactions employing solutions of metals (95, 392, 444). If, on the other hand, an ether contains at least one aromatic group, the action of liquid ammonia solutions of metals results in cleavage of a carbon–oxygen bond in all but a few of the many cases that have been examined.

TABLE 9

Reduction of alcohols, phenols, and naphthols in liquid ammonia by hydrogen generated by the interaction of sodium and ethanol[a]

COMPOUND REDUCED	PRODUCTS[b]	REFERENCES
Benzyl alcohol[c]	Toluene	(18)
Phenylmethylcarbinol	Ethylbenzene	(18)
Phenyldimethylcarbinol[c]	Isopropylbenzene	(18)
Phenylbutylcarbinol	*n*-Amylbenzene	(18)
p-Methoxyphenylcarbinol	*p*-Tolyl methyl ether (29%), dihydro-*p*-tolyl methyl ether (7%)	(18)
Furfuryl alcohol	2-Methylfuran (20%)	(18)
Furfurylbutylcarbinol	2-Amylfuran (3.5%)	(18)
4-Hydroxy-Δ^2-octene	Δ^2- or Δ^3-Octene (traces)	(18)
Geraniol	2,6-Dimethyl-2,6-octadiene	(97)
β-Geraniol	2,6-Dimethyl-2,6-octadiene	(101)
Linaloöl	2,6-Dimethyl-2,6-octadiene	(97)
β-Linaloöl	2,6-Dimethyl-2,6-octadiene	(101)
1-Vinylcyclohexanol	Ethylidenecyclohexane	(18)
3-Hydroxy-1-phenyl-Δ^1-butene	1-Phenyl-Δ^2-butene and 3-hydroxy-1-phenylbutane	(18)
1-Hydroxy-1-phenyl-Δ^2-butene	1-Phenyl-Δ^2-butene	(18)
3-Hydroxy-1-phenyl-3-methyl-Δ^1-butene	1-Phenyl-3-methyl-Δ^2-butene, 2-hydroxy-4-phenyl-2-methylbutane	(18)
D-Sabinol	α-Thujene	(18)
D-Carveol	(Not reduced)	(18)
Ethynylcyclohexanol	1-Vinylcyclohexanol	(18)
	Ethylidenecyclohexane	(18)
1-Δ^1-Heptynylcyclohexanol	1-Δ^1-Heptenylcyclohexanol	(18)
α-Naphthol*[d]	5,8-Dihydro-α-naphthol (65%)	(17)
6-Methoxy-5-methyl-1-naphthol	5-Hydroxy-1-methyl-2-tetralone	(87)
β-Naphthol*[e]	β-Tetralone (65%)	(17)

[a] In the cases marked with an asterisk, *tert*-amyl alcohol was used in place of ethanol.

[b] See footnote to table 1.

[c] Competitive reduction of benzyl alcohol and phenyldimethylcarbinol yielded toluene and probably isopropylbenzene.

[d] The same product was obtained, but in 85 per cent yield, by starting with sodium α-naphthoxide.

[e] Sodium β-naphthoxide under similar conditions gave a 55 per cent yield of β-tetralone.

Studies on the cleavage of aromatic ethers by sodium in ammonia described by Sowa and his associates (230, 351, 415) are summarized in table 10. The reactions may be represented by the general equation:

$$ROR' + 2Na + NH_3 \rightarrow RONa + R'H + NaNH_2$$

Two equivalents of sodium are consumed in all cases except where additional metal is utilized in reaction with —OH or —COOH. Considering the portion of the molecule which forms the phenolic compound to be the more electronegative (since it does not attract electrons, which cause the cleavage, to as great an extent as the other portion of the molecule), an order of *decreasing electro-*

negativity for a carbon-to-oxygen linkage may be drawn up as follows: 4-aminophenyl, 2-aminophenyl, 3-aminophenyl, 4-methoxyphenyl, 4-*tert*-butylphenyl, 4-methylphenyl, 3-methylphenyl, 2-methylphenyl, phenyl, 3-methoxyphenyl, 2-methoxyphenyl, 3-carboxyphenol, 2-carboxyphenyl, 4-carboxyphenyl.

TABLE 10

Cleavage of aromatic ethers by solutions of sodium in liquid ammonia

COMPOUND ROR'		CLEAVAGE PRODUCTS AS MOLE PER CENT			
R	R'	ROH		R'OH	
Phenyl	Phenyl	100	Phenol		
Phenyl	4-Methylphenyl	25.6	Phenol	74.9	*p*-Cresol
Phenyl	2-Methylphenyl	47.1	Phenol	52.9	*o*-Cresol
		46	Phenol	54	*o*-Cresol
Phenyl	3-Methylphenyl	38	Phenol	62	*m*-Cresol
2-Methylphenyl	4'-Methylphenyl	39	*o*-Cresol	61	*p*-Cresol
2-Methylphenyl	3'-Methylphenyl	47		53	
3-Methylphenyl	4'-Methylphenyl	23		77	
p-Tolyl	*p*'-*tert*-Butylphenyl	48	*p*-Cresol	52	*p*-*tert*-Butylphenol
Phenyl	4-Methoxyphenyl	19	Phenol	81	*p*-Methoxyphenol
Phenyl	2-Methoxyphenyl	55	Phenol	45	Guaiacol
Phenyl	3-Methoxyphenyl	53		47	
2-Methoxyphenyl	4'-Methoxyphenyl	1	Guaiacol	99	*p*-Methoxyphenol
2-Methoxyphenyl	3'-Methoxyphenyl	24		76	
3-Methoxyphenyl	4'-Methoxyphenyl	8		92	
p-Tolyl	*p*'-Anisyl	21	*p*-Cresol	79	*p*'-Hydroxyanisole
4-Methoxyphenyl	4'-Hydroxyphenyl	High-boiling products, not identified			
Phenyl	4-Aminophenyl			100	*p*-Aminophenol
Phenyl	2-Aminophenyl	1	Phenol	99	*o*-Aminophenol
Phenyl	3-Aminophenyl	28		72	
p-Tolyl	*p*'-Aminophenyl			100	*p*-Aminophenol
p-Anisyl	*p*'-Aminophenyl	8	*p*-Hydroxyanisole	92	*p*-Aminophenol
Phenyl	4-Carboxyphenyl	100	Phenol[a]		
Phenyl	2-Carboxyphenyl	90	Phenol[b]		
Phenyl	3-Carboxyphenyl	64		36	

[a] Approximately theoretical amount of dihydrobenzoic acid obtained.
[b] A mixture of dihydrobenzoic and benzoic acids obtained.

Table 11 includes results obtained by Birch and others in studies involving the action of sodium in liquid ammonia at its boiling point upon a variety of ethers. Information provided by Freudenberg and coworkers (127, 128) relative to the cleavage of aromatic ethers by solutions of potassium at 20°C. is incorporated in table 12. Finally, the work of Birch (17, 21, 23) on the reduction of ethers by sodium and ethanol (or methanol) in ammonia is summarized in table 13.

TABLE 11

Cleavage of ethers by solutions of sodium in liquid ammonia

ETHER	PRODUCTS IDENTIFIED[a]	REFERENCES
Anisole	Phenol (27%)	(21)
Dihydroanisole	Cyclohexanone	(19)
o-Tolyl methyl ether	*o*-Cresol (17%)	(21)
	Methylcyclohexenes	(23)
Dihydro-*o*-tolyl methyl ether	2-Methylcyclohexanone	(19)
o-Tolyl triphenylmethyl ether	*o*-Cresol (54%)[b], triphenylmethane	(367)
Phenyl benzyl ether	Phenol (48%)[c], bibenzyl	(367)
m-Tolyl methyl ether	*m*-Cresol (9%)	(21)
Dihydro-*m*-tolyl methyl ether	3-Methylcyclohexanone	(19)
5,6-Dihydro-*m*-tolyl methyl ether	1-Methylcyclohexene	(23)
p-Tolyl methyl ether	*p*-Cresol (4%)	(21)
Dihydro-*p*-tolyl methyl ether	Methyl-Δ^1-cyclohexene, 4-methylcyclohexanone	(19)
2,3-Dihydro-*p*-tolyl methyl ether	1,3- and 4-Methylcyclohexene	(23)
β-Bromoethyl phenyl ether	1,4-Diphenoxybutane, phenol	(95)
γ-Bromopropyl phenyl ether	Phenoxypropane, phenol, 1,6-diphenoxyhexane	(95)
Veratrole	Guaiacol (89%)	(21)
3,6-Dihydroveratrole	2,5-Dihydroanisole	(21)
4-Methylveratrole	3-Hydroxy-4-methoxytoluene	(21)
4-Methyl-3,6-dihydroveratrole	2,5-Dihydro-*m*-tolyl methyl ether	(21)
Resorcinol dimethyl ether	Resorcinol monomethyl ether (71%)	(21)
2,5-Dihydroresorcinol dimethyl ether	Cyclohexanone enol methyl ether	(21)
Resorcinol methyl *n*-amyl ether	Resorcinol *n*-amyl ether	(21)
Quinol dimethyl ether	Quinol monomethyl ether (3%)	(21)
2,5-Dihydroquinol dimethyl ether	Δ^1-Cyclohexene methyl ether	(21)
Guaiacol *n*-propyl ether	Catechol *n*-propyl ether	(21)
Guaiacol isopropyl ether	Catechol isopropyl ether	(21)
Guaiacol benzyl ether	Guaiacol, toluene, bibenzyl	(21)
Guaiacol methoxymethyl ether	Guaiacol, anisole	(21)
2-Methoxyphenoxyacetic acid	Guaiacol	(21)
2-Ethoxy-3,4-dihydronaphthalene	Tetralin	(23)
Methylenedioxybenzene	Phenol	(21)
3,4-Methylenedioxytoluene	*p*-Cresol	(21)
Safrole	*p*-Allylphenol, *p*-propenylphenol	(21)

[a] See footnote to table 1.

[b] Total reaction time = 7 days.

[c] Total reaction time = 5.5 days.

TABLE 12

Cleavage of aromatic ethers by solutions of potassium in liquid ammonia at 20°C.

ETHER	PRODUCTS IDENTIFIED[a]
Anisole	Phenol (*ca.* 100%)
Veratrole	Guaiacol, pyrocatechol
Propylveratrole	(Probably) 4-hydroxy-3-methoxy- and 4-methoxy-3-hydroxy-propylbenzenes
Dihydroeugenol	No cleavage of $-OCH_3$
Diisoeugenol methyl ether	Partial demethylation
Diisoeugenol	No cleavage of $-OCH_3$
Vanillin	No cleavage of $-OCH_3$[b]
Vanillic acid	No cleavage of $-OCH_3$
Egonol	No cleavage of $-OCH_3$
Dihydrosafrole	*p*-Hydroxyphenylpropane
Piperonylic acid	*m*-Hydroxybenzoic acid

[a] See footnote to table 1.

[b] The aldehyde group is reduced to a primary alcohol group.

TABLE 13

Reduction of ethers by sodium and ethanol (or methanol) in liquid ammonia[a]

ETHER	PRODUCTS IDENTIFIED[b]
Geranyl methyl ether	Geraniolene
Anisole[c]	Δ^2-Cyclohexenone (20%)
2,3-Dihydroanisole	1-Methylcyclohexene
2-Methylanisole	6-Methyl-Δ^2-cyclohexenone (12%)
3-Methylanisole	3-Methyl-Δ^2-cyclohexenone (42%)
5,6-Dihydro-*m*-tolyl methyl ether	1-Methoxy-3-methylcyclohexene
4-Methylanisole	4-Methyl-Δ^2-cyclohexenone (33%)
2,3-Dihydro-*p*-tolyl methyl ether	1-Methoxy-4-methylcyclohexene
2,6-Dimethylanisole	2,6-Dimethyl-Δ^2-cyclohexenone (10%) 2,4-Dimethylcyclohexene
2,5-Dimethylanisole	(?3,6)-Dimethyl-Δ^2-cyclohexenone (15%)
2,4-Dimethylanisole	4,6-Dimethyl-Δ^2-cyclohexenone (22%)
3,4-Dimethylanisole	(?3,4)-Dimethyl-Δ^2-cyclohexenone (35%)
3,5-Dimethylanisole	3,5-Dimethyl-Δ^2-cyclohexenone (16%) 2,4-Dimethylcyclohexene[d].
5-Methyl-2-isopropylanisole	3-Methyl-6-isopropyl-Δ^2-cyclohexenone ("low yield")
Veratrole	2,5-Dihydroanisole, 3,6-dihydroveratrole
4-Methylveratrole	2,5-Dihydro-*p*-tolyl methyl ether, 4-methyl-3,6-dihydroveratrole
Quinol dimethyl ether	2,5-Dihydroquinol dimethyl ether
Resorcinol dimethyl ether	2,5-Dihydroresorcinol dimethyl ether
Pyrogallol trimethyl ether	Dihydroresorcinol
5-Methoxytetralin	1-Keto-$\Delta^{9,10}$-octalin (trace)
6-Methoxytetralin	2-Keto-$\Delta^{1,9}$-octalin (44%)
6-Methoxy-5-methyltetralin	(No ketonic product)
5-Methoxyhydrindene	5-Keto-$\Delta^{4,9}$-tetrahydrohydrindene (30%)
Methylenedioxybenzene	Phenol
3,4-Methylenedioxytoluene	*p*-Cresol
Safrole	*p*-Allylphenol

[a] In many of the cases listed in this table, water was added following evaporation of the ammonia. Thus, hydrogen generated upon hydrolysis of sodium salts was potentially available for reaction.

[b] See footnote to table 1.

[c] Wooster (435) previously reported a 60 per cent yield of dihydroanisole from reactions employing sodium and methanol.

[d] Excess sodium was added following the treatment with sodium and ethanol.

VI. AMINES

A few of the lower aliphatic amines dissolve and react with some of the alkali metals to form substituted metal amides (339, 340), e.g., CH_3NHCs, C_2H_5NHCs, and iso-C_4H_9NHCs. These reactions usually do not occur readily except at elevated temperatures (105) and most amines may be stored safely over sodium as a means of complete dehydration.

Liquid ammonia is not a suitable medium for the preparation of salts of the aliphatic amines because such salts are readily ammonolyzed (340):

$$RNHM + NH_3 \rightarrow RNH_2 + MNH_2$$

Tributylamine has been recommended as a diluent to increase the solubility of certain organic halogen compounds in the application of the liquid ammonia–sodium method of analysis for halogens (392). Bis(β-cyanoethyl)methylamine is reduced by solutions of potassium in ammonia, but the principal product (probably an iminonitrile dimeride) has not been identified (86).

The monosodium salts of aniline, ethylaniline, *o*-toluidine, and diphenylamine have been formed by treating the amines with sodium in liquid ammonia in an autoclave at room temperature. These reactions did not occur readily at −40°C. Disodium anilide and sodium benzylamide could not be formed (333). Sodium diphenylamide (207, 420) has been prepared by the interaction of sodium

TABLE 14

Reduction of aromatic amines in liquid ammonia

AMINE	REDUCING SYSTEM	PRODUCTS REPORTED[a]	REFERENCES
Aniline	Na,CH_3OH	2,5-Dihydroaniline[b]	(24)
		Tetrahydroaniline[c]	(24)
Dimethylaniline	Na,CH_3OH	Dihydrodimethylaniline (39%)	(435)
	Na,C_2H_5OH	Δ^2-Cyclohexenone	(19)
Dihydrodimethylaniline	Na	Cyclohexanone	(19)
Dimethyl-*o*-toluidine	Na,C_2H_5OH	6-Methyl-Δ^2-cyclohexenone	(19)
Dihydrodimethyl-*o*-toluidine	Na	2-Methylcyclohexanone	(19)
Dimethyl-*m*-toluidine	Na,C_2H_5OH	3-Methyl-Δ^2-cyclohexenone	(19)
Dihydrodimethyl-*m*-toluidine	Na	2-Methylcyclohexanone	(19)
Dimethyl-*p*-toluidine	Na,C_2H_5OH	4-Methyl-Δ^3-cyclohexenone	(19)
Dihydrodimethyl-*p*-toluidine	Na	4-Methylcyclohexanone	(19)
Dimethyl-*p*-cumidine	Na,C_2H_5OH	4-Isopropyl-Δ^3-cyclohexenone	(19)
1-Naphthylamine	Na	5,8-Dihydro-1-naphthylamine (86%)	(412)
	Na,CH_3OH	5,8-Dihydro-1-naphthylamine[d]	(412)

[a] See footnote to table 1.
[b] Rapid reduction.
[c] Slow reduction.
[d] Probable product; reduction slow and incomplete.

and diphenylamine at −33°C. Triphenylamine is not attacked by sodium either in liquid ammonia (24 hr.) or in ether (1.5 years) (379). Both sodium and potassium in ammonia react with triphenylmethylamine to form alkali triphenylmethide and the corresponding amide (254).

$$(C_6H_5)_3CNH_2 + 2M \rightarrow (C_6H_5)_3CM + MNH_2$$

Although the work thus far reported is by no means extensive, there have been examined a few cases that permit a comparison of reactions of amines with solutions of metals and with hydrogen generated by the interaction of metals and ammonium salts, alcohols, etc. While the benzylphenylamide ion is not attacked by a solution of sodium in liquid ammonia (110), benzylaniline undergoes a reaction represented by the equation:

$$2C_6H_5CH_2NHC_6H_5 + 2e^- \rightarrow (C_6H_5CH_2NC_6H_5)^- + C_6H_5CH_3 + (C_6H_5NH)^-$$

With hydrogen from sodium and ammonium bromide, the reaction is

$$C_6H_5CH_2NHC_6H_5 + 2[H] \rightarrow C_6H_5CH_3 + C_6H_5NH_2$$

Results obtained in the study of reactions of amines with the reducing systems specified are incorporated in table 14.

VII. ALDEHYDES AND RELATED COMPOUNDS

Because most aldehydes react readily with liquid ammonia, this medium is ordinarily suitable only for reactions between aldehyde derivatives and solutions of metals. At −33.5°C. acetaldehyde ammonia and sodium react in a 1:1 ratio to provide one equivalent of hydrogen and a precipitate that is considered to be (260) $CH_3CH(ONa)NH_2$. Aldehyde ammonia, however, appears to be a hydrate of triethylidene triimine (382), $(CH_3CH{=}NH)_3 \cdot 3H_2O$, so that the precipitate might well have been sodium hydroxide. Similarly, benzaldehyde reacts with liquid ammonia to form a precipitate which is acted upon by sodium (261). At 20°C. vanillin reacts with solutions of potassium in ammonia to form vanillyl alcohol and a condensation product of vanillyl alcohol and vanillin (128).

In general, the acetals show only limited reactivity toward either liquid ammonia or solutions of metals in this solvent. Dimethylacetal has been recommended as a cosolvent in the liquid ammonia–sodium method of analysis for organic halogen (392). It has been reported that cyclohexanone catechol acetal and sodium react to form cyclohexanol and phenol (21).

Hexamethylenetetramine and *N*,*N*,*N*-tetramethylmethylenediamine, $[(CH_3)_2N]_2CH_2$, are unreactive toward sodium in ammonia. *N*-Ethylideneëthylamine, $CH_3CH{=}NC_2H_5$, forms *N*,*N*-diethyl-2,3-butanediamine, $CH_3CH(NHC_2H_5)CH(NHC_2H_5)CH_3$, when treated with sodium solution in an autoclave at room temperature (332). This reaction does not occur at −40°C. and is incomplete at −20°C. Benzylidenimine is reduced to benzylamine by sodium in liquid ammonia (380).

VIII. KETONES AND RELATED COMPOUNDS

The reactions of only a few ketones with solutions of metals have been studied. One mole of acetone reacts with 1 gram-equivalent of sodium without evolution of any gas, but the reaction product has not been definitely characterized (261). Benzophenone in ammonia solution reacts with one equivalent of sodium to form a monosodium ketyl, $(C_6H_5)_2CONa$, and with two equivalents to form a disodium ketyl, $(C_6H_5)_2CNaONa$ (261, 235, 261, 357, 432, 433, 438). A salt of the composition $C_7H_8O_2K$ has been obtained by the action of potassium on dimethylpyrone (357). 3-Phenylcyclopentanone and sodium in ammonia react to form a yellow oil which in turn reacts with ethyl chloroacetate (in ether) to form (phenylcyclopentylidene)phenylcyclopentanone (416). 2-Methoxy-5-methyl-2,7 naphthitadiene-1,4-dione forms a sodium salt by reaction with sodium in liquid ammonia (94).

The reduction of two chlorine-substituted ketones has been studied, but the

results are not entirely conclusive. α-Chloroacetophenone reacts in liquid ammonia with 2.2 atoms of sodium to give a nitrogen- and chlorine-free reddish oil (45 per cent by weight of original ketone) from which acetophenone (13 per cent), a colorless solid (1.3 per cent), and tar may be obtained. β-Chloropropiophenone similarly reacts with 1.53 atoms of sodium to give a nitrogen- and chlorine-free viscous oil (68.8 per cent), which solidifies to a hard resin (95).

At −33.5°C. benzophenone diethylketal reacts with sodium and potassium solutions to form sodium and potassium ethoxydiphenylmethides and the corresponding ethoxides (436).

$$(C_6H_5)_2C(OC_2H_5)_2 + 2Na \rightarrow (C_6H_5)_2C(Na)OC_2H_5 + C_2H_5ONa$$

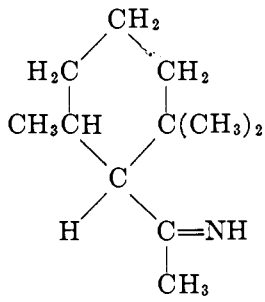
At the same time about 14.4 per cent of the acetal is doubly cleaved:

$$(C_6H_5)_2C(OC_2H_5)_2 + 4Na \rightarrow (C_6H_5)_2CNa_2 + 2C_2H_5ONa$$

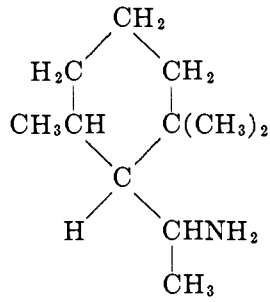
By the action of 1 gram-atom of potassium in liquid ammonia upon 1 mole of benzil, one obtains a deep blue-violet solution and, by the action of 2 gram-atoms, a deep red solution and precipitate. Neither the monopotassium nor the dipotassium salt is pure, because even at low temperatures benzil reacts with ammonia to form high-melting, nitrogen-containing products (375) that have been shown to include benzamide, triphenyloxazole, imabenzil, benzilimide, and (at higher temperatures) lophine and small quantities of tetraphenylpyrazine (281).

With solutions of sodium and potassium, benzophenoneimine reacts to form intensely red and very soluble products that cannot be freed of ammonia and excess metal for analysis. In each case, however, there is up to 50 per cent reduction to benzohydrylamine (or the product of its reaction with benzophenoneimine, i.e., benzophenonebenzohydrylamine). Other facts concerning the reaction indicate that this reduction takes place through the formation of the monosodium ketyl of benzophenoneimine, followed by ammonolysis to an equimolecular mixture of amine and imine together with sodium amide. Some disodium ketyl may be formed, but the relative quantity is very small (371). Upon treatment with excess sodium in liquid ammonia followed by ammonium bromide, benzophenoneanilide takes up four atoms of hydrogen to form diphenylmethane and aniline (110).

Two cases reported by Lochte and coworkers (283) are of particular interest in that they provide a comparison of rather strikingly different reducing systems. Methyl 2,2,6-trimethylcyclohexyl ketimine (I) is not reduced by either sodium amalgam in ethanol or hydrogen in the presence of the Adams catalyst. This apparently "hindered" imine, however, is slowly decomposed by solutions of sodium in ammonia to yield unidentified products. With sodium and methanol in ammonia, the imine is quantitatively reduced to α-methyl-2,2,6-trimethylcyclohexanemethylamine (II).

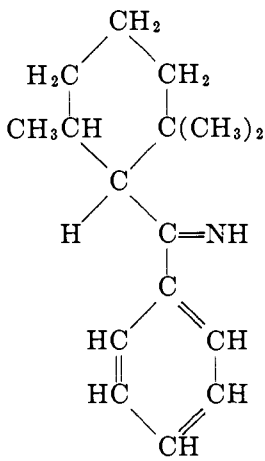


I

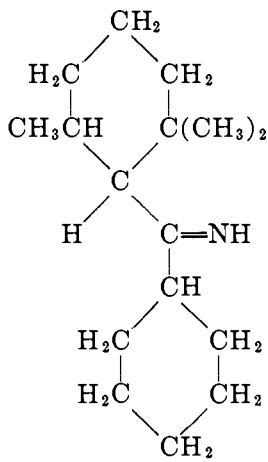


II

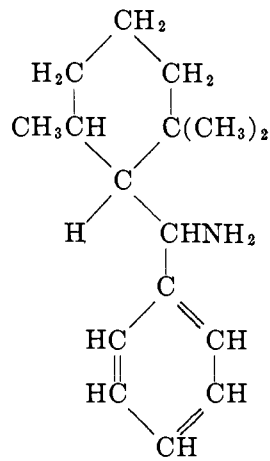
Phenyl 2,2,6-trimethylcyclohexyl ketimine (III) is not reduced by sodium amalgam in ethanol, but hydrogenation over the Adams catalyst reduces the benzene ring but not the imino group to form cyclohexyl 2,2,6-trimethylcyclohexyl ketimine (IV). On the other hand, the action of sodium in liquid ammonia reduces the imino group but not the benzene ring to provide α-phenyl-2,2,6-trimethylcyclohexanemethylamine (V). The same product, also in substantially quantitative yield, is obtained by the action of sodium and methanol in liquid ammonia.



III



IV



V

IX. CARBOHYDRATES AND RELATED SUBSTANCES

The earliest work concerned with reactions of carbohydrates with solutions of metals in liquid ammonia was that of Schmid and coworkers (359, 360), who demonstrated the rapid formation of monoalkali salts of glucose, fructose, α-methylglucoside, glycogen, inulin, soluble starch, lichenin, and chitin. Slower reactions leading to nitrogen-containing products were observed when excess alkali metal was employed.

As intermediates in the synthesis of carbohydrate derivatives, Muskat and

others (200, 285, 313, 314) have prepared (at −33.5°C.) but not isolated a number of potassium salts of carbohydrates, e.g., tetrapotassium α-methylmannoside, tripotassium monoacetoneglucose, monopotassium diacetoneglucose, monopotassium acetone methylrhamnoside (γ), monopotassium 2,3-acetone methylrhamnopyranoside, octapotassium sucrose (?), and monopotassium heptamethylisosucrose. Sugars containing potential aldehyde or ketone groups react with liquid ammonia to form the corrsponding amines. Treatment of 2,3,4-trimethyllevoglucosan with sodium in liquid ammonia at room temperature over a period of 18 days results in the formation of rather small quantities of phenol; thus, the conversion of a carbohydrate to cyclic substance is accomplished (366). Diacetone glucose reacts with sodium or potassium in ammonia to form alkali salts (125). The potassium salt melts at 150°C. with but little evidence of decomposition. These salts react with alkyl halides but do not lead to disaccharides when treated with acetohaloglucoses or diacetone-1-chloromannose.

The fact that carbohydrates containing available hydroxyl groups react with liquid ammonia solutions of alkali metals to form salts has been demonstrated repeatedly in recent years. The prevailing temperature does not appear to be at all critical, since salt formation has been reported as occurring at temperatures ranging from −80°C. up to room temperature. Salts thus produced are used most frequently in the preparation of carbohydrate derivatives, with *methylation* (*via* addition of methyl iodide in excess) being the procedure usually employed. Carbohydrates that form such salts include α-D-glucose, α-D-mannose, α-D-galactose (175), benzylideneglucosamine (90), maltose anhydride (131), partially methylated raffinose (187), partially methylated galactogen (358), partially methylated sorbitol (350), certain dextrans (286), dextrins (46, 129, 133, 288), certain hexitans and hexides (37), an insoluble polysaccharide isolated from yeast (162), and a carbohydrate residue obtained from ovomucoid (374). The attempted methylation of fructose methylphenylosazone led to cleavage of the nitrogen–nitrogen bond; the only crystalline product isolated was trimethylphenylammonium iodide (104). Since salt formation occurs in liquid ammonia with many carbohydrates that have been partially prealkylated, these salts are particularly useful in that they may be treated with suitable alkylation agents and thus afford *complete alkylation* which is commonly not accomplished by the more conventional procedures.

In a similar manner, the treatment of starch with liquid ammonia solutions of sodium or potassium results in alkali metal salts that are useful in alkylation procedures in general, most commonly methylation (46, 121, 122, 123, 124, 133, 186, 189). The starch employed may or may not be premethylated.

By regulating the quantity of alkali metal employed, cellulose may be converted to the mono-, di-, or tri-alkali salt; the latter, $[C_6H_7O_2(OM)_3]$, is stable toward excess metal solution (356, 361). Alkaline earth metals also may be employed. The alkali salts have found extensive application in the production of cellulose ethers, esters, xanthates, cellulose monoamine, etc. (25, 26, 32, 34, 121, 130, 132, 157, 309, 324, 325, 326, 352, 353, 354). According to Scherer and coworkers (354), the formation of trisodium cellulose is catalyzed by sodium halogenides. Methylcellulose forms a red sodium salt (368), α-methylglucoside

and β-methylglucoside are not reduced by sodium in ammonia, while α-methyltetramethylglucoside provides mixtures containing some unchanged glucoside. Cellulose nitrate is reduced to the monoamine (355) and cellulose ethers and esters undergo cleavage (365) upon treatment with sodium in liquid ammonia. Information relative to the conditions under which these reactions occur is not readily available; it is believed that cleavage may occur in either of the two following ways:

$$\text{Cell—O—R} + 2e^- \rightarrow \text{Cell—O}^- + \text{R}^-$$
$$\text{Cell—O—R} + 2e^- \rightarrow \text{Cell}^- + \text{R—O}^-$$

The benzyl ether reacts to form bibenzyl and cellulose, the methyl ether reacts partially in accordance with each of the schemes indicated above, while 1 mole of triacetylcellulose reacts with 6 atomic equivalents of sodium.

Studies that shed considerable light upon the chemical constitution of lignin (134) show that degradation by treatment with potassium in liquid ammonia at −33°C. or 20°C. results in extensive demethylation and formation of phenolic decomposition products (126). Spruce wood meal reacts with sodium at −33°C. to form products about one-half of which are soluble in aqueous alkali. This soluble portion contains about two-thirds of the lignin content of the original sample. Formaldehyde (potentially available from the methylenedioxy groups believed to be present in untreated lignin) cannot be liberated from lignin which has been treated with a liquid ammonia solution of potassium (120). Upon treatment with potassium solution at −50°C., cuproxam lignin is degraded in a manner such that it will not thereafter react with aniline and aniline hydrochloride to form acridan (127). In addition to phenolic products, the degradation of lignin by potassium in ammonia at room temperature results in the formation of cellulose and carbohydrate fragments (128). Under similar conditions, methylglucoside is not attacked, while phenylglucoside is degraded to glucose and other decomposition products.

X. ACIDS AND THEIR DERIVATIVES

The information concerning these compounds is summarized below under headings that are admittedly somewhat arbitrary.

A. Simple carboxylic acids

In liquid ammonia, carboxylic acids react to form ammonium salts. It has been shown that sodium acetate is unreactive, but that sodium benzoate does react with solutions of sodium in liquid ammonia (261, 351); the product in the latter case has been shown to consist of sodium dihydrobenzoate (113). Similarly, the sodium salt of α-naphthoic acid is reduced to 1,4- and (?3,4)-dihydro-α-naphthoic acids (17).

B. Acid amides, amidines, cyanamide, and dicyanodiamide

The acid amides react as monobasic acids with solutions of the alkali metals to liberate hydrogen and form salts. Sodium and potassium acetamidine have been prepared in this manner (120), as well as the sodium salts of benzenesul-

fonamide, succinimide, benzoic sulfimide, and urea (119). In studies on the reactions of acid amides with sodium in liquid ammonia at −50°C., Chablay (68, 75) observed not only the formation of sodium salts but also the reduction of a part of the amide to the corresponding alcohol:

$$3RCONH_2 + 3Na \rightarrow 3RCONHNa + 3[H]$$
$$RCONH_2 + 3[H] + Na \rightarrow RCH_2ONa + NH_3$$

Acetamide, propionamide, butyramide, and isovaleramide react rapidly, while caproamide, caprylamide, and higher homologues react only very slowly. Sodium and acetamide in liquid ammonia have been shown to react in a 1:1 mole ratio; at room temperature there is liberated only about one-fourth and at −33°C. about one-half of the expected quantity of hydrogen gas. At −33°C. benzamide reacts with more than two equivalents of sodium; dihydrobenzamide and benzyl alcohol are among the reduction products (113). Addition of methyl methacrylate to the sodium salt of formamide produced by the interaction of formamide and sodium in liquid ammonia provides monomethacrylylformamide (33). *o*-Formotoluide undergoes an intramolecular condensation when treated with potassium in liquid ammonia to form indole in 51 per cent yield (388). By reaction with sodium in ammonia, sodium *N*-phenylsulfamate is converted to the disodium salt (7), while *p*-toluenesulfonallylmethylamide yields allylmethylamine (419).

Urea reacts rapidly with solutions of the alkali metals in liquid ammonia to form the monoalkali salts and more slowly to form the dialkali salts (202). Similarly, monosubstituted ureas readily form monoalkali salts. The following have been prepared and subsequently employed in the synthesis of substituted ureas that are too numerous for inclusion here (50, 203, 204, 205, 206): monosodium, monolithium, and monopotassium ureas, disodium urea, monosodium thiourea, and monosodium methyl-, oleoyl-, benzyl-, and phenyl-ureas.

The alkaline earth metals and the very sparingly soluble magnesium exhibit similar reactions in liquid ammonia, but the resulting salts are commonly ammoniated. Thus, magnesium forms salts with acetamide, $(CH_3CONH)_2Mg \cdot 4NH_3$, benzenesulfonamide, $(C_6H_5CONH)_2Mg \cdot nNH_3$, succinimide, benzoic sulfimide, urea, and cyanamide (119, 120). With dicyanodiamide, calcium and magnesium form the salts $Ca(H_3C_2N_4)_2 \cdot 4NH_3$ and $Mg(H_3C_2N_4)_2 \cdot 2NH_3$ (117). Diphenylmethylformamidine, $C_6H_5N{=}CHN(CH_3)C_6H_5$, reacts with sodium in ammonia at room temperature to form a sodium salt (426).

C. Amino acids and proteins

The sodium salts of a number of amino acids have been prepared by Voss and Gutterman (408) by the action of liquid ammonia solutions of sodium at low temperatures, e.g., glycine, D,L-alanine, D,L-leucine, D,L-phenylalanine, sarcosine, L-tyrosine, β-alanine, γ-amino-*n*-butyric acid, and D-glutamic acid. They reported that the disodium salt of cystine could not be prepared in a satisfactory degree of purity using sodium in ammonia because of concurrent reduction to sodium cysteinate, but could be prepared pure by using sodium amide.

The reduction of cystine to cysteine (394, 400, 404) by solutions of sodium in liquid ammonia at −33.5°C.

$$S_2[CH_2CH(NH_2)COOH]_2 + 4Na \rightarrow 2NaSCH_2CH(NH_2)COONa$$

appears to be accompanied by the formation of limited quantities of sodium sulfide and alanine (137). This reaction, however, has come to be of major importance in connection with the synthesis of a wide variety of amino acids and amino acid derivatives of particular interest in biological chemistry. Largely as the result of work by du Vigneaud and his associates, it has been demonstrated that solutions of metals in ammonia constitute a valuable reagent for this type of synthesis. These reactions do not lead to racemization; hence optically active derivatives of active substances may be prepared readily by methylation, or by hydrolysis (plus oxidation) of the intermediate sodium salts. A summary of these syntheses is given in table 15. Treatment of glucosidocarbobenzyloxytyrosylglobulin with sodium in liquid ammonia fails to result in cleavage of the carbobenzyloxy residue, probably because of the very limited solubility of the parent compound (83).

Miller and coworkers (293, 306, 307, 344) have examined the reactions of solutions of sodium in liquid ammonia at its boiling point with a number of amino acids, proteins, and related substances. Listed in table 16 are the ratios of moles of hydrogen evolved to moles of substance used when the various substances and mixtures are treated with a slight excess of sodium. Similar ratios of 0.04, 0.06, and 0.32 were obtained when 0.50, 1.00, and 2.00 gram-atoms of sodium, respectively, were added per mole of diketopiperazine, and the ratio did not increase beyond 0.32 when the quantity of added sodium was increased. Together, these results lead to the following conclusions: (*1*) Glycine and alanine react as monobasic acids. (*2*) The phenolic hydroxyl group of tyrosine is slightly acidic. (*3*) Some tyrosine seems to be reduced by sodium in ammonia. (*4*) Leucine liberates more hydrogen than does a monoaminomonocarboxylic acid. (*5*) Cystine is reduced by sodium acting directly on the disulfide bond. (*6*) The peptide linkage in dipeptides is not acidic in liquid ammonia. (*7*) Diketopiperazine is reduced by sodium in liquid ammonia. (*8*) Mixtures of amino acids and of diketopiperazine do not liberate hydrogen additively, as is to be expected (307). Proteins (silk fibroin, casein, edestin, and silk) are acidic in liquid ammonia and react readily with sodium and potassium to form hydrogen and ammonolytic products containing alkali metal. The reaction of glycyl-D,L-alanine shows that the imide group of the peptide is not quantitatively reduced by sodium in ammonia. Glycine ethyl ester hydrochloride similarly treated yielded some of the glycine ester and an unidentified product, while *N*-methylacetamide was not completely reduced or decomposed (293). In general, the reactions of proteins with sodium in liquid ammonia occur more slowly than do similar reactions involving amino acids or dipeptides, and are sometimes complicated by the catalytic activity of the proteins (notably hemoglobin and hematin) toward the interaction of sodium and ammonia (38). Parathyroid hormone behaves as a typical protein toward sodium and is apparently without catalytic activity (346).

TABLE 15

Synthesis of amino acid derivatives

SUBSTANCE	PRODUCTS[a]	REFERENCES
Carbobenzoxy-β-alanine	β-Alanine, bibenzyl, toluene	(369)
β-(Phenylseleno)alanine	Diphenyl diselenide	(319)
β-(Benzylseleno)alanine	β,β'-Diselenodialanine	(319)
α-Amino-γ-(benzylseleno)butyric acid	Selenium analog of methionine	(225)
	Selenium analog of homocystine	(320)
α,α'-Diamino-γ,γ'-diselenodibutyric acid	Selenium analog of methionine	(320)
α-Amino-β-(benzylmercapto)valeric acid	α-Amino-β-mercaptovaleric acid	(88)
α-Amino-γ-benzylthio-γ-methyl-*n*-valeric acid	α-Amino-γ-thiol-γ-methyl-*n*-valeric acid	(58)
Carbobenzoxy-L-carnosine	L-Carnosine	(369)
Carbobenzoxy-D-carnosine	D-Carnosine	(399)
Cystine	*S*-Benzyl-L-cysteine	(406)
Homocystine	Sodium salt of homocysteine	(45, 397, 400, 403)
L-Cystine	1,2-Benzanthrylmethyl-*S*-L-cysteine	(427)
	L-(+)-Lanthionine	(39)
	S-Benzyl-L-cysteine	(428)
	L-β-(Carboxymethylmercapto)-alanine	(161)
Pentocystine	Sodium pentocysteinate	(398)
Hexocystine	Hexomethionine	(209)
	S-Benzylhexocysteine	(209)
Dicarbobenzoxyglycyl-L-cystine	Diglycyl-L-cystine	(59, 151)
Di-*p*-toluenesulfonyl-di-*N*-methyl-cystine	*N*-Methylcysteine	(27)
Cystine hydantoin	L-Cysteine hydantoin	(212)
Homocystine hydantoin	D,L-Homocysteine hydantoin	(212)
Cystinyldiglycine	Sodium salt of cysteinylgylcine	(284)
Carbobenzoxycystine	Sodium salt of cysteine	(369)
Dicarbobenzoxyglycyl-L-cystine	Diglycyl-L-cystine	(151)
N,N'-Dimethyl-*N,N'*-bis(*p*-toluenesulfonyl)cystine	*S*-Benzyl-*N*-methylcysteine	(222)
S-Benzylcysteine	Sodium salt of cysteine	(369)
	Cystine	(316)
S-Benzyl-D-cysteine	D-Cystine	(428)
	D-(−)-Lanthionine	(39)
S-Benzyl-D-homocysteine	Sodium D-cysteinate	(403)
S-Benzyl-L-cysteine	Sodium L-cysteinate	(403)
	Mesolanthionine	(396)
S-Benzyl-D,L-cysteine	D,L-Cystine	(429)
S-Benzylhomocysteine	*S*-(β-Amino-β-carboxyethyl)homocysteine	(38)
	Ethionine	(103)
S-Benzylhomocysteine-β,γ-d_2	Methionine-β,γ-d_2[b]	(323)
	Homocystine-β,β',γ,γ'-d_4	(323)
S-Benzyl-L-homocysteine	Sodium L-cysteinate	(403)
S-Benzyl-D,L-homocysteine	Sodium homocysteinate, bibenzyl, some toluene	(322, 385)

TABLE 15—*Concluded*

SUBSTANCE	PRODUCTS[a]	REFERENCES
S-Benzyl-*N*-methylcysteine	*N*,*N*'-Dimethylcystine	(222)
S-Benzyl-*N*-methylhomocysteine	Sodium cysteinate	(321)
L-*S*-Benzyl-β,β-dimethylcysteine	L-5,5-Dimethyl-4-carboxythiazolidine	(418)
D-*S*-Benzyl-β,β-dimethylcysteine	D-5,5-Dimethyl-4-carboxythiazolidine	(418)
S-Benzyl-β,β-dimethylcysteine	D,L-β,β-Dimethylcysteine (D,L-penicillamine)	(315)
D,L-Methionine	*S*-Benzyl-D,L-homocysteine	(376)
	N-Dibenzyl-*S*-Benzyl-D,L-homocysteine	(376)
N-Carbobenzoxy-*S*-benzylcysteine	Tyrosylcysteine	(160)
Cysteinylglycine	Sodium salt	(284)
Dicarbobenzoxycystinyldiglycine	Cystinyldiglycine	(284)
N-Carbobenzoxy-γ-glutaminyl-*S*-benzylcysteinylglycine	Glutathione	(402)
N-Carbobenzoxy-α-glutamyl-*S*-benzylcysteinylglycine	Isoglutathione	(401)
Carbobenzoxy-β-aspartyl-*S*-benzylcysteinylglycine	Asparthione	(304)
Benzyl ester of β-(benzylmercapto)-*N*-(N^{α}-carbobenzoxyglutaminyl)-alanine	*N*-Glutaminylcysteine	(158)
N-*p*-Toluenesulfonylisoglutamine	*N*-Carbobenzyloxyisoglutamine	(159)
N^{α}-[β-(Benzylmercapto)-*N*-carbobenzoxyalanyl]glutamine	N^{α}-(β-Mercaptoalanyl)glutamine, bibenzyl	(158)
S-Benzylhomocysteine hydantoin	D,L-Homocysteine hydantoin	(212)
S-Benzyl-*N*-carbobenzyloxycysteyltyrosine	Cysteyltyrosine	(160)
L-Histidine	Sodium salt	(395)
p-Toluenesulfonyl-*N*-methyl-1(or 3)-benzyl-L-histidine	L-Amino-*N*-methylhistidine	(395)
α-Amino-β-benzylmercaptobutyric acid	α-Amino-β-thiolbutyric acid	(57)
O-β-Glucosido-*N*-carbobenzyloxytyrosylgelatin	*O*-β-Glucosidotyrosylgelatin	(82)
D-Homocysteinediketopiperazine	*S*-Benzyl-D-homocysteinediketopiperazine	(405)
L-Homocysteinediketopiperazine	*S*-Benzyl-L-homocysteinediketopiperazine	(405)
Polymers from D- and L-homocysteinediketopiperazine	*S*-Benzyl-D(or L-)-homocysteinediketopiperazine	(405)

[a] See footnote to table 1.

[b] The synthesis of D,L-methionine containing C^{13} in the β- and γ-positions, and S^{34} has been reported by Kilmer and du Vigneaud (224). Similarly, Melville, Rachele, and Keller (298) have prepared L-methionine containing C^{14} in the methyl group.

Peptones behave as acids in liquid ammonia and liberate hydrogen upon treatment with sodium. These substances are more acidic than diketopiperazine but less acidic than amino acids or proteins; in general, peptones behave in a manner that suggests that they contain more diketopiperazine than do proteins (308). The behavior of insulin toward sodium in ammonia is similar to that of casein, egg albumin, edestin, and silk fibroin (343). So far as its capacity in the lowering of blood sugar is concerned, insulin is inactivated completely by treatment with sodium in ammonia. The digestibilities of egg albumin, silk fibroin, and wool are increased by the action of sodium in liquid ammonia, that of casein is decreased, while that of peptone is uninfluenced (294). According to Brown and du Vigneaud (40) the physiological activity of biotin is not destroyed by

TABLE 16

Reactions of amino acids and related substances with solutions of sodium in liquid ammonia

SUBSTANCE	MOLES OF H_2/MOLE OF SUBSTANCE	
Glycine	0.50	
Alanine	0.48	0.48
Tyrosine	0.65	0.67
Glycolic acid	0.94	0.96
L-Cystine	0.53	0.55
L-Leucine	0.64	
Diketopiperazine	0.32	
Glycylglycine	0.51	
Glycyl-D,L-alanine	0.51	0.52
N-Methylacetamide	0.53	0.54
Acetanilide	0.05	0.06
Glycylglycine and diketopiperazine, mole ratio 1:1	0.02	0.02
Glycylglycine (2 moles), and diketopiperazine (1 mole)	0.05	0.05
Glycine and tyrosine, mole ratio 1:1	0.39	
Glycine 53.3 per cent, alanine 31.1 per cent, tyrosine 15.6 per cent	0.36	

exposure to the strong reducing action of sodium in liquid ammonia. A quantitative separation of the alkaloids anabasine and lupinine that is useful for large-scale operations has been accomplished by treating the mixtures with sodium in liquid ammonia. The insoluble sodium lupinate is removed by filtration (349).

D. Esters

Nearly forty years ago Chablay (68, 76) observed that treatment of esters of carboxylic acids with solutions of sodium in liquid ammonia at −50°C. resulted in two reactions:

$$RCOOR' + 2Na + NH_3 \rightarrow RCONHNa + R'ONa + H_2$$
$$RCOOR' + H_2 + 2Na \rightarrow RCH_2ONa + R'ONa$$

These reactions were observed using the following esters: ethyl acetate, methyl butyrate, methyl isovalerate, ethyl caproate, and methyl caprylate. Esters dissolved in absolute ethanol and added to solutions of sodium in ammonia at −80°C. were reduced as shown by the equation (70):

$$RCOOR' + 2C_2H_5OH + 4Na \rightarrow RCH_2ONa + 2C_2H_5ONa + R'ONa$$

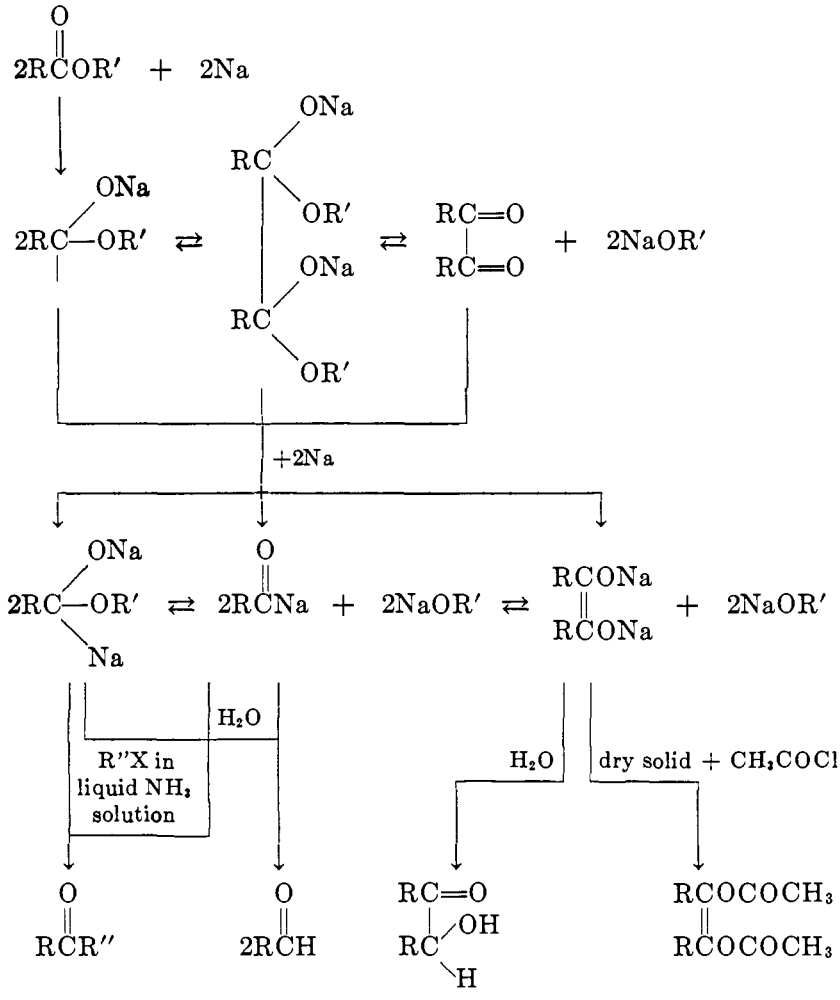
The esters treated in this manner and the alcohols obtained as products are listed in table 17.

TABLE 17

Reactions of esters with solutions of sodium in liquid ammonia in the presence of ethanol

ESTER REDUCED	ALCOHOLS OBTAINED
Esters of monocarboxylic acids:	
Methyl *n*-butyrate	Butanol
Methyl isovalerate	Isoamyl alcohol
Ethyl caproate	Hexanol
Methyl heptylate	Heptanol
Methyl caprylate	Octanol
Methyl laurate	Dodecanol ($C_{12}H_{25}OH$)
Methyl myristate	Tetradecanol ($C_{14}H_{29}OH$)
Methyl palmitate	Hexadecanol ($C_{16}H_{33}OH$)
Esters of dicarboxylic acids:	
Methyl sebacate, $CH_3OCO(CH_2)_8COOCH_3$	1,10-Decanediol
Dimethyl α,α'-dimethylglutarate, $CH_3OCOC(CH_3)_2(CH_2)_2COOCH_3$	2,2-Dimethyl-1,5-pentanediol
Esters containing an aromatic radical:	
Ethyl phenylacetate, $C_6H_5CH_2COOC_2H_5$	Phenethyl alcohol, $C_6H_5CH_2CH_2OH$
Methyl cinnamate, $C_6H_5CH{=}CHCOOCH_3$	β-Phenylpropyl alcohol, $C_5H_5(CH_2)_2CH_2OH$

More recently, Kharasch and coworkers (219, 220) have made extensive studies of the reactions between esters and liquid ammonia solutions of sodium at −33.5°C. These studies show that liquid ammonia is an advantageous medium for the conduct of such reactions since they occur rapidly, completely, and in an entirely homogeneous system. In this reaction medium it is also possible to study intermediate stages of reduction by using carefully controlled ratios of sodium to ester and thereby gain information relating to reaction mechanisms and the identity of intermediate products. In general, they have found that one mole of an ester reacts with one equivalent of sodium to form a free radical while the use of two equivalents of sodium results in the formation of very reactive sodium salts. The mechanism of these reactions is believed to be represented best by the following scheme (220):



In terms of the products finally isolated, the results obtained using the indicated ethyl esters are given in table 18, which is essentially that published by Kharasch *et al.* (220).

The cleavage of alkenyl esters by sodium in ammonia at −33.5°C. occurs as shown by the equation (370):

$$CH_3COOC(R)=CH_2 + 2Na \rightarrow CH_2=CHONa + CH_2=C(R)ONa$$

Thus, amyl methyl ketone is produced in 77 per cent yield by the cleavage of 2-acetoxy-1-heptene, followed by hydrolysis. Similarly, the cleavage of 2,4,6-tri-*tert*-butylphenyl benzoate followed by hydrolysis yields benzoic acid and 2,4,6-tri-*tert*-butylphenol (377). Treatment of the methyl ester of α-monodehydrodoisynolic acid with sodium and ethanol in liquid ammonia at −40°C. provides diastereomeric 7-methyldoisynolic acids (6).

TABLE 18

Reactions of esters with solutions of sodium in liquid ammonia

ETHYL ESTER	ATOMS OF Na PER MOLE OF ESTER	OTHER REAGENTS	YIELDS OF IDENTIFIED PRODUCTS[a]			
			Acyloin	Diketone	Aldehyde	Other products
			per cent	*per cent*	*per cent*	
Acetic	2		25			8% β-aminocrotonic ester, 25% acetic acid
Acetic	2	Acetyl chloride				83% acetoin diacetate
Acetic	1			Trace		
Propionic	2		22			24% propyl alcohol, 10% propionamide, 30% propionic acid
Propionic	1			18		46% propionic acid, 12% propionamide
Isobutyric	2		12		30	10% isobutyl alcohol, 25% isobutyric acid, 8% isobutyramide
Isobutyric	2	Ethyl bromide	28			32% ethyl isopropyl ketone
Trimethylacetic	2		29		35	15% *tert*-butyl carbinol, 6% trimethylacetic acid, 10% trimethylacetamide
Trimethylacetic	2	Ethyl bromide	22			33% ethyl *tert*-butyl ketone
Phenylacetic	2				7	27% phenethyl alcohol, 31% phenylacetamide
Diphenylacetic	2		11			36% diphenylethyl alcohol, 18% benzophenone, 32% diphenylacetic acid
Benzoic	2		14		50	9% benzamide, 12% benzoic acid
Benzoic	2	Benzyl chloride	15		30	5% desoxybenzoin, 10% isobenzamarone, 8% bibenzyl, 15% benzoic acid
Benzoic	2	Ethyl bromide	27			34% propiophenone
Benzoic	2	*n*-Butyl bromide	20			30% valerophenone
Benzoic	1			30		28% benzilic acid, 25% benzoic acid

[a] Based on ester used. In all cases there were unidentified substances, some of them tars.

E. Nitriles

Sodium in liquid ammonia reacts vigorously with α-tolunitrile to form a sodium salt,

$$C_6H_5CH_2CN + Na \rightarrow C_6H_5CHNaCN \text{ (or } C_6H_5CH{=}CNNa) + \tfrac{1}{2}H_2$$

which reacts with alkyl halides to form α-alkyl-α-tolunitriles. Some toluene (and presumably sodium cyanide) accompanies the formation of the sodium salt (12). Benzonitrile reacts rapidly with two equivalents of sodium to give a wine-red solution and a white precipitate; the reaction products have not been identified but only traces of cyanide are formed (261). 2,2,6-Trimethylcyclohexanecarbonitrile is decomposed slowly by the action of solutions of sodium at −33.5° C. With sodium and methanol, however, this compound is reduced smoothly and completely to 2,2,6-trimethylcyclohexanemethylamine (283). Treatment of 3,5-dimethylbenzyl cyanide with sodium in ammonia leads to the formation of a sodium salt which reacts with methyl iodide to give 2-(3,5-dimethylphenyl)-2-cyanopropane (372). In addition, some mesitylene is formed by the reductive cleavage of a carbon–carbon bond.

XI. NITROSO, NITRO, AZOXY, AND AZO COMPOUNDS. DERIVATIVES OF HYDROXYLAMINE AND HYDRAZINE

The interaction of sodium in liquid ammonia at −33.5°C. and nitrosoguanidine results in extensive degradation; cyanamide (10 per cent) and elemental nitrogen (27–30 per cent) are among the products (136). Nitrosobenzene reacts with solutions of either sodium or potassium to form dialkali phenylhydroxylamines (421).

$$C_6H_5NO + 2Na \rightarrow C_6H_5N(Na)ONa$$

In its reactions with solutions of sodium, the behavior of nitroguanidine is similar to that of the nitroso compound. If, however, sodium is added to solutions containing nitroguanidine together with ammonium chloride, aminoguanidine is formed (136) in yields as high as 70 per cent if the nitroguanidine–sodium ratio is at least 1:6. Nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, and 2-nitrobutane, which exist in liquid ammonia in the form of the corresponding ammonium salts, are not reduced at −33.5°C. by hydrogen arising from the interaction of sodium and ammonium bromide (411). These nitroparaffins are, however, reduced slowly and incompletely by liquid ammonia solutions of sodium to the corresponding alkylhydroxylamines.

The reduction of nitrobenzene by solutions of sodium in ammonia is of considerably greater complexity than has been recognized on the basis of published work. The reactions involved appear to lead to a variety of products that may differ with only slight changes in the experimental conditions employed. White and Knight (421) reported that nitrobenzene reacts with either sodium or potassium to form the dialkali phenylhydroxylamines,

$$C_6H_5NO_2 + 4Na + NH_3 \rightarrow C_6H_5N(Na)ONa + NaNH_2 + NaOH$$

while with an excess of sodium the product is probably disodium anilide:

$$C_6H_5N(Na)ONa + 2Na + NH_3 \rightarrow C_6H_5NNa_2(?) + NaNH_2 + NaOH$$

More recent experiments (413) show that slow addition of nitrobenzene to solutions of sodium in ammonia at −33.5°C. (i.e., sodium in excess) until the char-

acteristic blue color is discharged, leads to a blood-red ammonia solution and a reaction ratio of 4 gram-atoms of sodium per mole of nitrobenzene. At the end-point in the titration, the blue color is sharply replaced by the red and the end-point is readily reproducible. Addition of an excess of ethyl bromide provides a reaction mixture from which is obtained a small quantity of azobenzene and a yellow oil as the major product. Upon nitration, the latter yields two crystalline solids that have not yet been identified. Still different are the reactions observed in the presence of a source of active hydrogen. When water is added to partially reduced nitrobenzene in liquid ammonia, azoxybenzene and azobenzene result from the familiar reactions of phenylhydroxylamine in alkaline aqueous solution (421). Addition of sodium to liquid ammonia solutions containing nitrobenzene and either ammonium bromide or methanol provides high yields of aniline (412), which may be further reduced to 2,5-dihydroaniline (rapid reaction) or by a slower reaction to a tetrahydroaniline (24). From these and other experimental results it is evident that the reduction of nitrobenzene in ammonia warrants further study.

The reduction of 1-nitronaphthalene to dihydro-1-naphthylamine in 97 per cent yield by means of sodium in ammonia at −33.5°C. proceeds slowly because of the very limited solubility of the nitro compound (412). Upon addition of sodium to liquid ammonia containing 1-nitronaphthalene and ammonium bromide, reduction proceeds only to 1-naphthylamine in yields that are low but which may be increased to about 60 per cent by the use of toluene as a cosolvent. Under conditions similar except for the substitution of methanol for ammonium bromide, the product consists of a mixture of di- and tetra-hydro-1-naphthylamines, with the former predominating. 2-Nitrofluorene is reduced to tetrahydro-2-aminofluorene in 89 per cent yield by sodium in ammonia. The same compound is unreactive toward sodium and ammonium bromide, while sodium and methanol reduce 2-nitrofluorene to a mixture of tetra- and hexa-hydro-2-aminofluorenes.

The reduction of azoxybenzene by sodium in ammonia yields azobenzene, which in turn is reduced to the disodium salt of hydrazobenzene (421).

$$C_6H_5N{=}NC_6H_5 + 2Na \rightarrow C_6H_5N(Na)N(Na)C_6H_5$$

When 1 mole of azobenzene is treated with 2 gram-atoms of sodium, followed by an excess of ethyl iodide, *sym*-diethyldiphenylhydrazine results (108). Use of 4 gram-atoms of sodium provides the same product, together with ethane and ethylamine resulting from the action of sodium and ammonia upon the excess ethyl iodide. On the basis of these results, it is apparent that an earlier report (421) to the effect that the reaction involving 4 gram-atoms of sodium results in the formation of diethylaniline is in error. Azobenzene is reduced to aniline by the action of sodium and ammonium bromide (108).

Contrary to earlier reports (421), it has been shown (235) that the nitrogen–nitrogen bond in disodium benzhydrazide is not ruptured by an excess of sodium. Phenylhydroxylamine (421) is reduced directly to aniline without liberation of hydrogen,

$$C_6H_5NHOH + 2Na + NH_3 \rightarrow C_6H_5NH_2 + NaOH + NaNH_2$$

perhaps through the intermediation of monosodium anilide and its subsequent ammonolysis, thus:

$$C_6H_5NHOH + 2Na \rightarrow C_6H_5NHNa + NaOH$$
$$C_6H_5NHNa + NH_3 \rightarrow C_6H_5NH_2 + NaNH_2$$

The reaction between phenylhydrazine and sodium in liquid ammonia at its boiling point may be described by the equation (108):

$$2C_6H_5NHNH_2 + 2Na \rightarrow C_6H_5N(Na)NH_2 + C_6H_5NHNa + NH_3$$

The resulting monosodium salt of phenylhydrazine reacts with alkyl halides to form the corresponding alkylphenylhydrazines, and it has been demonstrated

TABLE 19

Reduction of substituted hydrazines in liquid ammonia

(R = C_6H_5—)

SUBSTITUTED HYDRAZINE	REDUCING SYSTEM	PRODUCTS REPORTED
$RNHNH_2$	Na	$RNNaNH_2$, RNHNa, NH_3
$RNKNH_2$	Na	No reaction
$RNHNH_2$	Na, NH_4Br	RNH_2
$RNKNH_2$	Na, NH_4Br	RNH_2
RNHNHR	Na	RNHNa
RNKNKR[a]	Na	No reaction
RNHNHR	Na, NH_4Br	RNH_2
RNKNKR	Na, NH_4Br	RNH_2
R_2NNH_2	Na	R_2NNa, $NaNH_2$
R_2NNHK	Na	R_2NNa, $NaNH_2$, KNH_2
R_2NNH_2	Na, NH_4Br	R_2NH
$RC_2H_5NNH_2$	Na	RC_2H_5NNa, $NaNH_2$
RC_2H_5NNHK	Na	RC_2H_5NK, $NaNH_2$
$RC_2H_5NNH_2$	Na, NH_4Br	RC_2H_5NH
$RC_6H_5CH_2NNH_2$	Na, NH_4Br	RNH_2, RCH_3(?)
$RC_6H_5CH_2NNHK$	Na	RNH_2, RCH_3(?)
RC_2H_5NNHR	Na	RC_2H_5NNNaR, RC_2H_5NH, RNH_2
RC_2H_5NNKR	Na	No reaction
RC_2H_5NNHR	Na, NH_4Br	RC_2H_5NH, RNH_2
R_2NNR_2	Na	R_2NNa
$RC_2H_5NNC_2H_5R$	Na	RC_2H_5NNa
$RC_2H_5NNC_2H_5R$	Na, NH_4Br	RC_2H_5NH
$R_2C{=}NNH_2$[b]	Na, NH_4Br	R_2CH_2
$RCH_3C{=}NNH_2$[b] [c]	Na, NH_4Br	$RCHNH_2CH_3$

[a] Converted to $RC_2H_5NNC_2H_5R$ by treatment with ethyl iodide.

[b] *Cf.* Section VIII.

[c] Reaction with sodium alone is slow, and the end-point is difficult to detect.

that this constitutes a broadly applicable method for the synthesis of α-alkylarylhydrazines (8). In this method, yields are increased by forming the monosodium salt through use of sodium amide rather than sodium, because as shown

by the foregoing equation, the reaction with sodium converts half of the starting material to sodium anilide owing to bond rupture by the liberated hydrogen.

Extensive studies of the reduction of substituted hydrazines by means of sodium or sodium and ammonium bromide in liquid ammonia at its boiling point have been made by Fernelius and coworkers (108, 110). From the results summarized in table 19, the following conclusions have been drawn: (*1*) In all cases, the N—N bond in substituted hydrazines is ruptured by sodium and ammonium bromide; (*2*) if two phenyl groups, or one phenyl and another group, are attached to the same nitrogen atom, the N—N bond is ruptured by sodium alone; (*3*) sodium replaces the active hydrogen in substituted hydrazines, and the hydrogen thereby liberated serves to reduce the N—N bonds.

Hydrazotriphenylmethane and hydrazophenylfluorene [*s*-bis(9-phenyl-9-fluoryl)hydrazine], $C_6H_5C_{13}H_8NHNHC_{13}H_8C_6H_5$, react vigorously with sodium in liquid ammonia at 0°C. to form products (probably sodium salts) which upon treatment with water yield triphenylmethane (90 per cent) and 9-phenylfluorene, respectively (334).

XII. HETEROCYCLIC COMPOUNDS

Among the earliest observations relating to the behavior of heterocyclic ring systems toward solutions of metals in liquid ammonia were those of E. C. Franklin (116). It was found that pyrrole discharges the blue color of solutions of potassium in ammonia with evolution of hydrogen, but the potassium salt so formed could not be crystallized. Calcium and magnesium react similarly, and the solubility of the salts is such as to permit their isolation: $(C_4H_4N)_2Ca \cdot 4NH_3$ and $(C_4H_4N)_2Mg \cdot 2NH_3$. That there is little reduction of pyrrole to tetrahydropyrrole is attested by the fact that 91.6 per cent of the anticipated quantity of hydrogen was collected from one reaction employing calcium. Pyrrole is not effectively reduced by sodium and ammonium bromide in liquid ammonia at its boiling point (106).

Franklin (116) also prepared the calcium and magnesium salts of indole, $(C_8H_6N)_2M \cdot 4NH_3$. Failure to obtain much more than half of the expected amount of hydrogen from the reaction with calcium suggested that extensive reduction to dihydroindole must also occur. More recently (108) it has been shown that 90 per cent of the hydrogen expected from the reaction between indole and sodium reacts further to form 2,3-dihydroindole.

In his experiments with carbazole, Franklin (116) observed that the reduction with potassium solutions is so extensive that only a very small quantity of hydrogen is liberated and the solutions become intensely colored. Subsequent experiments have shown that carbazole reacts with sodium solutions to form 1,4-dihydrocarbazole (106), while the same product together with 1,2,3,4-tetrahydrocarbazole is produced when sodium and ammonium bromide are used (108). *N*-Methylcarbazole is not reduced by sodium in liquid ammonia, but is converted to a dihydro-*N*-methylcarbazole upon treatment with sodium and ammonium bromide (109).

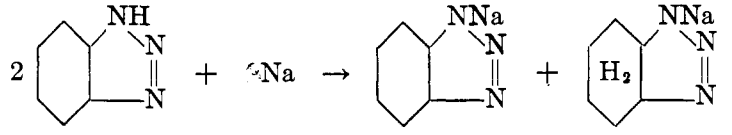
The work of W. C. Fernelius and his students (55, 107, 108. 110, 112, 113) on

TABLE 20

Reduction of triazoles in liquid ammonia

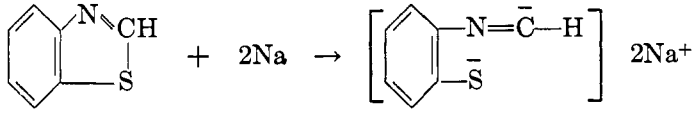
TRIAZOLE	REDUCING SYSTEM	PRODUCTS IDENTIFIED	NOTES	REFERENCES
1,2,3-Benzotriazole	Na	Sodium 1,2,3-benzotriazolate, sodium salt of dihydro-1,2,3-benzotriazole	No hydrogen liberated	(55)
		o-Phenylenediamine		(110)
Sodium 1,2,3-benzotriazolate	Na		No further reduction	(55)
	Na, NH_4Br	*o*-Phenylenediamine		(55)
1(or 2)-Methyl-1,2,3-benzotriazole	Na		No further reduction	(55)
2-Methyl-1,2,3-benzotriazole	Na, NH_4Br	*o*-Phenylenediamine		(55)
1-Methyl-1,2,3-benzotriazole	Na, NH_4Br	*N*-Methyl-*o*-phenylenediamine		(55)
4(7)-Methyl-1,2,3-benzotriazole	Na	2,3-Diaminotoluene, unchanged triazole	No hydrogen liberated	(110)
	Na, NH_4Br	2,3-Diaminotoluene		(110)
1-Methoxy-1,2,3-benzotriazole	Na	1,2,3-Benzotriazole		(112)
	Na, NH_4Br	*o*-Phenylenediamine		(112)
1-Methyl-1,2,3-benzotriazole 3-oxide	Na		Slow reaction, indefinite end-point	(112)
	Na, NH_4Br	*N*-Methyl-*o*-phenylenediamine		(112)
1-Hydroxy-1,2,3-benzotriazole	Na	1,2,3-Benzotriazole, sodium hydroxide	No hydrogen liberated	(112)
	Na, NH_4Br	*o*-Phenylenediamine		(112)
5-Hydroxy-1,2,3-benzotriazole	Na		No hydrogen liberated	(108)
	Na, NH_4Br	3,4-Diaminophenol		(113)
1(or 3)-Naphtho[1,2]-triazole	Na		No hydrogen liberated; some starting material recovered	(107)
1-Hydroxynaphtho-[1,2]triazole	Na	Sodium naphtho[1,2]-triazolate, sodium hydroxide		(107)
	Na, NH_4Cl	1,2-Diaminonaphthalene (small amount)	Complex mixture of products	(107)

the reduction of 1,2,3-benzotriazole and related compounds by means of sodium or sodium and ammonium bromide in liquid ammonia at its boiling point has provided some interesting comparisons of the relative effectiveness of these two reducing systems. The gross results of these studies are summarized in table 20. Cappel and Fernelius (55) postulated that the reaction between sodium in liquid ammonia at −33.5°C. and 1,2,3-benzotriazole results in the formation of an equimolar mixture of the sodium salt of the original compound and the sodium salt of an unstable dihydrobenzotriazole, without evolution of hydrogen:



In later experiments (110), however, the identification of *o*-phenylenediamine as one of the reaction products shows that the reactions are more complicated than originally believed and that the exact stoichiometry of the reactions has not yet been established. In connection with these studies, it is of particular interest to note that hydrogen displaced from 1,2,3-benzotriazole reduces the benzenoid ring, while that arising from the reaction between sodium and ammonium ions reduces the heterocyclic ring. Furthermore, it has been shown that hydrogen generated by the catalyzed interaction of potassium and ammonia is less effective in the reduction of the triazole than is hydrogen from ammonium ion.

Benzoxazole and benzothiazole are reduced by sodium in ammonia at −33.5°C. to sodium salts which are formed upon rupture of the heterocyclic rings (226), for example:



From these salts the corresponding bases are obtained by treatment with ammonium or ethyl bromide, or the corresponding aminophenols or thiophenols by hydrolysis of either the bases or the sodium salts. At the same temperature, hydrogen and ammonium bromide provide more extensive reduction, e.g., benzoxazole is reduced to *o*-(methylamino)phenol. Under the conditions of the experiments referred to above, 2-phenylbenzoxazole and 2-chlorobenzothiazole appear to exhibit similar behavior.

Several years ago, Wood and Bergstrom (426) observed that benzimidazole reacts with sodium in ammonia to liberate hydrogen and form a monosodium salt. More recently, Fernelius and Wesp (113) have confirmed this report and have shown that the hydrogen liberated does not participate appreciably in secondary hydrogenation reactions. Benzimidazole and 2-methylimidazole, however, react with sodium and ammonium bromide to form unstable dihydro compounds which are ammonolyzed or hydrolyzed to *o*-phenylenediamine and ammono or aquo aldehyde. 2-Phenylbenzimidazole differs in that the benzene ring of the ammonobenzaldehyde is reduced to a cyclohexyl ring. With sodium alone at room temperature, 2-phenylbenzimidazole yields 2-cyclohexylbenzimi-

TABLE 21

Reactions of heterocyclic compounds with solutions of metals in liquid ammonia

COMPOUND	REDUCING SYSTEM	PRODUCTS[a]	REFERENCES
Imidazole	Mg	$(C_3H_3N_2)_2Mg$, H_2	(417)
1,2,4-Triazole	Ca	Calcium salt	(381)
	Mg	Magnesium salt	(381)
Tetrazole	Ca	Calcium salt	(381)
2,4,5-Triphenylimidazole (lophine)	Ca	Calcium salt	(381)
	Mg	Magnesium salt	(381)
2-Phenyl-4-hydroxymethyl-1,3-dithiolan	Na, C_2H_5OH	2,3-Dimercaptopropanol	(378)
2-Methyl-4-hydroxymethyl-1,3-dithia-2-arsacyclopentane	Na, C_2H_5OH	2,3-Dimercaptopropanol	(378)
2-Amino-4-chloropyrimidine	Na	2-Aminopyrimidine	(267)
2-Amino-4-iodopyrimidine	Na	2-Aminopyrimidine	(267)
2-Amino-4-methyl-6-chloropyrimidine	Na	2-Amino-4-methylpyrimidine	(267)
2-Amino-4,6-dibromopyrimidine	Na	2-Aminopyrimidine	(267)
Pyridine	Na[b]	$(C_5H_5NNa)_2 \cdot NH_3$[c]	(278)
2-Methylpyridine	Na, C_2H_5OH	Dihydro-2-methylpyridine	(22)
2,4-Dimethylpyridine	Na, C_2H_5OH	Dihydro-2,4-dimethylpyridine	(22)
2,6-Dimethylpyridine	Na, C_2H_5OH	Dihydro-2,6-dimethylpyridine	(22)
2,4,6-Trimethylpyridine	Na, C_2H_5OH	Dihydro-2,4-6-trimethylpyridine	(22)
Quinoline	Na	Dihydroquinoline	(227)
	Na, NH_4Br	Dihydroquinoline	(227)
5-Aminoquinoline	Na	Dihydro-5-aminoquinoline	(227)
	Na, NH_4Br	Dihydro-5-aminoquinoline	(227)
5-Nitroquinoline	Na	Dihydro-5-aminoquinoline	(227)
	Na, NH_4Br	Dihydro-5-aminoquinoline	(227)
8-Aminoquinoline	Na	Dihydro-8-aminoquinoline	(227)
	Na, NH_4Br	Dihydro-8-aminoquinoline	(227)
8-Nitroquinoline	Na	Dihydro-8-aminoquinoline	(227)
	Na, NH_4Br	Dihydro-8-aminoquinoline	(227)
Phenacylquinoline	Na	Not reduced at −33° or 20°C.	(15)
Dibenzothiophene[d]	Na	1,4-Dihydrodibenzothiophene (85%)	(143)
Dibenzofuran[d]	Na	1,4-Dihydrodibenzofuran (82%)	(29, 142)
4-Hydroxydibenzofuran	Na	1,4-Dihydro-6-hydroxydibenzofuran	(142)
4-Methoxydibenzofuran	Na	Dihydrodibenzofuran (26%)	(142)
3-Aminodibenzofuran	Na	Tars	(142)
4-Aminodibenzofuran	Na	Tars	(142)
3-Diethylaminodibenzofuran	Na	Tars	(142)

[a] See footnote to table 1.

[b] At both room temperature and −60°C.

[c] This compound reacts with alkyl halides to form noncrystallizable ether-soluble basic products and yields a hydrate of tetrahydrodipyridyl, $(C_5H_6N)_2 \cdot H_2O$, upon decomposition with 95 per cent ethanol and small quantities of water in the presence of ether.

[d] There is some evidence (106) that these compounds may be reduced beyond the dihydro stage, presumably to the hexahydro compounds.

dazole. In their reactions with sodium at −33°C. both 2-phenylbenzimidazole and its potassium salt show indefinite end-points and yield mixtures of products. At −33°C. 1-methyl- and 1,2-dimethyl-benzimidazoles add two atoms of sodium; the action of sodium and ammonium bromide does not reduce these compounds beyond the dihydro stage.

The interaction of piperonylic acid and sodium or potassium at −70°C. results in rupture of the heterocyclic ring and the formation of *m*-hydroxybenzoic acid (127). Solutions of potassium at −70°C. reduce dihydrosafrole to *p*-hydroxypropylbenzene. Experiments involving reduction by liquid ammonia solutions of potassium at 20°C. show that this treatment ruptures the coumaran ring in diisoeugenol and its methyl ether, and the coumarone ring in egonal. Under the same conditions, scission of the heterocyclic ring in D,L-epicatechin does not occur.

The amidosulfonic acid derived from vitamin B_1 reacts with sodium in ammonia to form low yields of 2,5-dimethyl-6-aminopyrimidine (81, 424).

Information relating to reactions of other heterocyclic compounds is incorporated in table 21.

XIII. ORGANIC COMPOUNDS OF SULFUR

The reducing action of solutions of sodium in liquid ammonia toward certain organic sulfur compounds has been made the basis for the development of an analytical method for the determination of sulfur in such compounds. Sodium sulfide and/or sulfite formed in the reduction reactions are oxidized by means of sodium peroxide and precipitated as barium sulfate. Compounds satisfactorily analyzed for sulfur by this method include: thiourea, benzoyl sulfimide, acetone diethyl sulfone, diphenyl sulfone, dinitrophenyl thiocyanate, benzenesulfonamide, benzenesulfonyl chloride, *n*-propyl *p*-toluenesulfonate, *p*-toluenesulfonic acid, and 2-naphthylamine-5,7-disulfonic acid (373).

Alkyl mercaptans (244, 425) and phenyl mercaptan (244, 260, 422) react with liquid ammonia to form ammonium salts which in turn react with sodium to form the corresponding sodium mercaptides. The reduction of 4,4-bishydroxymethyl-1,2-dithiacyclopentane by sodium in liquid ammonia provides an 87.5 per cent yield of dithiopentaerythritol $(CH_2OH)_2C(CH_2SH)_2$ (10).

Aliphatic sulfides (ethyl, *n*-propyl, and *n*-heptyl) react with sodium in ammonia chiefly according to the equation,

$$R_2S + 2Na + NH_3 \rightarrow RSNa + RH + NaNH_2$$

although the observed ratio of sodium ethylmercaptide to sodium amide suggests the occurrence of a concomitant reaction, such as (425):

$$2R_2S + 2Na \rightarrow 2RSNa + RR$$

Addition of an ether solution of 2,3-dithia-5-spirodecane to a solution of sodium in liquid ammonia results in the formation of 1,3-dimercapto-2,2-pentamethyleneпropane in 93 per cent yield (10). Similarly, 4,4-dimethyl-1-thio-1,2-dithiacyclopentane is reduced to 1,3-dimercapto-2,2-dimethylpropane. The prod-

ucts of the reduction of diphenyl sulfide include benzene, sodium sulfide, and a small quantity of a water-insoluble gas (261). A particularly interesting reduction of a sulfide is that of (12-phenyl-12-β-benzoxanthylmercapto)acetic acid, which with sodium in liquid ammonia forms a deep orange-brown sodium triarylmethyl (2). After reaction with a slight excess of ammonium bromide, the resulting colorless trisubstituted methane is found to be optically active, showing that the sodium salt (or ion) must also be active.

Upon treatment with sodium in ammonia, aliphatic disulfides (ethyl, *n*-propyl, and isoamyl) are reduced quantitatively to the corresponding mercaptides (425). In a similar manner, 2,2′-difluoryl disulfide is reduced to 2-thiofluorenol (338).

From the reaction mixture obtained upon treatment of phenyl isothiocyanate, C_6H_5NCS, with sodium in ammonia, aniline, sodium sulfide (but no cyanide), and relatively small amounts of biphenyl have been isolated. Sodium benzenesulfonate reacts with 2 gram-atoms of sodium to furnish benzene (71 per cent), sodium sulfite, and a small amount of biphenyl (261). The reactivity of liquid ammonia solutions of sodium, potassium, calcium, and barium toward sulfur compounds has been utilized in the purification of petroleum (78).

Reactions of other organic sulfur compounds are included in Sections X and XII.

XIV. ORGANOMETALLIC COMPOUNDS

With but rare exceptions, presently available information concerning reactions of organometallic compounds with solutions of metals in liquid ammonia is the result of the work of C. A. Kraus and his students. These studies have contributed significantly to an understanding of the nature of free radicals and have provided a basis for the development of numerous methods of synthesis. It will be evident from the following discussion that despite the information accumulated thus far, numerous and almost totally unexplored areas of investigation remain.

A. Mercury

The only compound that has been studied is ethylmercuric chloride, which has been shown to react with sodium in liquid ammonia in accordance with the equation (247):

$$C_2H_5HgCl + 3Na + NH_3 \rightarrow NaCl + NaHg + C_2H_6 + NaNH_2$$

B. Boron, gallium, and thallium

Triphenylboron ammine reacts with sodium in liquid ammonia thus (234):

$$(C_6H_5)_3B\cdot NH_3 + Na \rightarrow (C_6H_5)_3B\cdot NH_3Na$$

The reaction of trimethylgallium ammine with sodium in liquid ammonia is in accord with the equations:

$$2(CH_3)_3Ga\cdot NH_3 + Na \rightarrow [(CH_3)_3Ga]_2NH_2Na + \tfrac{1}{2}H_2 + NH_3$$
$$2(CH_3)_3Ga\cdot NH_3 + 2Na \rightarrow [(CH_3)_3Ga]_2Na_2 + 2NH_3$$

Depending on conditions, reaction takes place according to the first equation to the extent of from 60 to 100 per cent of the total gallium and according to the second from 30 to 0 per cent. A similar reaction takes place when trimethylgallium is treated with lithium in ethylamine, except that the first reaction is replaced by the following (259):

$$(CH_3)_3Ga \cdot C_2H_5NH_2 + Li \rightarrow (CH_3)_3Ga \cdot C_2H_5NHLi + \tfrac{1}{2}H_2$$

Dimethylgallium chloride, $(CH_3)_2GaCl$, is reduced to dimethylgallium when treated with one atomic equivalent of sodium in liquid ammonia. The free dimethylgallium combines with ammonia and may be obtained as a solid at −33°C., where an internal oxidation–reduction takes place slowly (rapidly at room temperature) according to the equation:

$$(CH_3)_2Ga \cdot NH_3 \rightarrow (CH_3)_2GaNH_2 + \tfrac{1}{2}H_2$$

When dimethylgallium chloride is treated with two atomic equivalents of sodium, dimethylgallium is first formed, which reacts slowly with sodium, presumably according to the equation,

$$(CH_3)_2Ga \cdot NH_3 + Na \rightarrow [(CH_3)_2GaNH_2]^-Na^+ + \tfrac{1}{2}H_2$$

In this compound the amide ion apparently is linked to gallium by a coördinate bond (259).

The reduction of diphenylthallium bromide with sodium in ammonia at −33.5°C. results in the formation of triphenylthallium, elemental thallium, and sodium bromide (144).

C. Silicon, germanium, tin, and lead

As might be anticipated, most of the work relating to organometallic compounds has been concerned with the nontransitional elements of Group IV of the Periodic Table. Reactions of these compounds are discussed below under headings analogous to those employed in the preceding sections that have been devoted exclusively to carbon compounds.

(*1*) *Substituted stanno- and germano-methanes and -ethanes:* The compounds of germanium, tin, and lead that are analogous to the carbon compounds typified by hexaphenylethane have long been regarded as capable of existence as free radicals in liquid ammonia. There is at least limited evidence that, for example, $(C_6H_5)_3GeGe(C_6H_5)_3$ may exist as triphenylgermanyl, $(C_6H_5)_3Ge$. Selwood and coworkers (363), however, have used magnetic susceptibility measurements to demonstrate that dilute benzene solutions of compounds such as hexaphenyldigermane, "tri-*o*-tolyltin," "trimethyltin," "tricyclohexyllead," and hexaphenyldiplumbane are diamagnetic and hence should be formulated as the dimers. They have found that the extent of dissociation in benzene is quite limited (usually of the order of 1–2 per cent), if indeed the dimers dissociate at all. In view of the marked differences in the physical properties of benzene and liquid ammonia, it is questionable whether these results necessarily shed much light upon the mode of existence of this type of compound in the latter solvent. It is

nevertheless indicated that the free-radical character of these substances in liquid ammonia has probably been overemphasized.

In any event, the reactions between solutions of metals in ammonia and compounds such as triphenylgermanyl (hexaphenylgermanoethane) (236, 241, 245, 252, 258), triphenylstannyl (hexaphenylstannoethane) (245), and trimethylstannyl (hexamethylstannoethane) (232, 233, 244, 257) (see also table 22[3]) are analogous to those of the corresponding carbon compounds. That the electron in the trimethylstannomethide ion is not firmly held is shown by the equation (256):

$$(CH_3)_3Sn + Na + am = (CH_3)_3SnNa \cdot am - 3{,}830 \text{ cal.}$$

Triphenylsilicyl forms an addition compound with ethylamine, $(C_6H_5)_3Si \cdot C_2H_5NH_2$, which does not react with sodium in liquid ammonia to an appreciable extent. In liquid ethylamine the following reaction occurs (239):

$$(C_6H_5)_3Si \cdot C_2H_5NH_2 + Li \rightarrow (C_6H_5)_3SiLi + C_2H_5NH_2$$

Triethylsilicyl shows no reaction with sodium in liquid ammonia or with lithium in ethylamine (251). Triethylgermanyl reacts with lithium in ethylamine to form lithium triethylgermanide. The latter compound is partially aminolyzed in ethylamine and completely ammonolyzed in liquid ammonia:

$$(C_2H_5)_3GeLi + NH_3 \rightarrow (C_2H_5)_3GeH + LiNH_2$$

Potassium triethylgermanide prepared similarly in ethylamine is stable in liquid ammonia (240).

Tin and germanium form a type of free group which carbon does not form, i.e., dimethylstannyl (243), $[(CH_3)_2Sn]_x$, diphenylstannyl (77), $[(C_6H_5)_2Sn]_x$, and diphenylgermanyl (236), $[(C_6H_5)_2Ge]_4$. Each of these substances reacts with a solution of sodium to form the corresponding disodium salt: $(CH_3)_2SnNa_2$, $(C_6H_5)_2SnNa_2$, and $(C_6H_5)_2GeNa_2$. In two of these cases intermediate substances, $NaSn(CH_3)_2 \cdot Sn(CH_3)_2Na$ and $NaGe(C_6H_5) \cdot Ge(C_6H_5)_2Na$, respectively, are known to form first. All of the salts mentioned above may be employed for purposes of synthesis. By using them it has been found possible to prepare hydrides, alkyl and aryl derivatives, and chains of tin and germanium atoms: e.g., octaphenylgermanopropane, $(C_6H_5)_3Ge \cdot Ge(C_6H_5)_2 \cdot Ge(C_6H_5)_3$, and dodecamethylstannopentane, $(CH_3)_3Sn[Sn(CH_3)_2]_3Sn(CH_3)_3$.

(*2*) *Substituted ethanes:* Closely allied to the reactions given above are those between sodium and trimethylstannyltriphenylsilane in liquid ammonia (239) and that between triphenylgermanyltriethylsilane and lithium in ethylamine (251) (greater solubility of the silane):

$$(C_6H_5)_3Si \cdot Sn(CH_3)_3 + 2Na \rightarrow (C_6H_5)_3SiNa + (CH_3)_3SnNa$$
$$(C_6H_5)_3Ge \cdot Si(C_2H_5)_3 + 2Li \rightarrow (C_6H_5)_3GeLi + (C_2H_5)_3SiLi$$

[3] In table 22 certain compounds which may exist as the dimers are formulated as monomers, and *vice versa*. Since uncertainty remains, the general practice has been to employ the formulations used by the authors of the papers cited.

TABLE 22[a]

Reactions of organometallic compounds of tin and lead with solutions of metals in liquid ammonia

COMPOUND[b]	PRODUCTS[b][c]	REFERENCES
Tin:		
$(C_2H_5)_2Sn$	$[NaSn(C_2H_5)_2]_2$	(153)
$(C_2H_5)_3Sn$	$(C_2H_5)_3SnNa$	(153)
$(C_2H_5)_4Sn$	$(C_2H_5)_3SnNa$, C_2H_6	(153)
$(C_2H_5)_3SnX$	$(C_2H_5)_3Sn$	(153, 155, 156)
$(C_2H_5)_2SnX_2$	$(C_2H_5)_2Sn$	(153)
$(C_2H_5)_3SnOH$	$(C_2H_5)_3Sn$	(153, 155)
$[(CH_3)_3Sn]_3OI$	$(CH_3)_3SnNa$, hydrocarbon	(154)
$[(CH_3)_3SnOH]_2 \cdot [(CH_3)_3SnI]$	$(CH_3)_3SnNa$, hydrocarbon	(154)
$(C_6H_5)_3SnC(C_6H_5)_3$	$(C_6H_5)_3CNa$, $(C_6H_5)_3SnNa$	(11)
Lead:		
$(C_2H_5)_4Pb$	$(C_2H_5)_2Pb$	(16)
$(C_2H_5)_3(C_6H_5)Pb$	$(C_2H_5)_2(C_6H_5)PbNa$	(16)
$(C_2H_5)_3PbCl$	$(C_2H_5)_3Pb$	(139)
$(C_2H_5)_3PbBr$	$[(C_2H_5)_3Pb]_2$	(48)
$(CH_3)_3PbI$	$(CH_3)_4Pb$, $[(CH_3)_3Pb]_2$	(48)
R_3Pb[d]	R_3PbNa[d]	(11)
R_3PbX[d]	R_3PbNa[d]	(11, 139)
$(C_6H_5)_3PbCl$	$(C_6H_5)_3PbNa$	(115)
$(C_6H_{11})_2C_6H_5PbCl$	Red solution	(280)
$(C_6H_5)_3PbBr$	$(C_6H_5)_3PbNa$	(139)
$(m\text{-}CH_3C_6H_4)_3PbBr$	$(m\text{-}CH_3C_6H_4)_3Pb$	(139)
$(C_6H_5)_3PbI$	$(C_6H_5)_3Pb$	(139)
	$(C_6H_5)_3PbNa$	(115)
	$[(C_6H_5)_3Pb]_2$	(115)
$(C_6H_5)_2PbX_2$	$(C_6H_5)_3Pb$, inorganic lead	(5)
	$(C_6H_5)_2PbLi_2$, inorganic lead	(5)
	$(C_6H_5)_6Pb_2$, $(C_6H_5)_4Pb$	(280)
$[(C_6H_5)_3Pb]_2$	$(C_6H_5)_3PbNa$	(115)
	$(C_6H_5)_3PbM^I$[e]	(280)
	$(C_6H_5)_3PbM^{II} \cdot M^{II}Pb(C_6H_5)_3$[e]	(280)
$(C_6H_5)_3PbC(C_6H_5)_3$	$(C_6H_5)_3CNa$, $(C_6H_5)_3Pb$	(11)

[a] Reactions indicated in this table were carried out at or below the boiling temperature of ammonia. With but few exceptions (5, 280) the metal employed was sodium. X denotes a halogen.

[b] See footnote on page 366.

[c] See footnote to table 1.

[d] Where R = C_6H_5—, p-$CH_3C_6H_4$—, p-$C_2H_5OC_6H_4$—, o-$CH_3C_6H_4$—, or C_6H_{11}—.

[e] Where M^I = Li, Na, K, or Rb, and M^{II} = Ca, Sr, or Ba. These salts were treated with benzyl chloride to form triphenylbenzyllead. The highest yields were obtained using lithium and calcium and with each group of metals the yields decrease with increase in the atomic number.

(3) *Trisubstituted methanes:* Sodium in liquid ammonia reacts with trimethylstannane (233, 242) and triphenylstannane (77) to produce the sodium salt and

hydrogen:

$$(CH_3)_3SnH + Na \rightarrow (CH_3)_3SnNa + \tfrac{1}{2}H_2$$

The sodium salt of triphenylstannane is in small part converted to the disodium salt, $(C_6H_5)_2SnNa_2$. Triethylgermane appears not to react with sodium in liquid ammonia (240). Triphenylgermane, on the other hand, gives the sodium salt and hydrogen but not quantitatively, since some of the disodium salt is formed (241). While lithium in ethylamine solution has no direct action on triethylsilane, the metal does serve as a catalyst for the homogeneous reaction (251):

$$(C_2H_5)_3SiH + C_2H_5NH_2 \rightarrow (C_2H_5)_3SiNHC_2H_5 + H_2$$

The chief products of the reaction between triphenylsilane and sodium in liquid ammonia are sodium bis(triphenylsilicyl)imide, $[(C_6H_5)_3Si]_2NNa$, and hydrogen (341).

$$2(C_6H_5)_3SiH + Na + NH_3 \rightarrow [(C_6H_5)Si]_2NNa + H_2$$

(*4*) *Tetrasubstituted methanes:* Methyl- and *n*-propyl-triphenylgermanes are not attacked by sodium in liquid ammonia (258). Tetraethylgermane, which is practically insoluble in liquid ammonia, shows no appreciable reaction with sodium in that solvent (240); tetraphenylgermane, on the other hand, slowly reacts as follows:

$$(C_6H_5)_4Ge + 2Na + NH_3 \rightarrow (C_6H_5)_3GeNa + NaNH_2 + C_6H_6$$

With a concentrated sodium solution (241), a second phenyl group is substituted by sodium to form $(C_6H_5)_2GeNa_2$.

Tetramethylstannane undergoes the following reaction with an ammonia solution of sodium (249, 257):

$$(CH_3)_4Sn + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + NaNH_2 + CH_4$$

Tetraphenylstannane reacts similarly, with the exception that some of the sodium triphenylstannide is further substituted, forming the disodium compound (77).

Reactions with somewhat different types of compounds are those with bis(trimethylstannyl)methane and bis(trimethylstannyl)ethylene. The former reacts according to the equations (249):

$$CH_2[Sn(CH_3)_3]_2 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + (CH_3)_3SnCH_3 + NaNH_2$$
$$(CH_3)_3SnCH_3 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + CH_4 + NaNH_2$$

and the latter according to the following equations (250):

$$(CH_3)_3SnCH{=}CHSn(CH_3)_3 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + CH_2{=}CHSn(CH_3)_3 + NaNH_2$$
$$CH_2{=}CHSn(CH_3)_3 + 2Na + NH_3 \rightarrow CH_2{=}CHSn(CH_3)_2Na + CH_4 + NaNH_2$$

(*5*) *Organohalides:* As much as from five to six atomic equivalents of sodium are consumed when triphenylsilicyl chloride is treated with an excess of sodium

in liquid ammonia. It is evident that the phenyl–silicon bond is broken in this treatment (255). Triphenylsilicyl bromide and metallic lithium react in ethylamine solution according to the equation (239):

$$(C_6H_5)_3SiBr + Li + C_2H_5NH_2 \rightarrow LiBr + (C_6H_5)_3Si \cdot C_2H_5NH_2$$

While lithium does not act upon triethylsilicyl bromide in ethylamine solution, it does serve to neutralize the products of the aminolysis of the bromide and thus to bring the following reaction to completion (251):

$$(C_2H_5)_3SiBr + C_2H_5NH_2 + Li \rightarrow (C_2H_5)_3SnNHC_2H_5 + LiBr + \tfrac{1}{2}H_2$$

Triethyl-, tripropyl-, tributyl-, and triamyl-silicyl fluorides do not react with sodium in liquid ammonia at its boiling point (138).

Sodium triphenylgermanide has not been prepared by the action of the metal upon a triphenylgermanium halide, but only by the action of the metal upon hexaphenylgermanoethane. The reaction of sodium with diphenylgermanium dichloride must be carried on in an inactive solvent, since the chloride is ammonolyzed in liquid ammonia. Lithium in ethylamine solution acts upon diphenylgermanium dichloride to give a substance which retains ethylamine and which cannot be purified (236). Sodium does not act upon triethylgermanyl bromide in liquid ammonia, but instead reacts with the products of ammonolysis of the bromide:

$$2(C_2H_5)_3GeBr + 3NH_3 \rightarrow [(C_2H_5)_3Ge]_2NH + 2NH_4Br$$
$$2NH_4Br + 2Na \rightarrow 2NaBr + 2NH_3 + H_2$$

Similar reactions take place between lithium and triethylgermanyl chloride and bromide in ethylamine. Under the same conditions the fluoride has less tendency to ammonolyze and hence may be reduced:

$$2(C_2H_5)_3GeF + 2Li \rightarrow 2LiF + [(C_2H_5)_3Ge]_2$$

The reaction is unsatisfactory for the preparation of the digermane, however, since it seems to be complicated by the formation of lithium triethylgermanide (240).

Sodium in liquid ammonia reacts with triphenylstannyl bromide (77) and iodide (42, 43) to form sodium triphenylstannide. The trimethylstannide may be similarly prepared by the action of sodium on the corresponding bromide (43, 237, 249, 257) or chloride (242). If only one equivalent of sodium is used, this same reaction may be utilized to obtain a nearly quantitative yield of hexamethylstannoethane:

$$2(CH_3)_3SnBr + 2Na \rightarrow (CH_3)_3Sn—Sn(CH_3)_3 + 2NaBr$$

Sodium also converts dimethylethylstannyl bromide into the corresponding stannide (44). From measurements of the heats of reaction in liquid ammonia solution the following equations may be written (256):

$(CH_3)_3SnBr \cdot NH_3 \cdot am + Na \rightarrow (CH_3)_3Sn + NaBr \cdot am$	−30,470	cal.
$(CH_3)_3SnBr \cdot NH_3 \cdot am + 2Na \rightarrow (CH_3)_3SnNa + NaBr \cdot am$	−34,300	cal.
$(CH_3)_3SnBr + Na \rightarrow NaBr + (CH_3)_3Sn$	−37,470	cal.

Diphenyltin dibromide (77) and diiodide (43) on treatment with sodium solution are converted into the free group diphenyltin, $(C_6H_5)_2Sn$, or the salt, disodium diphenylstannide, $Na_2Sn(C_6H_5)_2$, depending upon the amount of sodium used. Similarly, dimethyltin dibromide is converted into the dimethyltin group, $(CH_3)_2Sn$, disodium dimethylstannide (243, 43), $(CH_3)_2SnNa_2$, or disodium tetramethylstannoethane (248), $NaSn(CH_3)_2Sn(CH_3)_2Na$, depending upon the reaction ratios.

For other reactions of organohalides of tin and lead, see table 22.

(6) Substituted oxides, hydroxides, and amines: While the bond between oxygen and carbon resists the action of metal solutions, that between oxygen and elements such as germanium and tin is broken by the action of a solution of sodium. Thus triphenylgermanium oxide reacts with sodium to form sodium triphenylgermanide and sodium triphenylgermanolate (262):

$$[(C_6H_5)_3Ge]_2O + 2Na \rightarrow (C_6H_5)_3GeNa + (C_6H_5)_3GeONa$$

Triethylgermanium oxide reacts similarly with lithium in ethylamine (240). Sodium in liquid ammonia converts trimethylstannyl phenoxide, $(CH_3)_3SnOC_6H_5$, into sodium phenoxide and either trimethylstannyl or sodium trimethylstannide, depending upon the quantity of sodium used (248).

Trimethylstannyl hydroxide reacts with sodium in liquid ammonia as follows (152):

$$(CH_3)_3SnOH + Na \rightarrow (CH_3)_3Sn + NaOH$$

The complex hydroxybromide, $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$, reacts in somewhat the same manner. At first trimethylstannyl precipitates, and then it goes into solution as more sodium is added to form sodium trimethylstannide, $NaSn(CH_3)_3$. As the reaction proceeds, gelatinous sodium hydroxide precipitates (238).

Trimethylstannylamine reacts with sodium in ammonia (249) in a manner entirely analogous to that previously indicated for triphenylmethylamine (392):

$$(CH_3)_3SnNH_2 + 2Na \rightarrow (CH_3)_3SnNa + NaNH_2$$

(7) Recent studies on synthesis: The foregoing survey is concerned almost exclusively with the earlier literature, most of which was published during the period 1925–1930. After a lapse of nearly ten years, renewed interest in these reactions has centered largely about their application to problems in synthesis and to further studies of free radicals. A summary of the more recent literature is given in table 22.

D. Antimony and bismuth

A few reactions of organoantimony and organobismuth compounds with solutions of metals in liquid ammonia have been studied by Gilman and others (146, 147, 430, 431), particularly from the standpoint of their use in synthesis (147). Compounds of the type $(C_6H_5)_2SbI$ react with solutions of sodium to form salts (431), $(C_6H_5)_2SbNa$, and possibly $(C_6H_5)_2Sb$ as well (430). Triphenylbismuth reacts to form a red solution (146, 147), while diphenylbismuth is reported as a possible product of the reduction of diphenylbismuth iodide (430).

The reaction,

$$R_2BiX + 2Na \rightarrow R_2BiNa + NaX$$

(where R = C_6H_5—, p-$CH_3C_6H_4$—, or p-ClC_6H_4—; X = Cl, Br, or I; and the reducing metal = Li, Na, K, Ca, or Ba) is one that has been shown to be particularly useful in the synthesis of organobismuth compounds. Triphenylbismuth dichloride and α-naphthylbismuth dibromide react with sodium to form solutions that are colored deep red and black, respectively.

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