ORGANO-ALKALI COMPOUNDS

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Received June 24, 1931
Revised to January 1, 1932

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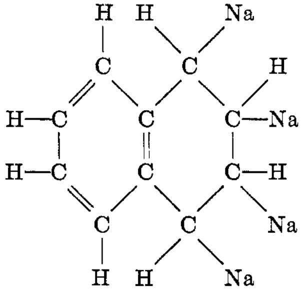
I. INTRODUCTION

The great difference in our familiarity with the organic chemistry of the halogens on the one hand and of the alkali metals on the other, fosters an erroneous conception of the relative reactivity toward organic molecules of these two classes of univalent elements. Both are capable of substituting the hydrogen of many hydrocarbons; cesium has even been found to react with certain paraffins. Both may add to unsaturated compounds, and although this reaction is restricted to the halogens in the case of simple aliphatic olefins, it is not in the case of conjugated systems and aromatic hydrocarbons. Indeed, the alkali metals may saturate some carbon-carbon double bonds to which bromine fails to add, and the present scarcity of these examples probably illustrates only the existing limitations of our knowledge. In one respect the alkali metals actually outstrip the halogens, for they can cleave carbon to carbon bonds in such compounds as tetraphenylethane, which shows no other evidence of dissociation.

Substances which contain alkali metals in direct union with carbon have been termed organo-alkali compounds (142, 183). This definition includes alkali metal carbides, but the dialkali acetylides are the only ones of definite constitution (52) known. A considerable number of organo-alkali compounds are on record, yet the majority are of recent synthesis. This is partly due to their exceptional reactivity, which necessitates rigid exclusion of air and moisture in handling them, but another factor is that the preparation of the structurally simpler representatives is attended by the greater difficulties and is subject to the most restricted choice of methods. Although organo-alkali compounds have now been obtained by more than sixteen essentially different methods, the successful application of these reactions is usually highly dependent on structural influences. For this reason these methods are best considered in connection with the compounds which they are used to prepare.

In this review the presentation of the simpler types of monoalkali compounds is followed immediately by a discussion of their physical properties and constitution as a background for the subsequent treatment of the more complicated classes. The relation of the subject to such problems as the structure of aromatic olefins, the existence of new types of bivalent carbon compounds, and the occurrence of organo-alkali compounds as intermediates in reactions employing alkali metals is also considered.

Nomenclature. The nomenclature employed for the simpler organo-alkali compounds is that recommended by the Committee on Nomenclature, Spelling, and Pronunciation of the American Chemical Society: "In naming metallo-organic compounds, the alkyl groups should precede and be directly attached to the name of the metal" (46). Thus the compound C_2H_5Na is called ethylsodium. Other names which are common in the literature are sodium ethide and sodium ethyl, the latter being the one used in the indices of Chemical Abstracts. For convenience the corresponding ammonium compounds have been named analogously, except that a hyphen is introduced to avoid confusion. Thus $(C_6H_5)_3C—N(CH_3)_4$ is called triphenylmethyl-tetramethylammonium. The recommendation of the American Committee offers no guidance in naming more complex substances, but an international committee (81) has suggested that the metal may be regarded as a substituent. The form adopted in this review is illustrated by 1,2,3,4-tetrasodium-1,2,3,4-tetrahydronaphthalene for the substance $C_{10}H_8Na_4$ having the structure,



II. MONOALKALI COMPOUNDS

1. *Alkali alkyls*

The simplest organo-alkali compounds are those which could theoretically be derived from the paraffin hydrocarbons by the substitution of a single atom of hydrogen by an alkali metal atom. These are termed the alkali alkyls. They cannot, in general, be prepared from the hydrocarbons by direct substitution, although metallic cesium does react in this manner with certain paraffins (107).

The most general method for the preparation of these compounds is by the action of alkali metals on the corresponding mercury alkyls (36). This reaction must be carried out under rigid exclusion of air and moisture. The original procedure (158, 142) employed nitrogen as an inert atmosphere; the nitrogen was carefully purified by passing it over heated copper, sodium hydroxide, calcium chloride, and phosphorus pentoxide, and then through a wash bottle containing a solution of triphenylmethylsodium in ether. This organo-alkali compound, which will be considered in detail later, acted both as a final, extremely active, drying agent and oxygen absorbent, and as a convenient indicator of the reliability of the purification process, since it is an intensely red substance which is converted by oxygen and water into the colorless products triphenylmethyl peroxide and triphenylmethane, respectively.

The preparation of methylsodium (158) may be represented by the equation,

$$2\ \mathrm{Na} + (\mathrm{CH_3})_2\mathrm{Hg} \rightarrow 2\ \mathrm{CH_3Na} + \mathrm{Hg} \qquad (1)$$

although in practice the liberated mercury forms an amalgam with the sodium, which must be used in excess, for Ziegler (216) has shown this type of reaction to be reversible. In order to separate the methylsodium, which forms a solid crust on the amalgam and which may be neither fused nor dissolved in any known solvent without decomposition, the reaction vessel is placed in a freezing mixture and when cold it is shaken vigorously. After the methylsodium is reduced to a powder, the supernatant liquid is decanted and the product washed. The pure compound is obtained as a white powder which explodes in air. Other compounds which have been prepared by similar reactions are ethyl-, *n*-propyl-, *n*-butyl-, and *n*-octyl-sodium (158) and methylpotassium (39).

Methyllithium (158) closely resembles the sodium compound in its properties, but since its preparation by a similar procedure leads to an impure product, it is made from ethyllithium and dimethylmercury. Both of the latter compounds are soluble without decomposition in benzene or purified gasoline and a double decomposition leads to the desired product, which may be separated by decantation or filtration and purified by washing.

$$\underset{\text{(soluble)}}{2\,LiC_2H_5} + \underset{\text{(soluble)}}{Hg(CH_3)_2} \rightarrow \underset{\text{(insoluble)}}{2\,LiCH_3} + \underset{\text{(soluble)}}{Hg(C_2H_5)_2} \qquad (2)$$

Ethyllithium (158) is obtained from diethylmercury and lithium in benzine.

$$2\,Li + Hg(C_2H_5)_2 \rightarrow Hg + 2\,C_2H_5Li \qquad (3)$$

The product is soluble and may be purified by crystallization from this solvent. It may thus be obtained in transparent crystals having the form of six-sided plates. It melts at 95°C. under nitrogen and may even be distilled largely unchanged at higher temperatures. Although it is soluble without decomposition in benzene, benzine, and gasoline, it reacts with ether and ignites spontaneously in air, burning with a light red flame.

The higher lithium alkyls are liquids, but otherwise resemble ethyllithium and may be prepared analogously. The original technique has been modified by Hager and Marvel (71) to permit the use of the solvent vapor as the inert atmosphere; they have prepared ethyl-, *n*-butyl-, isoamyl- and *n*-heptyl-lithium by this more convenient method. Ziegler and others have found that in many cases the lithium alkyls may also be prepared by the action of the metal on the corresponding alkyl halide (219, 217).

$$C_4H_9Cl + 2\,Li \rightarrow LiCl + C_4H_9Li \qquad (4)$$

This possibility is based on the relative stability of these organo-alkali compounds toward alkyl halides (222, 108) and is now the best method available for the preparation of lithium alkyls. The alkyl chlorides are preferable to the bromides, and the iodides cannot be used. Benzene or cyclohexane are more suitable as solvents than ether, which reacts with the lithium alkyls. Gilman and Zoellner (61) have recently shown that these reactions can be carried out about as conveniently as the corresponding Grignard reaction and with comparable yields. Isopropyllithium (223) has been prepared by the reaction

$$(CH_3)_2CHMgCl + 2\ C_6H_5Li \rightarrow LiCl + (C_6H_5)_2Mg + (CH_3)_2CHLi \qquad (5)$$

It is the first example of a purely aliphatic organo-alkali compound in which the metal is attached to a secondary carbon atom.

Ethylrubidium (65) has been isolated in the form of its diethylzinc compound, $Rb(C_2H_5) \cdot Zn(C_2H_5)_2$, m.p. 70–75°, by treating diethylzinc with rubidium. With cesium only the oily concentrated solution of ethylcesium in diethylzinc has been obtained. The action of the other alkali metals on diethylzinc leads to similar results (190, 191).

The sodium and potassium alkyls are, perhaps, the most highly reactive compounds ever isolated. Ethylsodium (158, 142), which may be taken as a typical example, is not only spontaneously inflammable in air and instantly decomposed by water and ammonia,

$$NaC_2H_5 + H_2O \rightarrow C_2H_6 + NaOH \qquad (6)$$

$$NaC_2H_5 + NH_3 \rightarrow C_2H_6 + NaNH_2 \qquad (7)$$

but enters into reaction with all classes of organic compounds with which it has been treated, except the paraffin hydrocarbons.

Acids, alcohols, phenols, as well as enolizable aldehydes, ketones, and esters replace the sodium with hydrogen. Toward non-enolizable aldehydes, ketones, and esters, ethylsodium behaves like a Grignard reagent.

$$(C_6H_5)_2C{=}O + C_2H_5Na \rightarrow (C_6H_5)_2(C_2H_5)CONa \qquad (8)$$

$$C_6H_5COOC_2H_5 + 2\ C_2H_5Na \rightarrow C_6H_5(C_2H_5)_2CONa + C_2H_5ONa \qquad (9)$$

It is converted by carbon dioxide into sodium propionate,

$$C_2H_5Na + CO_2 \rightarrow C_2H_5COONa \qquad (10)$$

and by carbon monoxide into ketones and a complex mixture of other products (169, 172, 176, 191). It is decomposed by ethyl ether with the formation of sodium ethylate, ethylene, and ethane (175),

$$C_2H_5OC_2H_5 + C_2H_5Na \rightarrow C_2H_5ONa + C_2H_4 + C_2H_6 \tag{11}$$

and reacts similarly with aromatic ethers.

$$C_6H_5OC_2H_5 + C_2H_5Na \rightarrow C_6H_5ONa + C_2H_4 + C_2H_6 \tag{12}$$

It is even decomposed by benzene,

$$C_6H_6 + C_2H_5Na \rightarrow C_6H_5Na + C_2H_6 \tag{13}$$

and the formation of phenylsodium may be demonstrated by the isolation of sodium benzoate after treating the mixture with carbon dioxide. A similar reaction ensues in toluene, xylene, etc., except that in these instances the sodium atom always enters the side chain of the aromatic hydrocarbon (174).

As might be expected, ethylsodium reacts with organic halides yielding coupling products,

$$RX + C_2H_5Na \rightarrow NaX + RC_2H_5 \tag{14}$$

but other materials such as might result from the disproportionation of organic radicals are often formed.

$$C_2H_5Br + C_2H_5Na \rightarrow NaBr + C_2H_4 + C_2H_6 \tag{15}$$

It should be noted that the isolation of the alkali alkyl is not always necessary in order to carry out these reactions, but that the same products may be obtained in many instances with a mixture of the alkali metal and the corresponding mercury alkyl (175).

The thermal decomposition of ethylsodium (38) (in the presence of sodium and mercury) begins very slowly at room temperature and is quite rapid at 100°. The gas formed at temperatures in the neighborhood of 90–100° consists of ethylene and ethane in the ratio of about 85 to 15, and sodium hydride is found in the residue. The principal reaction is, therefore,

$$NaC_2H_5 \rightarrow NaH + C_2H_4 \tag{16}$$

The gas formed at ordinary temperatures contains more ethane than ethylene. This is supposed to be due to the reaction,

$$2\ NaC_2H_5 \rightarrow Na_2C_2H_4 + C_2H_6 \qquad (17)$$

Certain observations indicate that this disodium compound is eventually converted into disodiumacetylene,

$$2\ Na_2C_2H_4 \rightarrow C_2H_6 + Na_2CH \cdot CHNa_2 \qquad (18)$$

$$Na_2CH \cdot CHNa_2 \rightarrow 2\ NaH + NaC{\equiv}CNa \qquad (19)$$

On heating methylsodium or methylpotassium (39), methane is evolved in accordance with the equation

$$4\ MCH_3 \rightarrow 3\ CH_4 + M_4C \quad (M = K \text{ or } Na) \qquad (20)$$

Hydrolysis of the residue yields chiefly acetylene and hydrogen, together with some ethylene and ethane, indicating the transformation

$$2\ M_4C \rightarrow M_2C_2 + 6\ M \qquad (21)$$

The thermolysis of methylsodium becomes rapid at about 200° and may be completed at a slightly higher temperature, whereas although the thermolysis of methylpotassium first becomes rapid at 100°, it is not completed below 250°. In this behavior, Carothers and Coffman (39) find evidence for the intermediation of K_2CH_2 or K_3CH in the passage from KCH_3 to K_4C.

2. Alkali phenyls

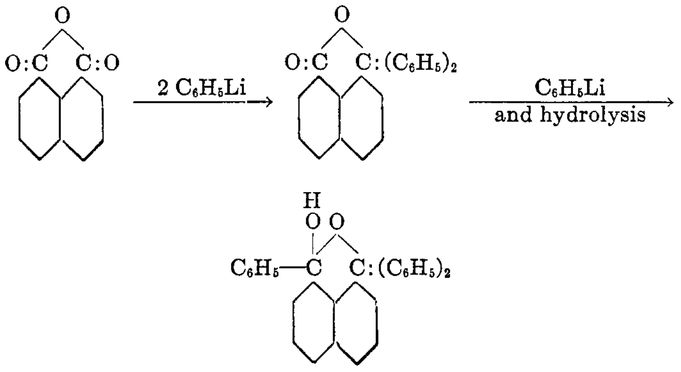
The alkali phenyls are at present the only representatives of organo-alkali compounds in which the alkali metal is attached directly to an aromatic nucleus. (For evidence suggesting the intermediate formation of other such compounds see reference 105.) Their preparation is analogous to that of the alkali alkyls, and like the latter, they are very reactive, colorless, insoluble solids. The reactions of benzene with cesium (70) and with potassium (1, 162) which have been reported do not lead to the formation of alkali phenyls (162). Only phenylsodium and phenyllithium (158, 2, 80) have been prepared. The latter compound has been made by treating diphenylmercury with either metallic lithium or ethyllithium and by the reaction between lithium and bromo- or iodo-benzene (179, 219, 166), which may be carried out under the same conditions as are used in preparing the Grignard reagent (61). Phenyllithium has also been obtained by treating phenylmagnesium bromide with lithium (167).

$$C_6H_5MgBr + 2\ Li \rightarrow LiBr + Mg + C_6H_5Li \tag{22}$$

When carbon dioxide is passed into ethereal solutions of the lithium aryls, the principal products are ketones and the yield of acids is small. The carboxylic acids may be obtained in satisfactory yields by spraying the solutions of the organo-lithium compounds into a carbon dioxide atmosphere or by dropping them onto "dry ice" (58). Phenyllithium and phenylsodium react with phenyl isothiocyanate (58),

$$C_6H_5Li + C_6H_5NCS \rightarrow C_6H_5N{=}C(C_6H_5)SLi \tag{23}$$

and the constitution of the reaction product has been established by methylation with dimethyl sulfate. In this respect the alkali phenyls resemble phenylmagnesium bromide (60), but different results were obtained when naphthalic anhydride was treated with these reagents. According to Wittig, Leo, and Wiemer (206), the reaction with phenyllithium follows the course indicated below.



(24)

The same final product is obtained when dimethylnaphthalate or 1,8-dibenzoylnaphthalene are used instead of naphthalic anhydride, but the Grignard reagent led to different results in every case.

Phenyllithium burns spontaneously in the air with a yellow flame (158).

3. *Alkali acetylides*

The oldest representatives of organo-alkali compounds are those derived from acetylene (48, 62, 26, 50, 66, 67, 110, 115). This is doubtless due to the fact that they are somewhat less reactive and may be readily prepared by direct substitution. When acetylene is passed over molten sodium at 190°, ethinylsodium or sodium acetylide results (142);

$$HC{\equiv}CH + Na \rightarrow HC{\equiv}CNa + \tfrac{1}{2}\,H_2 \qquad (25)$$

this is converted at temperatures above 210° into disodiumacetylene (109).

$$2\ HC{\equiv}CNa \rightarrow Na_2C_2 + C_2H_2 \qquad (26)$$

Monoalkali acetylides may also be prepared by the action of alkali metals or alkali metal amides on acetylene in liquid ammonia solution (116, 79, 100, 126). The higher acetylenes of the type, $R{-}C{\equiv}CH$, react in benzine solution with sodium amide (126, 35).

Ethinylsodium forms monoalkyl acetylenes with straight chain, primary, alkyl halides (99) and branched compounds of the type $RCH_2 \cdot CH_2X$ with the side chain in the γ or more distant position (124). The following compounds have been satisfactorily synthesized in this way: propine (99), butine, *n*-pentine (122), and *n*-hexine (99) (in liquid ammonia at −40°); *n*-heptine, *n*-decine, and *n*-octadecine (in liquid ammonia in an autoclave at room temperature (125)). Other types of alkyl halides, such as isobutyl iodide, secondary and tertiary halides which contain a side chain in the α position, yield unsaturated hydrocarbons and regenerate acetylene (123).

$$(CH_3)_2CHI + CH{\equiv}CNa \rightarrow C_2H_2 + NaI + CH_3 \cdot CH{=}CH_2 \qquad (27)$$

Like the alkali alkyls, ethinylsodium seldom reacts like a Grignard reagent with enolizable aldehydes, ketones, and esters, but usually sets free acetylene and yields condensation products of the ketone or aldehyde (79). There are exceptions; thus dehydrolinaloöl may be readily prepared by passing acetylene into a suspension of sodium amide in an ethereal solution of isobutyl acetone (138).

$$(CH_3)_2CH \cdot CH_2 \cdot CH_2COCH_3 + CH{\equiv}CNa \rightarrow (CH_3)_2CH \cdot CH_2 \cdot CH_2C(ONa)(CH_3)C{\equiv}CH \quad (28)$$

A marked difference between ethinylsodium and the sodium alkyls is indicated by the observation of Skossarewsky (177) that the former is converted into sodium propiolate *only* upon treatment with carbon dioxide under 50 *atmospheres pressure.* However, Strauss and Voss (184) state that it reacts vigorously at atmospheric and reduced pressures, at least when contaminated with sodium hydroxide.

The alkali metal derivatives of the monoalkyl acetylenes behave much more like the Grignard reagent with aldehydes, ketones, and esters (118, 119); phenylethinylsodium is especially applicable to synthesis. It is readily obtained from phenylacetylene and sodium in ethereal solution (62) and enters into reaction with ketones (120, 112),

$$RR'CO + C_6H_5C{\equiv}CNa \rightarrow RR'C(ONa){-}C{\equiv}C \cdot C_6H_5 \quad (29)$$

with carbon dioxide (62)

$$C_6H_5C{\equiv}CNa + CO_2 \rightarrow C_6H_5C{\equiv}C{-}COONa \quad (30)$$

with acyl halides (120), especially bromides (3),

$$RCOBr + C_6H_5C{\equiv}CNa \rightarrow C_6H_5C{\equiv}C{-}CO \cdot R + NaBr \quad (31)$$

with ethyl chloroformate (120),

$$ClCOOC_2H_5 + C_6H_5C{\equiv}CNa \rightarrow C_6H_5C{\equiv}C \cdot COOC_2H_5 + NaCl \quad (32)$$

and with isothiocyanates (214).

$$CH_3 \cdot C_6H_4NCS + C_6H_5C{\equiv}CNa \rightarrow C_6H_5C{\equiv}C \cdot C(SNa) : N \cdot C_6H_4 \cdot CH_3 \quad (33)$$

4. *Alkali triarylmethyls*

The alkali acetylides, like the alkali alkyls and alkali phenyls, are white solids when pure, but the compounds containing an alkali metal atom in the side chain of an aromatic hydrocarbon are usually intensely colored. Triphenylmethylsodium, which is a typical member of this class, has been rather extensively studied.

The alkali triarylmethyls may in general be prepared by the action of the alkali metal on an ethereal solution of the free radical, but triphenylmethyl is polymerized to *p*-benzohydryltetraphenylmethane,

$$(C_6H_5)_2CH \cdot C_6H_4 \cdot C(C_6H_5)_3$$

under these conditions (160). However, triphenylmethylsodium results when the reaction is carried out in liquid ammonia solution (93) or when sodium amalgam is substituted for the pure metal (160). The free energies of the latter and other similar reactions have been measured by Bent (8) as a means of determining the electron affinity of triphenylmethyl and its analogs. Curiously enough, in view of the ready hydrolysis of triphenylchloromethane, metallic sodium is without action on this substance dissolved in organic solvents (160), yet reacts smoothly with it in liquid ammonia (93).

$$(C_6H_5)_3CCl + 2\ Na \rightarrow NaCl + (C_6H_5)_3CNa \qquad (34)$$

A similar reaction can be carried out in organic solvents using sodium amalgam; this is at present the most convenient method of preparing triphenylmethylsodium (157). Potassium reacts with triphenylmethane at 200° (73, 196), and metallic sodium can directly displace hydrogen from this hydrocarbon in liquid ammonia,

$$(C_6H_5)_3CH + Na \rightarrow (C_6H_5)_3CNa + \tfrac{1}{2}\ H_2 \qquad (35)$$

but the reaction takes place slowly and a very pure preparation of triphenylmethylsodium may be more readily obtained by using sodium amide in liquid ammonia.

$$(C_6H_5)_3CH + NaNH_2 \rightarrow NH_3 + (C_6H_5)_3CNa \qquad (36)$$

Triphenylmethyl-potassium, -lithium, -rubidium, and -cesium have been prepared by similar reactions. Rubidium and cesium react with triphenylchloromethane in organic solvents (65). All of these substances are intensely red solids, soluble in ether and in benzene. The sodium and potassium compounds have also been shown to be soluble in liquid ammonia and to conduct the electric current in solution (94, 208, 84).

It is evident from its stability toward liquid ammonia that triphenylmethylsodium is less reactive than ethylsodium, but like the latter it is decomposed by enolizable ketones, aldehydes, and esters, as well as by water, acids, alcohols, and even gaseous ammonia at room temperature, with formation of triphenylmethane (148, 160). For this reason it has been employed by Schlenk, Hillemann, and Rodloff (156) in the preparation and study of crystalline enolates.

$$(C_6H_5)_3CNa + (C_6H_5)_2CHCOOCH_3 \rightarrow (C_6H_5)_3CH + (C_6H_5)_2C{=}C(ONa)OCH_3 \quad (37)$$

It also reacts like the Grignard reagent (160), but more rapidly, with non-enolizable ketones and aldehydes,

$$HCHO + (C_6H_5)_3CNa \rightarrow (C_6H_5)_3C{-}CH_2ONa \quad (38)$$

$$C_6H_5CHO + (C_6H_5)_3CNa \rightarrow (C_6H_5)_3C \cdot CH(ONa) \cdot C_6H_5 \quad (39)$$

The presence of halogen in the ring does not interfere with this process.

Certain ketones, however, constitute special cases; thus benzophenone is partly converted into a metal ketyl (163, 209),

$$(C_6H_5)_2CO + (C_6H_5)_3CNa \rightleftarrows (C_6H_5)_2\overset{|}{C}ONa + (C_6H_5)_3C{-} \quad (40)$$

and dibenzalacetone into a pinacolate (142).

$$2\,(C_6H_5CH{:}CH)_2C{=}O + 2\,(C_6H_5)_3CNa \rightarrow 2\,(C_6H_5)_3C{-} + [(C_6H_5CH{:}CH)_2CONa]_2 \quad (41)$$

The pinacol formed upon hydrolysis of this product passes spontaneously into a pinacolone.

It is interesting to note that in its reaction with esters and with ethyl chlorocarbonate triphenylmethylsodium ceases to react at an earlier stage than the simple Grignard reagents (160, 148, 29), a fact which is suggestive of the abnormal behavior of highly branched aliphatic compounds (43).

$$C_6H_5COOCH_3 + (C_6H_5)_3CNa \rightarrow (C_6H_5)_3C—CO—C_6H_5 + CH_3ONa \tag{42}$$

$$C_2H_5OCOCl + (C_6H_5)_3CNa \rightarrow NaCl + (C_6H_5)_3C—CO—OC_2H_5 \tag{43}$$

Triphenylmethylsodium is rapidly converted by air to sodium peroxide and triphenylmethyl peroxide (160, 94),

$$2\ (C_6H_5)_3CNa + 2\ O_2 \rightarrow (C_6H_5)_3COOC(C_6H_5)_3 + Na_2O_2 \tag{44}$$

by carbon dioxide to sodium triphenylacetate,

$$(C_6H_5)_3CNa + CO_2 \rightarrow (C_6H_5)_3C—COONa \tag{45}$$

and by sulfur dioxide to the corresponding sulfinate.

$$(C_6H_5)_3CNa + SO_2 \rightarrow (C_6H_5)_3C—SOONa \tag{46}$$

However it is quite unaffected by carbon monoxide (160).

Nitrous oxide adds to the organo-alkali compound (148, 142), yielding a salt-like substance which upon hydrolysis with alcohol is decomposed to triphenylcarbinol, nitrogen, and sodium ethylate,

$$N_2O + (C_6H_5)_3CNa \rightarrow (C_6H_5)_3CN_2ONa \tag{47}$$

$$(C_6H_5)_3CN_2ONa + C_2H_5OH \rightarrow C_2H_5ONa + N_2 + (C_6H_5)_3COH \tag{48}$$

whereas nitric oxide may furnish two products, one a red solid for which the possible free radical formulas, $(C_6H_5)_3C—\overset{|}{N}—ONa$, and $(C_6H_5)_3C—\overset{|}{N}{=}O(Na)$ have been suggested, and the other a white solid resulting from the further action of nitric oxide, $(C_6H_5)_3C—N(NO)\cdot ONa$(?).

When ammonium chloride is added to a solution of triphenylmethylsodium in liquid ammonia a pink solid is at first precipitated; this is unstable and decomposes with loss of color upon evaporation of the ammonia (93). The final products are, of course, sodium chloride and triphenylmethane; the intermediate pink compound is regarded as triphenylmethyl-ammonium.

$$(C_6H_5)_3CNa + NH_4Cl \rightarrow (C_6H_5)_3CNH_4 + NaCl \tag{49}$$

$$(C_6H_5)_3CNH_4 \rightarrow NH_3 + (C_6H_5)_3CH \tag{50}$$

This view is supported by the fact that triphenylmethyltetramethylammonium results from the action of tetramethylammonium chloride on triphenylmethylsodium in ether (157). This product may be crystallized out as a red solid closely resembling the sodium compound from which it is prepared. When trimethylmethoxyammonium iodide is used, the products are sodium iodide, trimethylamine, triphenylmethane, and triphenylethanol, although the intermediate formation of triphenylmethyltrimethylmethoxyammonium is supposed to occur (83).

$$(CH_3)_3NI \cdot OCH_3 + (C_6H_5)_3CNa \rightarrow NaI + (CH_3)_3(CH_3O)NC(C_6H_5)_3 \tag{51}$$

$$(CH_3)_3(CH_3O)NC(C_6H_5)_3 \rightarrow (CH_3)_3N + (C_6H_5)_3CH + HCHO \tag{52}$$

$$HCHO + (C_6H_5)_3CNa \rightarrow (C_6H_5)_3C \cdot CH_2ONa \tag{53}$$

The types of organic halides which react anomalously with the Grignard reagent do so also with triphenylmethylsodium,

$$(CH_3)_2CHCl + (C_6H_5)_3CNa \rightarrow NaCl + (C_6H_5)_3CH + CH_3{-}CH{=}CH_2 \tag{54}$$

but the reactivity of the halogen is as important a factor in governing the course of the reaction as is the ease with which hydrogen halide may be removed. Thus chloromethyl ether behaves normally in spite of its readiness to split off hydrogen chloride (148).

$$(C_6H_5)_3CNa + ClCH_2OCH_3 \rightarrow NaCl + (C_6H_5)_3C{-}CH_2OCH_3 \tag{55}$$

Many organic halides react smoothly with the alkali triphenylmethyls (160); this fact has been employed as a basis for a number of syntheses which are unique in that the preparation of a hydrocarbon from its next lower homolog is effected in a single process. 1,1,1-Triphenylethane, 1,1,1,2-tetraphenylethane, and tetraphenylmethane have been made in this way (211, 93). The procedure in the case of the first of these consists in treating triphenylmethane with potassium in liquid ammonia,

$$(C_6H_5)_3CH + K \rightarrow (C_6H_5)_3CK + \tfrac{1}{2} H_2 \qquad (56)$$

and then adding methyl iodide.

$$(C_6H_5)_3CK + CH_3I \rightarrow KI + (C_6H_5)_3C{-}CH_3 \qquad (57)$$

In this instance an additional complication is introduced by the reactivity of methyl iodide towards liquid ammonia. A portion of the precipitate formed is light pink in color and apparently consists of triphenylmethyl-methylammonium formed as a result of the reactions,

$$CH_3I + NH_3 \rightarrow CH_3NH_3I \qquad (58)$$

$$CH_3NH_3I + (C_6H_5)_3CK \rightarrow (C_6H_5)_3CNH_3CH_3 + KI \qquad (59)$$

This substance would decompose on warming to room temperature with regeneration of triphenylmethane, but by renewing the treatment with potassium, followed by more methyl iodide, a sufficient proportion of this by-product may be converted into the desired triphenylethane to permit yields of 85 to 94 per cent.

In certain instances the action of organic halides on triphenylmethylsodium results in the formation of free radicals, as when triphenylchloromethane (160, 93) and diphenyldichloromethane (161) are employed.

$$(C_6H_5)_3CCl + (C_6H_5)_3CNa \rightarrow NaCl + 2\,(C_6H_5)_3C{-} \qquad (60)$$

$$(C_6H_5)_2CCl_2 + 2\,(C_6H_5)_3CNa \rightarrow 2\,NaCl + (C_6H_5)_3C{-} + (C_6H_5)_3C{-}\overset{|}{C}(C_6H_5)_2 \qquad (61)$$

Triphenylmethylsodium adds readily to isocyanates and isothiocyanates (148),

$$RNCO + (C_6H_5)_3CNa \rightarrow (C_6H_5)_3C{-}C(ONa):N \cdot R \qquad (62)$$

$$RNCS + (C_6H_5)_3CNa \rightarrow (C_6H_5)_3C{-}C(SNa):N \cdot R \qquad (63)$$

and forms an insoluble violet-red compound of the composition.

$$(C_6H_5)_3CNa\,.\,(C_6H_5)_2SO$$

with diphenyl sulfoxide (54, 55).

The other alkali triarylmethyls closely resemble triphenylmethylsodium in their chemical properties. They vary somewhat in their color, as may be seen from the brief list in table 1 (160).

5. *Other monoalkali derivatives of aromatic hydrocarbons*

The simplest examples of the highly colored compounds containing an alkali metal atom in the side chain of an aromatic hydrocarbon are the alkali benzyls. Benzylsodium may be prepared from sodium and dibenzylmercury in benzene (158).

$$2\ Na + (C_6N_5CH_2)_2Hg \rightarrow Hg + 2\ C_6H_5CH_2Na \qquad (64)$$

TABLE 1

Colors of sodium triarylmethyls

SUBSTANCE	COLOR
Triphenylmethylsodium	Red
Biphenylene-*p*-anisylmethylsodium	Red
Biphenylenephenylmethylsodium	Orange red
Dibiphenyl-α-naphthylmethylsodium	Dark violet
Phenyl-α-naphthylbiphenylmethylsodium	Blue violet
Tribiphenylmethylsodium	Blue

It is soluble in ether but may be precipitated by the addition of gasoline, and is purified and separated in this manner. It also results from the action of sodium on benzyl halides in liquid ammonia (211, 95, 37), but this method is not suitable for its preparation. Benzyllithium has been obtained by the action of phenyllithium and of lithium alkyls on dibenzylmercury (158, 76, 223), and by the action of lithium on benzylmagnesium halides, but according to Ziegler and Dersh (223) the action of phenyllithium on benzylmagnesium chloride is the most convenient method of preparing solutions of benzyllithium for use in reactions where the presence of diphenylmagnesium is no disadvantage.

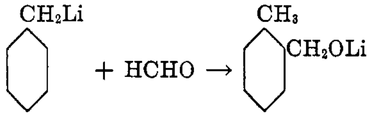
$$C_6H_5CH_2MgCl + C_6H_5Li \rightarrow LiCl + C_6H_5MgCH_2C_6H_5 \qquad (65)$$

$$C_6H_5MgCH_2C_6H_5 + C_6H_5Li \rightarrow (C_6H_5)_2Mg + C_6H_5CH_2Li \qquad (66)$$

The reactions of benzylsodium have not been extensively investigated. The action of carbon dioxide yields sodium phenyl-acetate (158), dibenzyl is formed with benzyl halides (211), and benzyl-tetramethylammonium with tetramethylammonium halides (159). It is, of course, spontaneously inflammable; stilbene has been found among the products of slow oxidation (158). It reacts with mercuric chloride (216),

$$2\ C_6H_5CH_2Na + HgCl_2 \rightarrow 2\ NaCl + (C_6H_5CH_2)_2Hg \qquad (67)$$

and with ether (227). Benzyllithium, on the contrary, is stable in ether, but both the sodium and lithium compounds react alike and anomalously with formaldehyde (58).



(68)

The same anomalous behavior is exhibited by benzylmagnesium chloride (59).

Ziegler and his coworkers (229) have found the action of alkali metals on aromatic ethers a convenient method of preparing organo-alkali compounds of this class as, for instance, phenylisopropylpotassium (228).

$$C_6H_5C(CH_3)_2OCH_3 + 2\ K \rightarrow CH_3OK + C_6H_5CK(CH_3)_2 \qquad (69)$$

This important substance has been extensively employed in a study of certain types of organo-alkali reactions which will be discussed later.

The preparation of diphenylmethylsodium originally presented considerable difficulty. Neither sodium nor sodium amide react with diphenylmethane in organic solvents (142), although it has since been found that these reactions do take place in liquid ammonia solution (102, 211). The mercury compound of diphenylmethyl has not been prepared and consequently cannot be employed. The difficulty was solved by a double decomposition reaction, using diphenylmethane and benzylsodium (149, 142).

$$C_6H_5CH_2Na + (C_6H_5)_2CH_2 \rightarrow C_6H_5CH_3 + (C_6H_5)_2CHNa \qquad (70)$$

The product is orange-red and stable in ether. Since both the reactants and the products are soluble, the occurrence of this reaction must be attributed to other than solubility influences. This point will be discussed in greater detail later. Alkali diphenylmethyls have subsequently been very conveniently prepared from benzohydrol methyl ether by the Ziegler method and from *sym*-tetraphenylethane by cleavage with sodium–potassium alloy (229).

$$(C_6H_5)_2CH—CH(C_6H_5)_2 + 2\ K \rightarrow 2\ (C_6H_5)_2CHK \qquad (71)$$

This cleavage reaction is of interest not only as a method of preparing organo-alkali compounds, but also as a test for weakened carbon to carbon bonds. By using 40 per cent and 1 per cent sodium amalgams as well as sodium–potassium alloy, Conant and Garvey (45) have developed a method for differentiating between certain compounds containing carbon-carbon linkages of varying reactivities. Table 2 summarizes the results of some of their studies. This test has been applied extensively by Marvel and others (140, 136, 141, 57, 44, 47, 180).

TABLE 2

The cleavage of certain compounds by alkali metal

SUBSTANCE	Na-K IN ETHER	Na-K IN BENZENE	40% Na-Hg IN ETHER	40% Na-Hg IN BENZENE	1% Na-Hg IN ETHER	1% Na-Hg IN BENZENE
Hexaphenylethane	+	+	+	+	+	+
Dibenzyldixanthyl	+	+	+	+	−	−
Di-*n*-butyldixanthyl	+	+	+	+	−	−
Diethyldixanthyl	+	+	+	+	−	−
Dimethyldixanthyl	+	+	+	+	−	−
Dixanthyl	+	+	+	−	−	−
Tetraphenylethane	+	+	−	−	−	−
Dibenzyl	−	−	−	−	−	−

A + sign indicates appreciable cleavage in five minutes as judged by appearance of red color.

A − sign indicates no cleavage in five minutes.

In each case 0.00025 mole of the ethane in 5 cc. of the solvent was shaken with 1 cc. of the liquid metal. The tubes were all shaken violently by hand for five minutes.

Diphenylmethylsodium reacts like triphenylmethylsodium with phenyl isothiocyanate (149),

$$C_6H_5NCS + (C_6H_5)_2CHNa \rightarrow C_6H_5N : C(SNa) \cdot CH(C_6H_5)_2 \qquad (72)$$

but like the Grignard reagent with benzophenone and fluorenone.

$$(C_6H_5)_2CO + (C_6H_5)_2CHNa \rightarrow (C_6H_5)_2C(ONa) \cdot CH(C_6H_5)_2 \qquad (73)$$

Although the reaction between the Grignard reagent and thioketones is abnormal and results in reduction, diphenylmethylsodium adds smoothly, yielding tertiary thioalcohols which are readily converted into ethylenes with loss of hydrogen sulfide when heated with acetyl chloride (21).

$$(C_6H_5)_2CS + (C_6H_5)_2CHNa \rightarrow (C_6H_5)_2C(SNa)CH(C_6H_5)_2 \qquad (74)$$

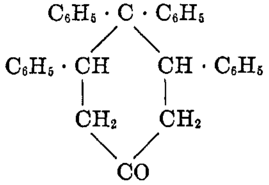
One mole of diphenylmethylsodium reacts with the conjugated system of dicinnamalacetone yielding a substituted ketone upon hydrolysis (21).

$$(C_6H_5CH : CH \cdot CH : CH)_2CO + (C_6H_5)_2CHNa \rightarrow$$

$$C_6H_5CH : CH \cdot CH : CHC(ONa) : CH{-}CH[CH(C_6H_5)_2]CH : CHC_6H_5 \xrightarrow{H_2O}$$

$$C_6H_5CH : CH \cdot CH : CH \cdot CO \cdot CH_2 \cdot CH[CH(C_6H_5)_2]CH : CHC_6H_5 \qquad (75)$$

and forms with dibenzalacetone a cyclic compound of the formula,



The reaction between diphenylmethylsodium and 9-chlorofluorene yields benzohydrylfluorene, *sym*-tetraphenylethane, and bifluorenyl (145, 88, 9, 89). Similarly 9,9′-bianthryl has been obtained using 9-bromoanthracene. [Note: In two papers (145, 151) Schlenk and Bergmann have reported the preparation of a number of new isomers whose existence has been disputed. Therefore, in reading these papers the content of accompanying citations should not be overlooked.] Ziegler has shown (216) that diphenylmethylsodium and mercuric chloride do not lead to the formation of an organo-mercury compound.

$$2\ (C_6H_5)_2CHNa + HgCl_2 \rightarrow (C_6H_5)_2CH \cdot CH(C_6H_5)_2 + Hg + 2\ NaCl \qquad (76)$$

The oxidation of diphenylmethylsodium takes place smoothly when a stream of dry air is passed through a liquid ammonia solution of the organo-alkali compound (209) and, in contrast to the oxidation of alkali triarylmethyls, leads to the formation of a hydrocarbon,

$$2\ (C_6H_5)_2CHNa + O_2 \rightarrow Na_2O_2 + (C_6H_5)_2CH \cdot CH(C_6H_5)_2 \qquad (77)$$

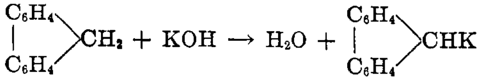
thus suggesting that the formation of an organic peroxide as an oxidation product is typical only of those organo-alkali compounds which are derivatives of free radicals.

A dipotassium derivative of diphenylmethane, which probably possesses the structure $(C_6H_5)_2CK_2$, results from the action of the metal on the hydrocarbon at 230° (139).

No alkali metal derivatives of vinyl or substituted vinyl radicals are known. An attempt to prepare diphenylvinylsodium, $(C_6H_5)_2C{=}CHNa$, from the corresponding mercury compound resulted in the formation (145) of 1,4-disodium-1,1,4,4-tetraphenylbutene-2,

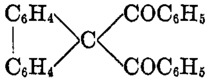
$$(C_6H_5)_2CNa{-}CH{=}CH{-}CNa(C_6H_5)_2$$

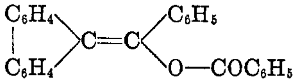
Fluorenyl-sodium, -potassium, and -lithium (145, 88, 9, 89), indenylsodium (193, 102) and pentaphenylcyclopentadienylpotassium (224) have been prepared by methods similar to those used in making diphenylmethylsodium and by the direct action of alkali metals on the hydrocarbons. These compounds react normally with water, carbon dioxide, and alkyl halides, and are useful in separating fluorene and indene from the raw materials (142, 194). Fluorenylpotassium may also be prepared in a highly interesting manner from fluorene and potassium hydroxide at 280° (192).



$$\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle CH_2 + KOH \rightarrow H_2O + \left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle CHK \qquad (78)$$

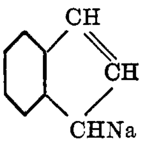
In this instance the usual process of hydrolysis is evidently capable of reversibility under suitable conditions. Disodium and dilithium derivatives of fluorene have been made by the action of triphenylmethylsodium and of ethyllithium on the hydrocarbon (145). When treated with benzoyl chloride they yield different products, to which the following formulas have been assigned (151, 127, 90).



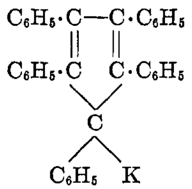


9-Sodium-9-methoxyfluorene has been prepared by cleavage of 9,9-dimethoxyfluorene (145, 88, 9, 89,) and 9-sodium-9-phenylfluorene results similarly from the corresponding methyl ether. The latter organo-alkali compound reacts smoothly with benzyl chloride (151, 171); Bachmann (5) has thus obtained 9-phenyl-9-benzylfluorene in 99 per cent yield.

The sodium derivative of indene possesses the structure,



and is probably an intermediate in condensation reactions employing sodium ethylate and indene (186, 106). Pentaphenylcyclopentadienylpotassium is represented by the following formula:



When treated with potassium metal cyclopentadiene, itself, yields a bimolecular potassium compound, $(C_5H_5K)_2$ of unknown structure (187).

III. THE PHYSICAL PROPERTIES AND CONSTITUTION OF ORGANO-ALKALI COMPOUNDS

1. The electrolytic properties and salt-like character of organo-alkali compounds

The exceptional reactivity of the organo-alkali compounds suggests a marked difference between their constitution and that of the more stable organic molecules with which we are most familiar. In consideration of the pronounced electropositive character of the alkali metals and the amphoteric nature of the organic radicals, it may well be expected that their union would produce polar substances more or less closely analogous to the alkali metal hydrides.

Experimental confirmation of this view has been sought in a study of the electrical conductivity of these substances, but it has been rendered particularly difficult by their chemical and physical properties. Only certain of the lithium alkyls may be liquefied without decomposition, and suitable solvents are very rare.

Ethyl-sodium, -lithium, and -potassium, and methyl-, phenyl- and benzyl-lithium yield conducting solutions in diethylzinc, which is itself a non-conductor (75, 76, 77). The orders of increasing molar conductances and melting points and of decreasing miscibilities with the solvent are parallel, and confirm the expectation that the salt-like character is more pronounced in the compounds of the more electropositive metals.

Benzyllithium conducts the best of all the lithium alkyls investigated in diethylzinc solution, whereas phenyllithium and phenylsodium exhibit an unexpectedly low conductance which has been ascribed to a hindering effect of excessive solvation. In general, the molar conductances are of the same order of magnitude as those of such typical salts as tetraethyl- and tetra-*n*-propylammonium iodides in the same solvent.

The electrolytic character of the alkali alkyls is not confined to solutions in a single solvent, but is also exhibited in triethylaluminum and dipropylzinc. The triethylaluminum solvates possess higher melting points and better conductances and are thus more salt-like than the diethylzinc solvates, but the reverse is true for solutions of propylsodium and propylpotassium in dipropylzinc. The dilute solutions of alkali alkyls in dimethylzinc and trimethylaluminum, and the concentrated solutions of ethyllithium and of ethylsodium in diethylcadmium are non-conducting.

Electrolysis of solutions of ethylsodium in diethylzinc yields a mixture of hydrocarbon gases at the anode. About 80 per cent of this mixture consists of equal proportions of ethane and ethylene, probably resulting from disproportionation of the ethyl group. The remainder contains butane, propane, and some methane. When lead anodes were used, a loss in weight approximately in accordance with Faraday's law was observed as a result of the formation of tetraethyllead. Although this fact has been regarded as evidence confirming the transient existence of free ethyl groups at the anode, it is not impossible that the tetraethyllead results directly from the union of ethyl ions with lead ions on the surface of the anode.

The decomposition potential of ethylsodium is less than 0.1 volt, which is not surprising in view of its low decomposition temperature.

The conductance of these solutions is probably purely electrolytic, for the temperature coefficient of the conductance is positive and the deposition of zinc at the cathode (apparently as a result of the action of free sodium on diethylzinc) takes place in quantitative agreement with Faraday's law. Furthermore, transference experiments have shown that the conducting ions are derived from the ethylsodium itself. Consequently, there can be no doubt regarding the polar nature of this substance. Considerable variation in the intensity of the polar character is shown by the several compounds, and the constitution of the fusible lithium alkyls probably approaches in some respects that of the alkyl derivatives of the multivalent metals, since fused ethyllithium, in contrast to lithium hydride, is a non-conductor. This conclusion is also in harmony with the lower reactivities of these compounds.

M. Skossarewsky (178) has measured the conductance of ethinylsodium in liquid ammonia and finds that it is dissociated to approximately the same extent as sodium acetate in water.

Guntz (68) has electrolyzed solutions of dilithiumacetylene in fused lithium hydride.

A few representatives of the colored organo-alkali compounds, in particular triphenylmethylsodium, have been found to conduct the electric current in ether solution (160, 157, 145, 158). Since the equivalent conductance of these solutions decreased upon dilution, Schlenk and Marcus (160) decided that the carriers could not be the simple sodium [Na^+] and triphenylmethyl [$(C_6H_5)_3C^-$] ions, but suggested complex ion formation of the type,

$$m\ (C_6H_5)_3CNa \rightarrow \{[(C_6H_5)_3C]_m\ Na_{m-n}\}^- + n\ Na^+ \qquad (79)$$

However, as has been pointed out by Kraus and Rosen (94), this behavior is common to all salts dissolved in solvents of low dielectric constant (D, ether = 4.5) and need not, necessarily, be ascribed to the formation of complex ions.

In this instance a solvent of much higher dielectric constant (D = 22.0) is available, for triphenylmethylsodium is soluble without decomposition in liquid ammonia at its boiling point. The conductance values obtained under these conditions give no evidence of any such complex ionization. Although the conductance has been determined (94, 208, 84) only within the dilution range of 6 to 250 liters per mole, the equivalent conductance increases with dilution and does not differ greatly in magnitude from that of typical uni-univalent salts dissolved in the same solvent, as may be seen upon inspection of figure 1. This equivalent conductance has been calculated on the basis of normal ionization (74, 207),

$$(C_6H_5)_3CNa \rightarrow (C_6H_5)_3C^- + Na^+ \qquad (80)$$

and should be multiplied by the factor m/n to express it on the basis of the complex ionization indicated in equation 79. It is evident, therefore, that the conductance values obtained in liquid ammonia cannot be attributed to complex ionization without assuming an abnormally high equivalent conductance for the complex salt.

The same considerations apply even in solvents of considerably lower dielectric constant. The results obtained by Ziegler and

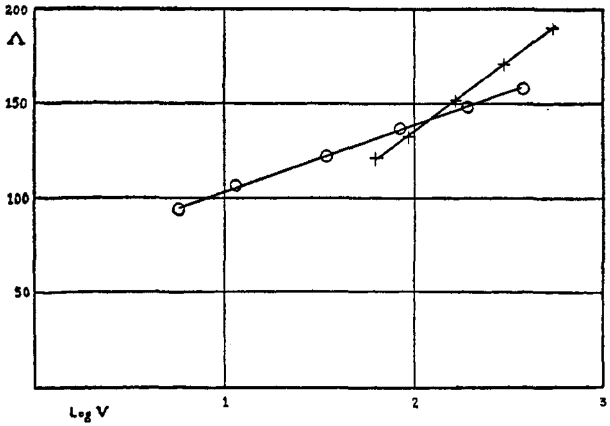


FIG. 1. THE CONDUCTANCE OF TRIPHENYLMETHYLSODIUM IN LIQUID AMMONIA
○ $(C_6H_5)_3CNa$; + $NaBrO_3$

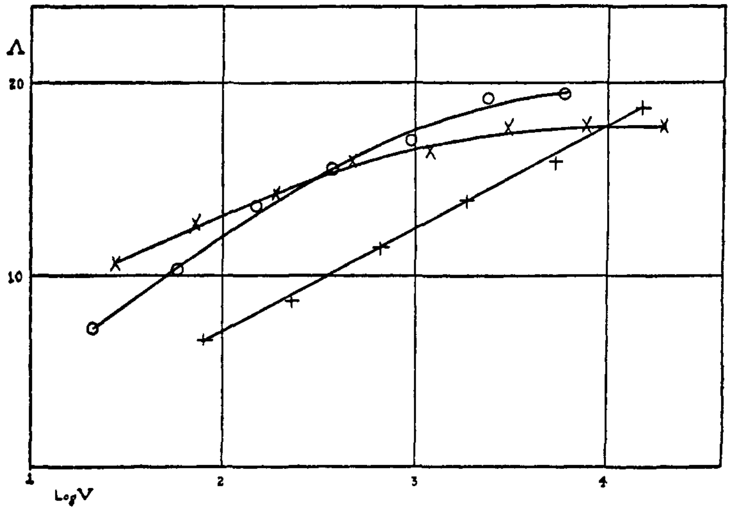


FIG. 2. THE CONDUCTANCE OF ORGANO-ALKALI COMPOUNDS IN PYRIDINE
× $(C_6H_5)_3CNa$; ○$(C_6H_5)_3CK$; + $(NO_2C_6H_4)_3CNa$

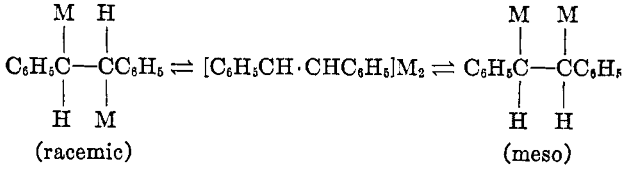
Wollschitt (230) with triphenylmethyl-sodium and -potassium in pyridine ($D = 12.5$) are reproduced in figure 2 together with values for the more typical salt, $(NO_2C_6H_4)_3CNa$, for comparison.

There still remains one item of evidence which must be considered in this connection. Schlenk and Bergmann (145) have observed that the alkali metals add to stilbene forming compounds of the type, $C_6H_5CHM—CHMC_6H_5$, and that when these are converted by the action of carbon dioxide into diphenylsuccinic acids, the acid obtained from the lithium compound is not identical with that yielded by the sodium and potassium analogs. The former acid is the racemic mixture, whereas the latter possesses the meso configuration. These authors regard this fact as an insurmountable objection to the formulation of such organo-alkali compounds as polar substances

$$[C_6H_5CH\cdot CHC_6H_5]^{--}\ Na_2^{++}$$

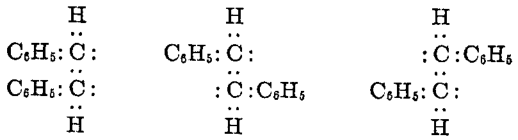
because in the ionized condition the absolute possession of the individual alkali metal atoms by the individual carbon atoms would be lost.

Ziegler and Wollschitt (230) have already suggested the possible existence of a purely heteropolar form in equilibrium with two stereochemically different forms of the dialkali addition product whose relative stabilities depend upon the nature of the alkali metal,



$$\underset{\text{(racemic)}}{C_6H_5\overset{M}{\underset{H}{C}}—\overset{H}{\underset{M}{C}}C_6H_5} \rightleftharpoons [C_6H_5CH\cdot CHC_6H_5]M_2 \rightleftharpoons \underset{\text{(meso)}}{C_6H_5\overset{M}{\underset{H}{C}}—\overset{M}{\underset{H}{C}}C_6H_5} \qquad (81)$$

and the possibility that the steric differences might first arise in the reaction between carbon dioxide and the organo-alkali compounds. On closer inspection it is evident that Schlenk and Bergmann's argument also overlooks the possible existence of stereoisomeric anions, having the following electronic configurations.



$$\begin{array}{ccc} H & H & H \\ C_6H_5\!:\!\ddot{C}\!: & C_6H_5\!:\!\ddot{C}\!: & :\!\ddot{C}\!:\!C_6H_5 \\ C_6H_5\!:\!\ddot{C}\!: & :\!\ddot{C}\!:\!C_6H_5 & C_6H_5\!:\!\ddot{C}\!: \\ H & H & H \end{array}$$

It is true that such stereoisomeric anions are unknown, but in the absence of any proof that they are incapable of existence the evidence of Schlenk and Bergmann remains inconclusive.

In spite of considerable variations in the behavior of the individual organo-alkali compounds, it has thus been clearly demonstrated that in general they possess a salt-like character, and that under favorable circumstances this character is exhibited in a very typical manner. Although no comprehensive and satisfactory theory, capable of summarizing and predicting the reactions of these substances, has yet been attained, there can be little doubt that a recognition of their polar nature will be one of the most fundamental principles of such a theory. In fact, by considering these substances simply as salts of very weak acids of varying strength, it is possible to correlate and understand many of their reactions. In this light their ready hydrolysis may be viewed as a decomposition by the relatively strong acid, water. The ammonolysis of the alkali alkyls and the alkali phenyls is analogous, but owing to the fact that certain other hydrocarbons are more acidic than ammonia, the corresponding alkali metal salts are stable in this solvent. Thus triphenylmethane reacts with the ammono base, potassium amide, in liquid ammonia solution to form triphenylmethylpotassium (93).

$$(C_6H_5)_3CH + KNH_2 \rightarrow (C_6H_5)_3CK + NH_3 \tag{82}$$

The analogy to the familiar neutralization process is clearly evident. Moreover, Kraus and Rosen (94) have shown that even the hydrolysis of this compound is reversible, for in spite of its exceedingly low solubility, potassium hydroxide imparts a distinct color to a solution of triphenylmethane in liquid ammonia.

$$(C_6H_5)_3CH + KOH \rightarrow (C_6H_5)_3CK + H_2O \tag{83}$$

Another case of such salt formation by neutralization of this very typical base is the preparation of fluorenylpotassium from the hydrocarbon and the base at 280° (equation 78). It is probably the volatility of the water formed under these conditions which permits this reaction to proceed to completion.

Instances of salt formation by direct substitution of the hydrogen are not lacking. Sodium and potassium liberate hydrogen from triphenylmethane in liquid ammonia solution (equation 35), and potassium reacts similarly with the fused hydrocarbon at elevated temperatures (73, 64).

It is not possible to apply the usual methods to determine the ionization constants of such very weak and sparingly soluble acids as those corresponding to the organo-alkali salts, but a solution of potassium amide in liquid ammonia may be used to differentiate between those whose ionization is greater and those whose ionization is less than that of this solvent, for the former will react with the ammono base and the latter will not (211). The results of applying this test to a series of phenylated paraffins appear in table 3. The formation of organo-alkali salts was very easily observable in these instances, since these salts are all intensely colored. From these data it is apparent that the ability of potassium amide to replace with potassium a hydrogen atom in compounds of this class is confined to those compounds (nos. 2, 3, 7, 8, 10, and 13 in table 3) in which at least two phenyl groups are attached to a single carbon atom. Since no reaction occurs unless a hydrogen atom is also attached to the same carbon atom as are the two or more phenyl groups (see nos. 4, 9, and 11), it is very

TABLE 3

The action of potassium and sodium amides on phenylated paraffins

NO.	HYDROCARBON	POTASSIUM AMIDE	SODIUM AMIDE
1	$C_6H_5CH_3$	No action	No action
2	$(C_6H_5)_2CH_2$	Reacts	Reacts
3	$(C_6H_5)_3CH$	Reacts	Reacts
4	$(C_6H_5)_4C$	No action	———
5	$C_6H_5CH_2CH_3$	No action	No action
6	$C_6H_5CH_2CH_2C_6H_5$	No action	No action
7	$(C_6H_5)_2CHCH_3$	Reacts	Reacts
8	$(C_6H_5)_2CHCH_2C_6H_5$	Reacts	Reacts
9	$(C_6H_5)_3CCH_3$	No action	No action
10	$(C_6H_5)_2CHCH(C_6H_5)_2$	Reacts	Reacts
11	$(C_6H_5)_3CCH_2C_6H_5$	No action	No action
12	$C_6H_5CH(CH_3)_2$	No action	No action
13	$(C_6H_5)_2CHCH_2CH(C_6H_5)_2$	Reacts	———

likely that it is this hydrogen atom which is replaced. This conclusion has been confirmed by more rigid methods in the case of 1,1,2-triphenylethane (209, 137). It is also evident that similar generalizations apply to the reactions with sodium amide.

Somewhat different considerations permit a rough approximation of the relative acidity of certain other hydrocarbons. Thus the ionization of toluene is apparently intermediate between that of diphenylmethane and those of benzene and saturated aliphatic hydrocarbons, for although toluene does not react with potassium amide, benzyl bromide and potassium metal yield benzylpotassium, which is capable of a transient existence in liquid ammonia, as evidenced by its red color and by its reaction with excess benzyl bromide to form dibenzyl (211, 49). Under similar conditions the alkali alkyls are ammonolyzed too rapidly to show such reactions. The fact that traces of biphenyl result from the reaction between phenyl halides and alkali metals in liquid ammonia (197) suggests that benzene is at least a slightly stronger acid than the saturated aliphatic hydrocarbons.

It is at once obvious that these relative acidities are in harmony with the influences which have been found to favor the cleavage of carbon to carbon bonds (table 2) and of aromatic ethers by alkali metals. They are also in agreement with such facts as that the cleavage of methyl phenylisopropyl ether by potassium yields exclusively phenylisopropylpotassium and potassium methylate, not the reverse (equation 69). It will, moreover, be evident later that a similar correspondence exists between these relative acidities and the influences governing addition of alkali metals to multiple bonds.

The analogy of the Shoruigin reaction (174),

$$\mathrm{RM} + \mathrm{R'H} \rightarrow \mathrm{RH} + \mathrm{R'M} \tag{84}$$

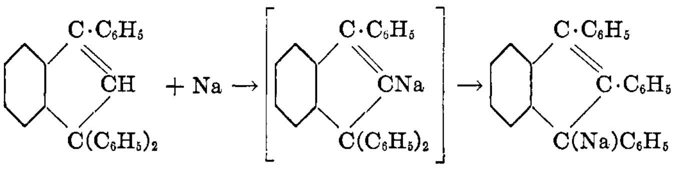
to that between a strong acid and the salt of a weak acid is clear, and even the very rough series of relative acidities just developed suffices to account for the direction which the reaction follows in homogeneous systems and in heterogeneous systems where solubility influences are not paramount. Thus the conclusion that diphenylmethane is a stronger acid than toluene is in harmony with the preparation of diphenylmethylsodium by the action of diphenylmethane on benzylsodium in ether solution (equation 70). Note also that ethylsodium is decomposed by benzene, yielding ethane and phenylsodium (equation 13).

In certain instances the organo-alkali compounds originally formed in reactions undergo molecular rearrangement to a more stable constitution, and factors similar to those governing the stability of such compounds toward ammonolysis account for the direction of the rearrangements. Thus when β-chloro-α,α,α-triphenylethane is treated with sodium in liquid ammonia, the structure of the resulting compound indicates a migration of the sodium atom from the β to the α position (212, 137).

$$(C_6H_5)_3C\cdot CH_2Cl + 2\,Na \rightarrow NaCl + [(C_6H_5)_3C—CH_2Na] \qquad (85)$$

$$[(C_6H_5)_3C—CH_2Na] \rightarrow (C_6H_5)_2CNa—CH_2C_6H_5 \qquad (86)$$

A similar rearrangement occurs when 1,1,3-triphenylindene is treated with sodium in ether (221, 145).

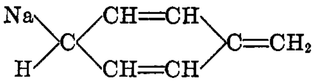


(87)

Not the least striking point about the correlation of the reactions, methods of preparation, and stabilities of organo-alkali compounds on the basis of their salt-like character is that the agreements pointed out are much better than one could have had any *a priori* reason to expect. Since both the temperature and the nature of the solvent unquestionably influence the degree of dissociation of the hydrocarbon acids under consideration, the parallelism between observations in liquid ammonia at −33.5° and organic solvents at room and more elevated temperatures could be expected only on the assumption of a corresponding parallelism between the effects of these factors on the salt-like properties of the individual compounds. It is also probable that the differences between the individuals chosen were relatively large. In general, therefore, apparent exceptions are to be expected until more complete information is available, since a variation in temperature or of the solvent may well, in certain instances, reverse the order of particular substances in a table of relative acidities.

2. The relation between the constitution and color of organo-alkali compounds

The visual division of organo-alkali compounds into two classes, one intensely colored and the other colorless, suggests the possible existence of a fundamental difference in constitution between these two groups; it is a curious fact that until recently all those compounds (and only those compounds) for which a quinonoid formula could be written were colored. Thus benzylsodium with the possible isomeric structure,



is intensely red, whereas the alkali alkyls, the alkali acetylides, and even the alkali phenyls for which such an alternative formula is lacking are colorless. However, the apparent significance of this fact has now been destroyed, since certain compounds of the first type, such as pentaphenylcyclopentadienylpotassium, have been found to be colorless, and colored alkali metal derivatives of aliphatic hydrocarbons have been discovered by Schlenk and Bergmann (144) and by Salzberg and Marvel (140), the simplest example being tri-*tert*-butylethinylmethyl-potassium (or -sodium),

$$[(CH_3)_3C\cdot C{\equiv}C]_3CK$$

which results from the cleavage of hexa-*tert*-butylethinylethane with sodium-potassium alloy.

Hanriot and Saint-Pierre (73) obtained two products from the action of benzyl chloride upon triphenylmethylpotassium, one of which they believed to be *p*-benzyltriphenylmethane, which could conceivably result from a quinonoid modification of the organo-alkali compound,

$$C_6H_5CH_2Cl + KC_6H_5{:}C(C_6H_5)_2 \rightarrow KCl + C_6H_5CH_2\cdot C_6H_5{:}C(C_6H_5)_2 \qquad (88)$$

$$C_6H_5CH_2\cdot C_6H_5{:}C(C_6H_5)_2 \rightarrow C_6H_5CH_2C_6H_4CH(C_6H_5)_2 \qquad (89)$$

but Gomberg and Cone (64) repeated the experiment carefully without obtaining this product, and when the reaction is carried out in liquid ammonia (211) only *unsym*-tetraphenylethane results. A well established case of such para substitution has been more recently discovered in the reaction between triphenylmethylsodium and triphenylacetyl chloride (200, 155, 142),

$$(C_6H_5)_3C\cdot COCl + (C_6H_5)_3CNa \rightarrow NaCl + (C_6H_5)_3C\cdot CO\cdot C_6H_4CH(C_6H_5)_2 \quad (90)$$

and it may be recalled that ortho substitution occurs when the alkali benzyls are treated with formaldehyde (equation 68).

Nevertheless it is evident that a possible quinonoid constitution is neither a necessary nor sufficient basis for predicting color in an organo-alkali compound, and although such a constitution may conceivably be a factor in producing the color of certain individuals or classes, no conclusive evidence for this view exists at present.

The only organo-alkali compound whose absorption spectrum has been studied is triphenylmethylsodium (74).

3. The constitution of sodiumphenylacetonitrile

The substance obtained from the action of sodium or sodium amide on benzyl cyanide may be considered as a special case of organo-alkali compound (30–4, 188, 131–4). From its method of preparation two structures are possible.

$$C_6H_5CH_2CN + NaNH_2 \rightarrow NH_3 + C_6H_5CH{:}C{:}NNa, \text{ or } C_6H_5CHNa\cdot CN \quad (91)$$

Only the second of these is a true organo-alkali compound, but this structure is supported by the nature of the products formed with alkyl halides and esters (142),

$$C_6H_5CHNa\cdot CN + RX \rightarrow C_6H_5CHR\cdot CN + NaX \quad (92)$$

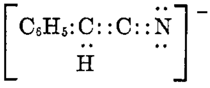
$$CH_3COOC_2H_5 + C_6H_5CHNa\cdot CN \rightarrow C_2H_5OH + CH_3(ONa){:}C(CN)(C_6H_5) \quad (93A)$$

$$CH_3C(ONa){:}C(CN)(C_6H_5) + HCl \rightarrow NaCl + CH_3COCH(CN)(C_6H_5) \quad (93B)$$

and by its peculiar reactions with aromatic aldehydes and ketones.

$$C_6H_5CHNa\cdot CN + (C_6H_5)_2CO \rightarrow (C_6H_5)_2C{=}C(CN)(C_6H_5) + NaOH \quad (94)$$

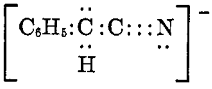
On the other hand, some reactions favor the "nitride" type of formula (188), and certain studies indicate that a tautomeric equilibrium mixture of both forms is in best accord with the evidence (131–4). It seems very probable that the isomerism is in the organic ion,



$\left[C_6H_5:\underset{\underset{H}{..}}{C}::C::\overset{..}{\underset{..}{N}}\right]^-$

"nitride"

or



$\left[C_6H_5:\overset{..}{\underset{\underset{H}{..}}{C}}:C:::\underset{..}{N}\right]^-$

"carbide"

and the suggestion has been made (188) that the substance exists only in the nitride form and that condensation reactions at the carbon atom involve rearrangement of the anion during the reaction. However, the distinction between preëxisting tautomerism and rearrangement which occurs only during reactions is a fine one which appears to lie beyond the scope of the existing experimental evidence.

4. Ammonium analogs of the organo-alkali compounds

Triphenylmethyl-tetramethylammonium, $(C_6H_5)_3C—N(CH_3)_4$, was characterized by its discoverers (157) as the first instance of a compound with *five* hydrocarbon radicals in combination with a nitrogen atom. Its constitution presents an interesting problem and if, as seems likely, the tetramethylammonium group functions in this compound as a metallic radical the substance may conveniently be considered in connection with organo-alkali compounds, just as in inorganic chemistry the ammonium salts are conveniently classed with those of the alkali metals.

In quaternary ammonium salts nitrogen has usually been considered as having a valence of five, but it has also been recognized that the fifth valency is of a type different from the other four (195, 114, 104). The older ideas concerning the stereochemistry of quinquivalent nitrogen (189, 201, 27) predicted many isomers that have never been obtained experimentally.

In all of the ammonium compounds that have been studied carefully, the groups attached to nitrogen have differed widely in character. The compounds triphenylmethyl-tetramethylammonium (159, 158) and benzyl-tetramethylammonium (159) are highly colored and very reactive. They react with water to give tetramethylammonium hydroxide, and triphenylmethane and toluene, respectively. Triphenylmethyl-tetramethylammonium in pyridine solution conducts the electric current. Although this behavior indicates that the fifth group is held by a valency different from the other four, there could be room for doubt, since there is still considerable difference between the methyl group on the one side and the benzyl or triphenylmethyl group on the other.

An attempt has been made to extend this work to give compounds in which five closely related aliphatic groups were attached to the nitrogen atom (71). It was hoped that the preparation of R_4NR' by the two methods,

$$R_4NX + LiR' \rightarrow R_4NR' + LiX \tag{95}$$

$$R_3R'NX + LiR \rightarrow R_3R'NR + LiX \tag{96}$$

would lead to the formation of isomers if the fifth valency of nitrogen were different from the other four, whereas, if the five valencies were equivalent, the two compounds would be identical.

Actually, no pentaalkyl nitrogen could be isolated. The lithium alkyls reacted with the quaternary ammonium halides and tertiary amines were obtained. The following reactions were carried out and the tertiary amines were identified.

$$LiC_2H_5 + (C_2H_5)_3(C_4H_9)NBr \xrightarrow{70^\circ} (C_2H_5)_2NC_4H_9 \tag{97}$$

$$LiC_2H_5 + (C_2H_5)_3(C_4H_9)NBr \xrightarrow{-70^\circ} (C_2H_5)_2NC_4H_9 + (C_2H_5)_3N \tag{98}$$

$$LiC_5H_{11}(iso) + (C_2H_5)_3(C_4H_9)NBr \xrightarrow{-70^\circ} (C_2H_5)_3N + (C_2H_5)_2NC_4H_9 \tag{99}$$

$$LiC_4H_9 + (C_2H_5)_4NBr \rightarrow (C_2H_5)_3N \tag{100}$$

$$LiC_4H_9 + (C_2H_5)_3(C_6H_5CH_2)NBr \rightarrow (C_2H_5)_2NCH_2C_6H_5 \tag{101}$$

$$LiC_4H_9 + (C_4H_9)_3(C_7H_{15})NI \rightarrow (C_4H_9)_2NC_7H_{15} \tag{102}$$

$$LiC_7H_{15} + (C_4H_9)_4NI \rightarrow (C_4H_9)_3N \tag{103}$$

If, as seems rather likely, a pentaalkyl nitrogen is formed as the first product in these reactions, it cannot have a structure in which the valencies are equivalent, since such a compound should give some tertiary amine containing the alkyl group introduced through the lithium alkyl. Inspection of equations 97 to 103 shows that this alkyl group never appeared in the tertiary amine unless it was also present in the original quaternary ammonium salt.

A much better explanation of these reactions is that a penta-alkyl nitrogen is formed, in which one of the alkyl groups is held by a polar valency to the ammonium ion, $(R_4N)^+ R'^-$. This compound then at once breaks down into more stable products. It might first separate into the two ions $(R_4N)^+$ and R'^-. The ammonium ion, $(R_4N)^+$ could decompose further to give R_3N and R^+. One would then expect the positive R^+ ion to combine with the negative R'^- to give a hydrocarbon RR'. A second possible decomposition mechanism would involve the intermediate formation of free alkyl groups and a tetraalkylammonium "metal" (92).

$$(R_4N)^+ R'^- \rightarrow R_4N + —R' \qquad (104)$$

$$R_4N \rightarrow R_3N + —R \qquad (105)$$

The free alkyl groups undoubtedly would then undergo disproportionation (228), giving a mixture of saturated and unsaturated hydrocarbons. The reaction between ethyllithium and tetraethylammonium bromide points to the latter hypothesis, for the gaseous hydrocarbon products were found to contain no butane, but to consist of a mixture of ethane and ethylene.

The question of whether or not phosphorus may exhibit five equivalent (covalent) valencies is still open (104, 96, 128, 185). The reaction between quaternary phosphonium halides and alkali metal alkyls (40) appears to result in the formation of phosphine methylenes (182).

$$(C_6H_5)_3PI \cdot C_2H_5 + LiC_4H_9 \rightarrow C_4H_{10} + LiI + (C_6H_5)_3P{=}CHCH_3 \qquad (106)$$

No pentaalkyl phosphorus compounds were obtained, but preliminary results on compounds in which the carbon atoms in direct union with phosphorus were devoid of hydrogen, indicated possible formation of such pentaalkyl derivatives.

The reactions between quaternary arsonium halides and lithium alkyls are analogous to those of quaternary ammonium halides and, consequently, the possible intermediate formation of pentaalkyl arsenic compounds in which the alkyl groups are equivalent is excluded (53).

IV. THE ADDITION OF ALKALI METALS TO MULTIPLE CARBON-CARBON BONDS

A large number of organo-alkali compounds have been prepared by the action of alkali metals on substances containing multiple carbon-carbon bonds. Such addition usually occurs to unsaturated carbon atoms which are in combination with aryl residues, but it may take place in other instances, such as to 2,6-dimethyl-4-methyleneheptadiene-2,5,

$$[(CH_3)_2C{=}CH]_2\,C{=}CH_2$$

and in special cases to the carbon atoms of an aromatic ring. These reactions have been carried out by shaking the unsaturated compounds with finely divided alkali metals (143, 144) or with liquid sodium-potassium alloy[1] (42) in organic solvents under nitrogen, and by the use of alkali metal solutions in liquid ammonia (168, 220, 211, 212).

1. Alkali metal additions to carbon-carbon double bonds

The addition products obtained in this way from compounds containing simple ethylenic linkages may be distinctly divided into two classes. One class comprises those compounds formed by normal or 1,2 addition of the alkali metal atoms to a double bond. It is illustrated by the reaction between sodium and tetraphenylethylene.

$$(C_6H_5)_2C{=}C(C_6H_5)_2 + 2\,Na \rightarrow (C_6H_5)_2CNa{-}CNa(C_6H_5)_2 \qquad (107)$$

The members of the other class result from a "dimerizing" addition reaction. The action of sodium on *unsym*-diphenylethylene is illustrative.

$$2\,(C_6H_5)_2C{=}CH_2 + 2\,Na \rightarrow (C_6H_5)_2CNa\cdot CH_2CH_2CNa(C_6H_5)_2 \qquad (108)$$

---

[1] Conant and Blatt (41) have employed this reagent to isolate thermolabile substances from petroleum.

These two classes are sharply distinguished not only in their structure but also in their chemical reactions. Although both are hydrolyzed by water and converted into salts of carboxylic acids by carbon dioxide in the usual manner, even the action of alkyl halides leads to different results. Whereas normal substitution occurs with members of the second class,

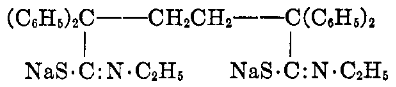
$$(C_6H_5)_2CNa\cdot CH_2CH_2CNa(C_6H_5)_2 + 2\,CH_3I \rightarrow 2\,NaI + (C_6H_5)_2C(CH_3)\cdot CH_2CH_2C(CH_3)(C_6H_5)_2 \qquad (109)$$

the unsaturated parent hydrocarbon is regenerated when members of the first class are similarly treated.

$$(C_6H_5)_2CNa\cdot CNa(C_6H_5)_2 + 2\,CH_3I \rightarrow 2\,NaI + C_2H_6 + (C_6H_5)_2C{=}C(C_6H_5)_2 \qquad (110)$$

The isothiocyanates also react normally with dimerized addition products,

$$(C_6H_5)_2CNa\cdot CH_2CH_2CNa(C_6H_5)_2 + 2\,C_2H_5NCS \rightarrow$$

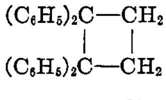


$$\underset{\displaystyle NaS\cdot C{:}N\cdot C_2H_5}{(C_6H_5)_2C}\text{——}CH_2CH_2\text{——}\underset{\displaystyle NaS\cdot C{:}N\cdot C_2H_5}{C(C_6H_5)_2} \qquad (111)$$

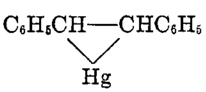
but remove the alkali metal from 1,2 addition products.

$$(C_6H_5)_2CNa\cdot CNa(C_6H_5)_2 + 2\,C_2H_5NCS \rightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + C_2H_5N{:}C(SNa)\cdot C(SNa){:}NC_2H_5 \qquad (112)$$

Mercury abstracts the alkali metal from both classes of compounds, giving rise to an alteration of the molecule in the case of the dimerized addition compounds. Thus *unsym*-diphenylethylene is regenerated from its alkali metal addition product and cyclic compounds, such as



never result (144). The intermediate formation of unstable mercury compounds of the type,



during the decomposition of the 1,2 addition products has been suggested (219, 216) and discussed (9). Enolizable compounds, with the exception of phorone, substitute hydrogen for the alkali metal in both classes of compounds.

From the data in table 4 it is evident that the reactions of the normal addition products are characterized by a tendency toward regeneration of the double bond, whereas inspection of table 5 discloses a resemblance between the reactions of the dimerized addition products and those of the Grignard reagent.

TABLE 4

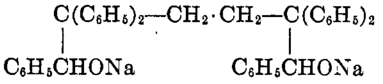
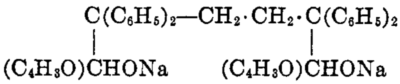
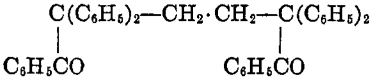
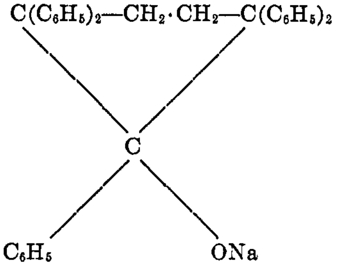
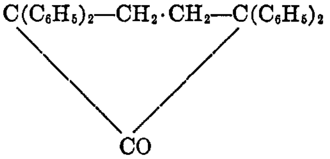
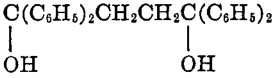
Reactions of disodiumtetraphenylethane, $(C_6H_5)_2CNa \cdot CNa(C_6H_5)_2$ (144, 29)

NO.	REAGENT	PRODUCTS
1	Bromobenzene	Tetraphenylethylene and biphenyl
2	Benzaldehyde	Tetraphenylethylene, sodium benzoate, and benzyl alcohol
3	Furfural	Tetraphenylethylene, sodium pyromucate, and furyl alcohol
4	Paraformaldehyde	Tetraphenylethylene, sodium formate (methyl alcohol?), and a little  $(C_6H_5)_2\underset{HOH_2C}{C}\text{——}\underset{CH_2OH}{C}(C_6H_5)_2$
5	Phenyl benzoate (Methyl formate) (Diethyl oxalate) (Methyl benzoate) (Ethyl carbonate) (Phenyl carbonate)	Tetraphenylethylene, biphenyl, and sodium benzoate (The other esters reacted analogously.)
6	Benzoyl chloride	Tetraphenylethylene and benzil
7	α-Naphthoyl chloride	Tetraphenylethylene and α, α'-naphthil
8	Methyl chlorocarbonate	Tetraphenylethylene and dimethyl oxalate
9	Phorone	Tetraphenylethylene and diisobutyl ketone
10	Nitric oxide	Tetraphenylethylene and sodium hyponitrite
11	Carbon monoxide	No reaction
12	Sulfur dioxide	Sodium tetraphenylethanedisulfinate
13	Ammonia	No reaction
14	Aniline	Tetraphenylethane and sodium anilide

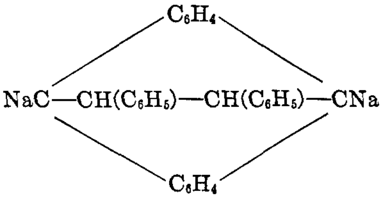
The results of a study of the action of alkali metals on a number of unsaturated compounds appear in table 6. Examples 1 to 4 are typical illustrations of the two methods of addition, and num-

TABLE 5

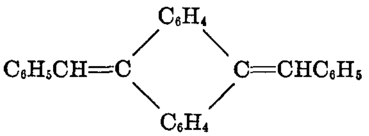
Reactions of disodiumtetraphenylbutane, $(C_6H_5)_2CNa\cdot CH_2CH_2CNa(C_6H_5)_2$ (144)

NO.	REAGENT	PRODUCTS
1	Benzaldehyde	 $\underset{C_6H_5CHONa}{C}(C_6H_5)_2—CH_2\cdot CH_2—\underset{C_6H_5CHONa}{C}(C_6H_5)_2$
2	Furfural	 $\underset{(C_4H_3O)CHONa}{C}(C_6H_5)_2—CH_2\cdot CH_2\cdot \underset{(C_4H_3O)CHONa}{C}(C_6H_5)_2$
3	Phenyl benzoate	 $\underset{C_6H_5CO}{C}(C_6H_5)_2—CH_2\cdot CH_2—\underset{C_6H_5CO}{C}(C_6H_5)_2$ and (sodium phenolate?)
4	Benzoyl chloride	 and its benzoyl derivative
5	Phosgene	
6	Phorone	Tetraphenylbutane and the sodium derivative of an enol form of phorone
7	Nitrosyl chloride	 $\underset{OH}{C}(C_6H_5)_2CH_2CH_2\underset{OH}{C}(C_6H_5)_2$ (after hydrolysis of the original reaction product)

bers 13 to 24 show the similar behavior of substances containing systems of crossed and conjugated double bonds. It is interesting to note that the attempt of Bergmann and Fujise (17) to prepare the bridged compound,



by adding sodium to dibenzaldihydroanthracene,

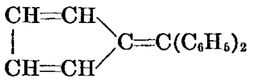
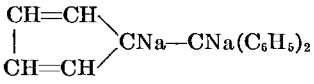
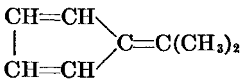
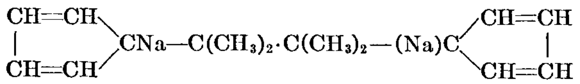
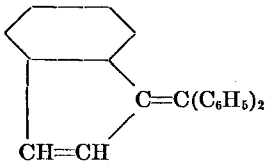
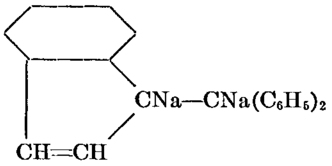


was unsuccessful. Instead of the expected dimerizing reaction (note table 6, no. 18) a normal tetrasodium addition product resulted. This substance, therefore, resembles benzalxanthene and 10-benzal-9,9-diphenyl-9,10-dihydroanthracene (table 6, nos. 25 and 26) in its behavior with sodium.

In recent papers Schlenk, Bergmann, and coworkers (152, 16, 11, 15, 121, 12) have concluded, somewhat to their surprise, that, as a rule, the greater the residual affinity or partial valence on a carbon atom the less is its ability to add sodium, and vice versa. Since most of the evidence regarding this residual affinity is based on the reactivity toward halogens, oxidizing agents, etc., it is not impossible that this fact really means that the "residual affinity" with respect to the addition of electropositive atoms or groups differs from and is in general inversely related to the residual affinity with respect to the addition of electronegative atoms or groups. This interesting possibility suggests the advisability of a review (and perhaps revision) of our accepted views of partial valence.

TABLE 6

The addition of alkali metals to C-C double bonds (144)

NO.	SUBSTANCE	PRODUCTS
1	$[(CH_3)_2NC_6H_4]_2C{=}C[C_6H_4N(CH_3)_2]_2$	$[(CH_3)_2NC_6H_4]_2CNa{-}CNa[C_6H_4N(CH_3)_2]_2$
2	$(C_6H_5 \cdot C_6H_4)_2C{=}CH_2$	$(C_6H_5 \cdot C_6H_4)_2CNa{-}CH_2CH_2{-}CNa(C_6H_4 \cdot C_6H_5)_2$
3	$(C_6H_5)_2C{=}CHC_6H_5$	$(C_6H_5)_2CNa{-}CHNa \cdot C_6H_5$
4	$(C_6H_5)_2C{=}C(CH_3)C_6H_5$	$(C_6H_5)_2CNa{-}CNa(CH_3)C_6H_5$
5	$(C_6H_5)_2C{=}CH \cdot CH_3$	No reaction
6	$(C_6H_5)_2C{=}C(CH_3)_2$	No reaction with sodium $(C_6H_5)_2CLi{-}C(CH_3){=}CH_2$(?)
7	$C_6H_5CH{=}C(CH_3)_2$	No reaction
8	$C_6H_5(CH_3)C{=}C(CH_3)_2$	No reaction
9	$(C_6H_5)_2C{=}C(CH_2C_6H_5)_2$	No reaction
10	$(C_6H_5)_2C{=}CHCH_2C_6H_5$	Substitution $(C_6H_5)_2CNa{-}CH{=}CHC_6H_5$(?)
11	$(C_6H_5)_2C{=}CH \cdot CH(C_6H_5)_2$	Complicated reaction
12	$(C_6H_5)_2C{=}C(CN)C_6H_5$	$(C_6H_5)_2CNa{-}CNa(CN)C_6H_5$
13		
14		
15		

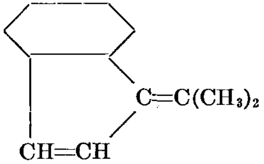
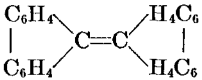
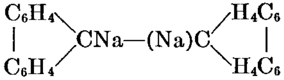
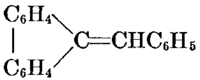
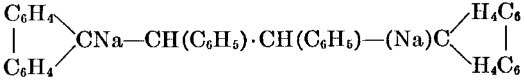
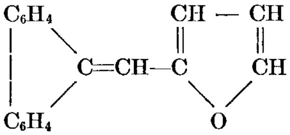
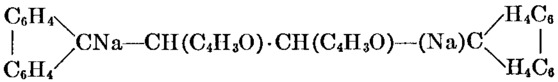
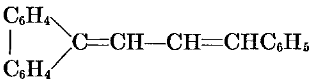
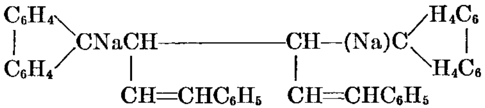
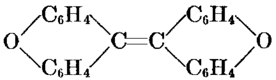
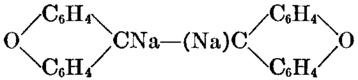
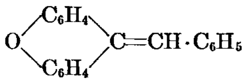
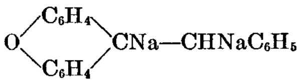
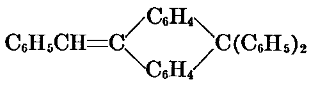
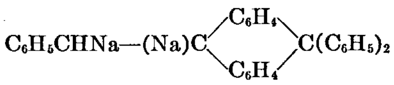
16		Polymerization (without addition)
17		
18		
19		
20		
21		
22	$(C_6H_5CH{=}CH)_2C{=}C(C_6H_5)_2$..................	$(C_6H_5\cdot CH{=}CH)_2CNa{-}CNa(C_6H_5)_2$

TABLE 6—*Concluded*

NO.	SUBSTANCE	PRODUCTS
23	$(C_6H_5CH{=}CHCH{=}CH)_2C{=}C(C_6H_5)_2$..........	$(C_6H_5CH{=}CHCH{=}CH)_2CNa{-}CNa(C_6H_5)_2$
24	$[(CH_3)_2C{=}CH]_2C{=}CH_2$.......................	$[(CH_3)_2C{=}CH]_2CNa{-}CH_2CH_2{-}CNa[CH{=}C(CH_3)_2]_2$
25		
26		

2. *The addition of organo-alkali compounds to unsaturated hydrocarbons*

The absence of reaction observed in cases 5 to 9, table 6, is noteworthy and has inspired a valuable inquiry into both the mechanism of alkali metal additions and the question of the true structure of these apparently abnormal hydrocarbons. An interesting insight into these problems has resulted from a study of the addition of organo-alkali compounds to unsaturated hydrocarbons. This type of reaction was first observed in the case of the addition of phenylisopropylpotassium to *sym*-diphenylethylene by Ziegler and Bähr (215, 218).

$$C_6H_5CK(CH_3)_2 + C_6H_5CH{=}CHC_6H_5 \rightarrow (C_6H_5)[C_6H_5C(CH_3)_2]CH{-}CHKC_6H_5 \quad (113)$$

A more extensive investigation (222) showed that this type of reaction was not unique, although the possibility of its occurrence was influenced both by the nature of the organo-alkali compound and that of the unsaturated hydrocarbon.

It is evident from what has gone before that simple organo-alkali compounds may be divided into three distinct classes. (A). The colorless monosodium or monopotassium alkyls and aryls which are insoluble in organic solvents, act as electrolytes when dissolved in zinc alkyls, and are probably heteropolar in the solid state. (B). The more or less intensively colored compounds in which the carbon atom united with the alkali metal is also in direct union with aromatic rings or a system of multiple bonds and which yield conducting solutions in many organic solvents. (C). The colorless lithium alkyls which are soluble in organic solvents, are readily fusible or liquid, sublime or distill unchanged, conduct poorly or not at all in zinc alkyls, and in their physical properties resemble the zinc and cadmium alkyls.

With respect to their ability to add to double bonds the following characteristics are shown: The evidence indicates that members of type A would readily yield addition products. The addition tendency of members of type B is largely determined by the number of aromatic nuclei and unsaturated groups attached to the carbon atom in union with the alkali metal. Only compounds having but one such group in the position defined are capable of smooth addition. The others add slowly or not at all (i.e., to diphenylethylene) or else give rise to complicated side reactions (i.e., polymerization in the case of styrene and 1,3-butadiene). The lithium alkyls comprising type C add smoothly but more slowly, the rate changing with the nature of the alkyl radical and apparently alternating as the number of carbon atoms is regularly increased. In table 7 are given the velocity constants, $K = x/at(a - x)$ [t = time in hours], of the reaction of three lithium *n*-alkyls with *unsym*-diphenylethylene at 50°. The extent of addition after a definite interval was very ingeniously measured by determination of the lithium bromide formed on decomposition of the reaction mixture with *n*-butyl bromide, which reacts readily with the addition product but not appreciably with the lithium alkyls in the course of twenty-four hours. The addition tendency of even the most suitable members of type B is very variable according to the nature of both the alkali metal and the organic group. It is also very dependent on the nature of the unsaturated compound, as is evident from the data in table 8.

TABLE 7

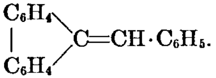
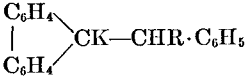
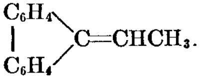
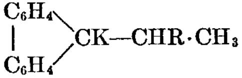
The rates of addition of lithium alkyls to diphenylethylene

SUBSTANCE	*K*
LiC_2H_5	1.5
LiC_3H_7	3.4
LiC_4H_9	2.8

Addition has been observed only to unsaturated carbon atoms directly linked or conjugated with a benzene ring or other unsaturated system. The presence of as many as three such aromatic rings tends to hinder the reaction, unless they are so united as to constitute a sort of "fulvene derivative" (table 8, no. 6). Examples 9 to 13 show that saturated alkyl radicals also hinder the reaction. Since in these cases another reaction (i.e., substitution) occurs, it is pertinent to inquire whether the result is actually due to a hindrance of the addition reaction or to a facilitation of the substitution. The fact that all the addition reactions

TABLE 8

The action of phenylisopropylpotassium on unsaturated hydrocarbons

NO.	HYDROCARBON	REACTION TYPE	PRODUCT R equals $C_6H_5C(CH_3)_2$
1	$CH_2{=}CH_2$	No reaction	—
2	$C_6H_5CH{=}CH_2$	Addition	$C_6H_5CHK{-}CH_2R$
3	$C_6H_5CH{=}CHC_6H_5$	Addition	$C_6H_5CHK{-}CHRC_6H_5$
4	$(C_6H_5)_2C{=}CH_2$	Addition	$(C_6H_5)_2CK{-}CH_2R$
5	$(C_6H_5)_2C{=}CHC_6H_5$	No reaction	—
6	 $(C_6H_4)_2C{=}CH\cdot C_6H_5$	Addition	 $(C_6H_4)_2CK{-}CHR\cdot C_6H_5$
7	$C_6H_5CH{=}CH\cdot CH_3$	Addition	$C_6H_5CHK{-}CHR\cdot CH_3$
8	$C_6H_5(CH_3)C{=}CH_2$	Addition	$C_6H_5(CH_3)CK{-}CH_2R$
9	$C_6H_5CH{=}C(CH_3)_2$	Substitution	$C_6H_5CH{=}C(CH_2K)CH_3$
10	$(C_6H_5)_2C{=}CH\cdot CH_3$	Substitution	$(C_6H_5)_2C{=}CH\cdot CH_2K$
11	$(C_6H_5)_2C{=}C(CH_3)_2$	Substitution	$(C_6H_5)_2C{=}C(CH_2K)CH_3$ and $(C_6H_5)_2C{=}C(CH_2K)_2$
12	$(C_6H_5)_2C{=}CH\cdot CH_2CH_3$	Substitution	$(C_6H_5)_2C{=}CH\cdot CHKCH_3$
13	$(C_6H_5)_2C{=}CHCH_2C_6H_5$	Substitution	$(C_6H_5)_2C{=}CH\cdot CHKC_6H_5$
14	$C_6H_5C(CH_3){=}CHC_6H_5$	Substitution	$(C_6H_5)C(CH_2K){=}CHC_6H_5$
15	 $(C_6H_4)_2C{=}CHCH_3$	Addition	 $(C_6H_4)_2CK{-}CHR\cdot CH_3$
16	$C_6H_5CH{=}CHCH_2CH_2C_6H_5$	Addition	$C_6H_5CHK{-}CHR\cdot CH_2CH_2C_6H_5$
17	$C_6H_5CH_2CH{=}CHCH_2C_6H_5$	Substitution	$C_6H_5CHK\cdot CH{=}CH\cdot CH_2C_6H_5$ and $C_6H_5CHK\cdot CH{=}CH\cdot CHKC_6H_5$
18	$C_6H_5CH{=}CH\cdot CH{=}CHC_6H_5$	Addition	? ? ? ?
19	$C_6H_5CH_2CH{=}CH\cdot CH{=}CHCH_2C_6H_5$	Substitution	$C_6H_5CHK\cdot CH{=}CH\cdot CH{=}CH\cdot CHKC_6H_5$

were instantaneous, whereas the substitution reactions proceeded very slowly, decides in favor of the former alternative. It has been suggested that the similar action of aromatic and saturated aliphatic radicals in this instance is due to different causes, for they do not exert a similar effect on the addition of free alkali metal.

3. Mechanism of the addition of alkali metals to multiple bonds

We are now in a position to discuss the mechanism of the addition of alkali metals to unsaturated compounds. The first explanation of the dimerizing type of addition attributed its occurrence to the difference in the affinity of the two ethylenic carbon atoms toward the alkali metal. It was suggested by Schlenk and Bergmann (144) that the initial step resulted in the formation of a free radical,

$$(C_6H_5)_2C{=}CH_2 + Na \rightarrow (C_6H_5)_2CNa{-}CH_2{-} \qquad (114)$$

which subsequently polymerized.

$$2\ (C_6H_5)_2CNa{-}CH_2{-} \rightarrow (C_6H_5)_2CNaCH_2CH_2CNa(C_6H_5)_2 \qquad (115)$$

In the cases of normal addition they assumed that the structural influences favored the reaction of the radical with more alkali metal to the exclusion of the polymerization reaction.

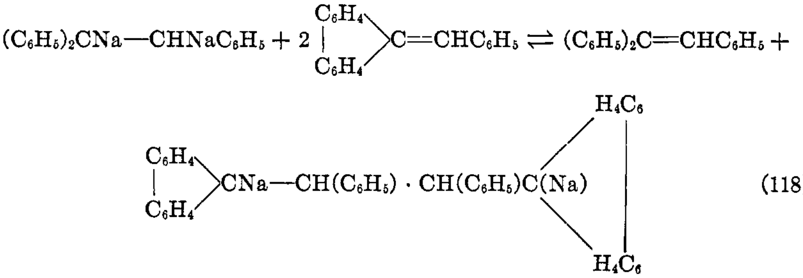
An alternative hypothesis, proposed by Ziegler, Colonius, and Schäfer (220) is that normal or 1,2 addition always occurs,

$$(C_6H_5)_2C{=}CH_2 + 2\ Na \rightarrow (C_6H_5)_2CNa{-}CH_2Na \qquad (116)$$

and that addition of the resulting organo-alkali compound to another molecule of the unsaturated hydrocarbon may follow under favorable circumstances.

$$(C_6H_5)_2C{=}CH_2 + (C_6H_5)_2CNa{-}CH_2Na \rightarrow (C_6H_5)_2CNa{-}CH_2{\cdot}CH_2{-}CNa(C_6H_5)_2 \qquad (117)$$

Thus the fact that benzalfluorene, for instance, yields a dimerized addition product, whereas triphenylethylene gives a normal addition product, is ascribed by Ziegler, Colonius, and Schäfer not to a greater inequality in the rates of the addition to the two sides of the double bond (144) in the former than in the latter instance, but to the general difference in the ability of these two substances to add suitable organo-alkali compounds, as evidenced by their behavior toward phenylisopropylpotassium (nos. 5 and 6, table 8). This illustration has been critized by Schlenk and Bergmann (153) on the ground that disodiumtriphenylethane, $(C_6H_5)_2CNaCHNaC_6H_5$, not only fails to add to triphenylethylene but when treated with benzalfluorene or *unsym*-diphenylethylene leads to the equilibria,



$$(C_6H_5)_2CNa{-}CHNaC_6H_5 + 2\,(C_6H_4)_2{>}C{=}CHC_6H_5 \rightleftharpoons (C_6H_5)_2C{=}CHC_6H_5 + (C_6H_4)_2{>}CNa{-}CH(C_6H_5)\cdot CH(C_6H_5)C(Na)(C_6H_4)_2 \qquad (118)$$

$$(C_6H_5)_2CNa{-}CHNaC_6H_5 + 2\,(C_6H_5)_2C{=}CH_2 \rightleftharpoons (C_6H_5)_2C{=}CHC_6H_5 + (C_6H_5)_2CNa\cdot CH_2CH_2\cdot CNa(C_6H_5)_2 \qquad (119)$$

instead of to addition reactions. However, as has been pointed out by Ziegler and Schäfer (227), this fact merely shows that the addition tendency of the organo-alkali compound as well as the nature of the unsaturated hydrocarbon is a factor in determining the type of reaction.

If the reaction between sodium and *unsym*-diphenylethylene actually follows the course indicated in equations 116 and 117, the formation of the normal 1,2 addition product should be observable when the second reaction is eliminated by performing the experiment in the presence of an excess concentration of the alkali metal. This requirement is fulfilled when the diphenylethylene is added to an excess of sodium or potassium dissolved in liquid ammonia, and although the product is semi-ammonolyzed, it is evident that normal and not dimerizing addition takes place (220).

$$(C_6H_5)_2C{=}CH_2 + 2\,Na \rightarrow (C_6H_5)_2CNa{-}CH_2Na \qquad (120)$$

$$(C_6H_5)_2CNa{-}CH_2Na + NH_3 \rightarrow (C_6H_5)_2CNa{-}CH_3 + NaNH_2 \qquad (121)$$

The ammonolysis product yields 1,2,2-triphenylpropane, $C_6H_5CH_2C(C_6H_5)_2CH_3$, on treatment with benzyl chloride, and 1,1-diphenylethane, $(C_6H_5)_2CHCH_3$, with ammonium chloride. No trace of the 1,1, 4,4-tetraphenylbutane which should result from the decomposition of a dimerized addition product was observed. The fact that some of this tetraphenylbutane *was* obtained *when the potassium was added to an excess of the diphenylethylene* in liquid ammonia demonstrates that the results are, indeed, due to the presence of excess metal and not to some specific action of the solvent ammonia.

The suggestion of Schlenk and Bergmann (153) that the results were due to the reaction,

$$(C_6H_5)_2CNa{-}CH_2{-} + NH_3Na \rightarrow NaNH_2 + (C_6H_5)_2CNa{-}CH_3 \quad (122)$$

although not contested by Ziegler (227), is hardly tenable in view of the evidence against the existence of "sodammonium," NH_3Na, presented by Kraus (91). On the other hand, there does exist a possible interpretation of these facts on the basis of the Schlenk and Bergmann hypothesis. It is that the presence of excess metal greatly favors the reaction,

$$(C_6H_5)_2CNa{-}CH_2{-} + Na \rightarrow (C_6H_5)_2CNa{-}CH_2Na \quad (123)$$

in competition with the polymerization expressed in equation 115.

It is fortunate, therefore, that Ziegler and Schäfer (227) have sought to substantiate their conclusion by a reaction employing solid alkali metals and ethereal solutions of the organic materials. They found that when the action of sodium on diphenylethylene was carried out in the presence of indene (2 moles), the concurrent reaction yielding diphenylethane

$$(C_6H_5)_2CNa{-}CH_2Na + 2\ C_9H_8 \rightarrow 2\ C_9H_7Na + (C_6H_5)_2CH{-}CH_3 \quad (124)$$

proceeds so rapidly that the ordinary course, as represented by equations 117 and 125, is followed only to the extent of 20 per cent or less.

$$(C_6H_5)_2CNa{-}CH_2CH_2CNa(C_6H_5)_2 + 2\ C_9H_8 \rightarrow 2\ C_9H_7Na + (C_6H_5)_2CHCH_2CH_2CH(C_6H_5)_2 \quad (125)$$

The possibility that the diphenylethane resulted from reduction of the ethylene by nascent hydrogen liberated in a reaction between indene and sodium was excluded by a study of the rates of reaction of sodium with diphenylethylene alone, with indene alone, and with the mixture of the two hydrocarbons.

In figure 3A the ordinates represent amounts of metal reacting, in atoms per mole of diphenylethylene or per two moles of indene, and the abscissae the time in hours. Curve I gives the rate at which sodium reacted with an ethereal solution of diphenylethylene. After two or three hours the reaction is practically completed, and one atom of sodium per molecule of the ethylene has dissolved, as is required by the usual dimerizing reaction. Curve III is the rate of formation of indenylsodium from sodium and indene under the same conditions. It is evident that in the short time of two or three hours no significant quantities of indenylsodium result, so this reaction is too slow to account for the the formation of the diphenylethane. Finally, curve II gives the sodium consumption of solutions containing two molecules of indene per molecule of the diphenylethylene. It is clear that this is very much like the curve of the rate of addition of sodium to the diphenylethylene but, owing to the presence of the indene, two atoms of metal are dissolved. The slight difference

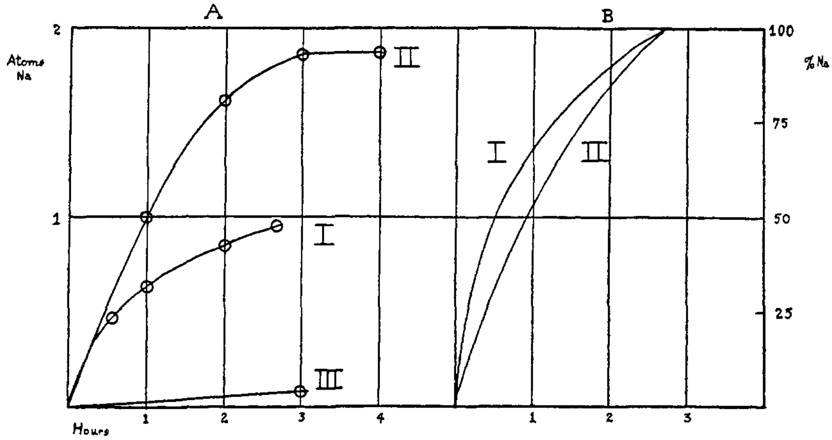


FIG. 3. THE RATE OF ADDITION OF SODIUM TO DIPHENYLETHYLENE

is the result of the concurrent reaction (equations 117 and 125), and if allowance is made for this factor the consumption of sodium becomes exactly two atoms. The close similarity of curves I and II is best revealed when they are plotted on comparable scales (i.e., per cent of total metal consumption as ordinates) as in figure 3B.

Ziegler and Schäfer have also considered whether some of the indene could have acted directly as a hydrogen donator.

$$(C_6H_5)_2CNaCH_2\text{—} + 2\ C_9H_8 \rightarrow C_9H_7Na + C_9H_7\text{—} + (C_6H_5)_2CHCH_3 \quad (126)$$

$$C_9H_7\text{—} + Na \rightarrow C_9H_7Na \quad (127)$$

They concluded that the reaction expressed in equation 127 could not be expected to go to completion in such a heterogeneous system, because all of the indenyl radicals would not remain in the free condition long enough to come into contact with an alkali metal surface, and that consequently this hypothesis could not account for the consumption of two atoms of sodium as observed. It appears that they have overlooked here one necessary link in their chain of evidence. If the indenyl radicals resulting from the reaction expressed in equation 126 polymerized to biindenyl, this substance *might* then have been completely converted into indenylsodium by the cleavage reaction,

$$C_9H_7\text{—}C_9H_7 + 2\ Na \rightarrow 2\ C_9H_7Na \quad (128)$$

thus accounting for the total sodium consumption actually observed. It is quite possible that this weakness may be eliminated by a study of the rate of the cleavage reaction (equation 128), but until this has been done the hypothesis of Ziegler, Colonius, and Schäfer rests largely on the similarity of curves I and II and the alternative hypothesis of Schlenk and Bergmann cannot be rigidly excluded.

4. The structure of certain aromatic olefins and their alkali metal derivatives

The fact that several unsaturated hydrocarbons (table 6, nos. 5 to 10) unexpectedly failed to add sodium[2] led Schlenk and

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[2] However, Conant and Blatt (42) had previously reported the preparation of typical dimerized addition products from propylstyrene, $C_6H_5CH{=}CHC_3H_7$, and dimethylstyrene, $C_6H_5CH{=}C(CH_3)_2$, by the action of sodium-potassium alloy in ether.

Bergmann (144) to propose for these substances the following isomeric structures,

(5) a. $(C_6H_5)_2CH—CH{=}CH_2$

(6) b. $(C_6H_5)_2CH—C(CH_3){=}CH_2$

(7) c. $C_6H_5CH_2—C(CH_3){=}CH_2$

(8) d. $(C_6H_5)(CH_3)CH—C(CH_3){=}CH_2$

(9) e. $(C_6H_5)_2CH—C(CH_2C_6H_5){=}CHC_6H_5$

(10) f. $(C_6H_5)_2CH—CH{=}CHC_6H_5$

which need not be expected to add alkali metals and which were in agreement with the formation of substitution products with sodium and lithium as in cases 10 and 6 (table 6), respectively. However, these authors later (152) withdrew this proposal in favor of the assumption of a tautomeric equilibrium between the pairs of alternative structures, in view of certain objections to the isomeric formulas a, b, and f marshalled by Ziegler, Colonius, and Schäfer (220). These objections were based on the refractometric data of Richter (130), the spectrochemical studies of Auwers (4), and the following two syntheses of 1,1,3-triphenyl-1-methoxypropylene-2 by Ziegler, Richter, and Schnell (226) which are difficult to reconcile with the alternative formula f.

$$(C_6H_5)_2C{=}CH \cdot CH_2C_6H_5 + Br_2 \rightarrow (C_6H_5)_2CBr—CHBr \cdot CH_2C_6H_5 \tag{129A}$$

$$(C_6H_5)_2CBr—CHBr \cdot CH_2C_6H_5 + CH_3OH \rightarrow (C_6H_5)_2C(OCH_3)CHBr \cdot CH_2C_6H_5 + HBr \tag{129B}$$

$$(C_6H_5)_2C(OCH_3)CHBr \cdot CH_2C_6H_5 \rightarrow (C_6H_5)_2C(OCH_3)—CH{=}CHC_6H_5 + HBr \tag{129C}$$

$$(C_6H_5)_2CO + C_6H_5CH{:}CHMgBr + H_2O \rightarrow Mg(OH)Br + (C_6H_5)_2C(OH)—CH{=}CHC_6H_5 \tag{130A}$$

$$C_6H_5C(OH)—CH{=}CHC_6H_5 + K + CH_3I \rightarrow KI + (C_6H_5)_2C(OCH_3)—CH{=}CH{\cdot}C_6H_5 \tag{130B}$$

Furthermore, the substitution products formed with phenylisopropylpotassium (table 8, nos. 10, 11, and 13), whose structures were *apparently* established by converting them into the carboxylic acids through the action of carbon dioxide and subsequent hydrolysis, are in accord with the classical formulas rather than the new ones (a, b, and f). This is particularly noteworthy in the cases of 1,1-diphenyl-2,2-dimethylethylene, and 1,1-diphenyl-2-

benzylethylene (table 8, nos. 11 and 13), since Schlenk and Bergmann obtained substitution products by the direct action of alkali metal to which they attributed an isomeric structure (table 6, nos. 6 and 10). Ziegler, Colonius, and Schäfer (220) concluded that the formulas of Schlenk and Bergmann were erroneous and at first suggested for their formation reactions of the following type:

$$(C_6H_5)_2C{=}C(CH_3)_2 + 2\ K \rightarrow (C_6H_5)_2CK{-}CK(CH_3)_2 \qquad (131)$$

$$(C_6H_5)_2CK{-}CK(CH_3)_2 + (C_6H_5)_2C{=}C(CH_3)_2 \rightarrow (C_6H_5)_2CK{-}CH(CH_3)_2 + (C_6H_5)_2C{=}C(CH_3)CH_2K \qquad (132)$$

since by carrying out the reaction with sodium–potassium alloy and treating the product with carbon dioxide, they were able to isolate the two carboxylic acids corresponding to the analogous saturated and unsaturated potassium (or sodium) compounds. However, Schlenk and Bergmann (153) were able to show that the use of lithium led directly to the formation of only one lithium compound (not the saturated one), and that some 1,1-diphenyl-2-methylpropane also resulted; consequently Ziegler and Schäfer (227) suggested that the additional reaction,

$$(C_6H_5)_2CLi{-}CH(CH_3)_2 + (C_6H_5)_2C{=}C(CH_3)_2 \rightarrow (C_6H_5)_2CH{-}CH(CH_3)_2 + (C_6H_5)_2C{=}C(CH_3)CH_2Li \qquad (133)$$

took place with the lithium compounds, supporting their suggestion by the analogy,

$$(C_6H_5)_2CNa{\cdot}CH_3 + (C_6H_5)_2C{=}CH{\cdot}CH_3 \rightarrow (C_6H_5)_2CHCH_3 + (C_6H_5)_2C{=}CH{\cdot}CH_2Na \qquad (134)$$

On the other hand, having found that the action of lithium on 1,1-diphenyl-2-benzylethylene resulted in products analogous to those obtained by Ziegler and Schäfer with 1,1-diphenyl-2,2-dimethylethylene and sodium–potassium alloy (equations 131 and 132), Schlenk and Bergmann (154) considered this to represent a third general type of addition reaction—"disproportionating addition"—for which they proposed the following reaction scheme based on their intermediate free radical interpretation of dimerizing addition.

$$2\,(C_6H_5)_2C{=}CH{-}CH_2C_6H_5 + 2\,Li \rightarrow 2\,(C_6H_5)_2CLi{-}\overset{|}{C}H{\cdot}CH_2C_6H_5 \qquad (135)$$

$$2\,(C_6H_5)_2CLi{-}\overset{|}{C}H{\cdot}CH_2C_6H_5 \rightarrow (C_6H_5)_2CLi{-}CH_2{\cdot}CH_2C_6H_5 + (C_6H_5)_2CLi{-}CH{=}CHC_6H_5 \qquad (136)$$

Now it is evident that Schlenk and Bergmann's formulation of these unsaturated metal derivatives,

A. $(C_6H_5)_2CM{-}CR{=}CR_2$

differs from that of Ziegler, Colonius, and Schäfer,

B. $(C_6H_5)_2C{=}CR{-}CR_2M$

and it would appear that the structure of the reaction products with carbon dioxide, in which the carboxyl group occupies the position of M in formula B, excluded the structures and reaction mechanisms of Schlenk and Bergmann. However, it has been shown recently by these authors (154) and by Crössmann (227) in Ziegler's laboratory, that the organo-alkali compounds prepared by cleavage of the two ethers,

$$(C_6H_5)_2C{=}CH{\cdot}CH(OCH_3){\cdot}C_6H_5$$

and

$$(C_6H_5)_2C(OCH_3){-}CH{=}CH{\cdot}C_6H_5$$

as well as those resulting from the action of phenylisopropylpotassium on the two corresponding hydrocarbons (H in the place of OCH_3 in the above formulas) are identical and yield identical reaction products with benzyl chloride, carbon dioxide, and phenyl isothiocyanate, in which the substituted group occupies the same position as the alkali metal atom in Ziegler, Colonius, and Schäfer's formulation of the organo-alkali compounds.

This clearly implies that at least one of the two isomeric organo-alkali compounds is capable of rearranging to the other, and leaves open the question of the structure of the stable isomer, for the reaction products may be considered as resulting from direct substitution in compounds of the structural type B (227) or from compounds of type A by a reaction involving the allyl displacement (153). None of the evidence for the alternative structures thus far presented (154, 205, 10) is decisive. The possibility that these two isomers exist in tautomeric equilibrium,

$$(C_6H_5)_2CNa{-}CH{=}CH{\cdot}C_6H_5 \rightleftharpoons (C_6H_5)_2C{=}CH{\cdot}CHNa{\cdot}C_6H_5 \qquad (137)$$

is of interest from the standpoint of the various electronic interpretations of organic reactions, since such a transformation could readily occur in the anions by a mere shift of electron pairs from shared to unshared positions without leaving their respective carbon atoms.

$$(C_6H_5)_2\ddot{C}{:}CH{::}CHC_6H_5 \rightleftharpoons (C_6H_5)_2C{::}CH{:}\ddot{C}HC_6H_5 \qquad (138)$$

Bergmann and Weiss (23) have recently reported a case in which the two types of unsaturated compounds exist independently and react differently with sodium. The substance of the structure,

$$C_6H_5CH_2(C_6H_5)C{=}C(C_6H_5)_2$$

adds two atoms of sodium. The isomer,

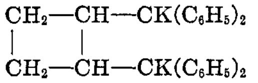
$$C_6H_5CH{=}C(C_6H_5)CH(C_6H_5)_2$$

yields a brown product from which the alkali metal is removed by mercury, leaving (among other products) a hydrocarbon $C_{54}H_{42}$. This suggests that the reaction between sodium and the second isomer consists of *substitution.*

$$2\,C_{27}H_{22} + 2\,Na \rightarrow 2\,C_{27}H_{21}Na + H_2 \qquad (139)$$

$$2\,C_{27}H_{21}Na + Hg \rightarrow C_{54}H_{42} \qquad (140)$$

In this connection some experiments of Wittig and Leo (205, 204) relating to the transmission of the influence of aromatic nuclei through the double bond are of interest. These investigators found that the action of potassium on 1,1,6,6-tetraphenylhexadiene-1,5 did not result in the formation of a cyclobutane derivative,



$$\begin{array}{l}CH_2\text{—}CH\text{—}CK(C_6H_5)_2\\ |\qquad\;\; |\\ CH_2\text{—}CH\text{—}CK(C_6H_5)_2\end{array}$$

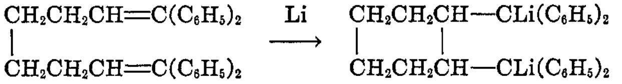
but consisted of cleavage.

$$(C_6H_5)_2C{=}CHCH_2\text{—}CH_2CH{=}C(C_6H_5)_2 + 2\,K \rightarrow 2\,(C_6H_5)_2C{=}CHCH_2K \quad (141)$$

Since a similar reaction occurred with 1,2-dibiphenylylethane,

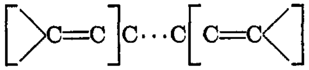
$$C_6H_5\cdot C_6H_4CH_2\text{—}CH_2C_6H_4\cdot C_6H_5 + 2\,K \rightarrow 2\,C_6H_5\cdot C_6H_4CH_2K \quad (142)$$

Wittig and Leo doubted that the cyclobutane derivative was formed even as an intermediate product. On the other hand, Bergmann (10) took the opposite view, because he observed ring formation in a somewhat similar reaction.

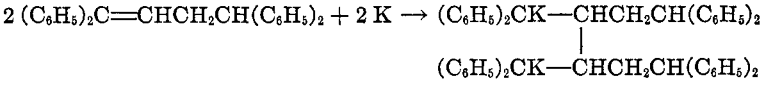


$$\begin{array}{lcl}CH_2CH_2CH{=}C(C_6H_5)_2 & & CH_2CH_2CH\text{—}CLi(C_6H_5)_2\\ | & \xrightarrow{Li} & |\qquad\qquad |\\ CH_2CH_2CH{=}C(C_6H_5)_2 & & CH_2CH_2CH\text{—}CLi(C_6H_5)_2\end{array} \quad (143)$$

However, Wittig and Leo contend that this evidence has no bearing on the question, because Bergmann's compound lacks a "cleavage position," that is a



grouping. In further support of their views they have studied the action of potassium on 1,1,4,4-tetraphenylbutene-1. This reaction might be expected to follow either of two courses: (1) addition and coupling in analogy with the mechanisms favored by Bergmann,



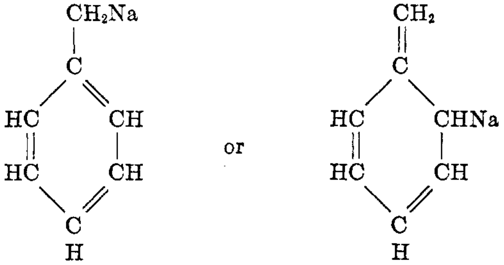
$$2\,(C_6H_5)_2C{=}CHCH_2CH(C_6H_5)_2 + 2\,K \rightarrow \begin{array}{l}(C_6H_5)_2CK\text{—}CHCH_2CH(C_6H_5)_2\\ \qquad\qquad\quad |\\ (C_6H_5)_2CK\text{—}CHCH_2CH(C_6H_5)_2\end{array} \quad (144)$$

or (2) cleavage analogous to the mechanisms of Wittig and Leo.

$$(C_6H_5)_2C{=}CHCH_2CH(C_6H_5)_2 + 2\,K \rightarrow (C_6H_5)_2CHK + (C_6H_5)_2C{=}CHCH_2K \quad (145)$$

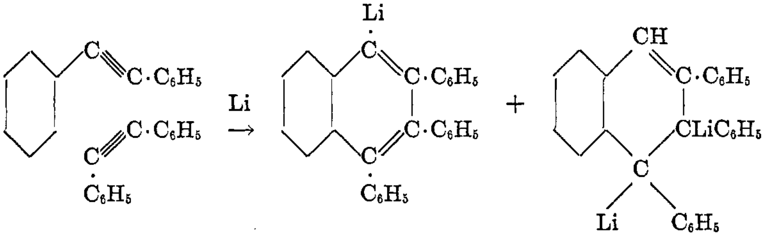
It is evident that the proportion of alkali metal consumed would be different in the two cases. The experimental determinations favored the proportion required by reaction 145, and the cleavage was further confirmed by isolation of diphenylmethane and 1,1-diphenylpropylene-1 after hydrolysis of the reaction products.

In conclusion it may be pointed out that the nuclear substitution observed in some reactions of sodium benzyl (equation 68) may also be interpreted in terms of an allylic (or *ortho* quinonoid) system.



5. *The addition of alkali metals to aromatic acetylenes*

Aromatic acetylenes whose structure precludes substitution may, nevertheless, in some instances react with alkali metals (144, 24). Thus tolane forms with lithium addition products which upon hydrolysis yield triphenylnaphthalene.



(146)

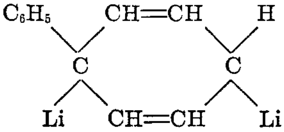
The action of carbon dioxide, followed by hydrolysis, yielded a monocarboxylic acid and the anhydride of a dicarboxylic acid, whereas phenyl isothiocyanate formed a derivative of a monolithium compound. The fact that the action of lithium on 1,1-dichloro- and 1,1-dibromo-2,2-diphenylethylene leads also to the same results has been ascribed to the intermediate formation of tolane.

$$(C_6H_5)_2C{=}CCl_2 + 2\,Li \rightarrow 2\,LiCl + \left[(C_6H_5)_2C{=}C\langle\right] \qquad (147)$$

$$\left[(C_6H_5)_2C{=}C\langle\right] \rightarrow C_6H_5C{\equiv}CC_6H_5 \qquad (148)$$

6. *Alkali metal additions to aromatic nuclei*

Although cesium, rubidium (70), and perhaps also potassium (1, 162), react with benzene to some extent, no definite alkali metal compounds have been isolated, nor have any decomposition products been obtained which clearly indicate the nature of the reaction. On the other hand, biphenyl yields a dilithium addition product of the probable structure,



and naphthalene one in which the lithium atoms occupy the 1,4 positions (144). Sodium, which is without action on these hydrocarbons except in liquid ammonia (213), reacts with certain others in ether under the same conditions as lithium, but more slowly. In some instances the products obtained with these two alkali metals are analogous, but in others they may be quite different, as is evident from table 9. The structural formulas are those suggested by the original investigators and they have not in all cases been completely established. Anthracene also appears to form a *mono*sodium derivative (145, 111, 29).

7. *Schlenk and Bergmann's "new type of compound with bivalent carbon"*

The action of lithium on tetraphenylallene results in the formation of the substance whose formula is given below,

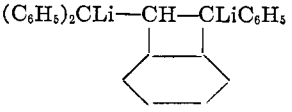


TABLE 9

The addition of alkali metals to aromatic nuclei (144, 145, 69)

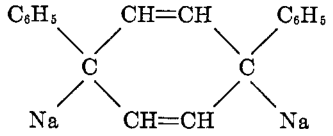
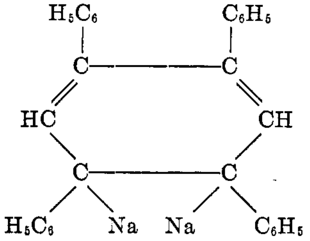
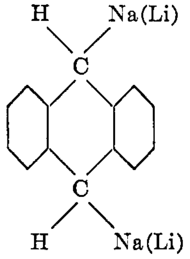
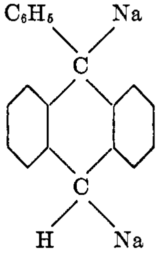
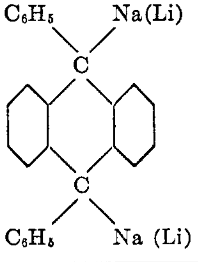
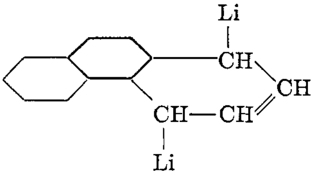
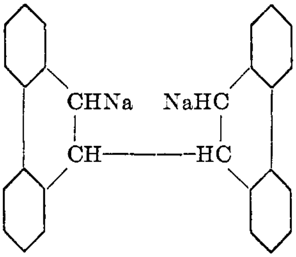
NO.	SUBSTANCE	PRODUCT
1	*p*-Diphenylbenzene..........	
2	1, 2, 4, 5-Tetraphenylbenzene.	
3	Anthracene..................	
4	9-Phenylanthracene..........	
5	9, 10-Diphenylanthracene....	

TABLE 9—*Concluded*

NO.	SUBSTANCE	PRODUCT
6	Phenanthrene.	 

but the use of sodium yields a different type of compound, which is supposed by Schlenk and Bergmann (146) to contain a bivalent carbon atom.

The assumption of Schlenk and Bergmann is based upon the reactions of a red disodium derivative of tetraphenylallene. Hydrolysis of this substance yields 1,1,3,3-tetraphenylpropylene,

$$(C_6H_5)_2CH—CH{=}C(C_6H_5)_2$$

and the action of carbon dioxide produces an insoluble white compound containing the correct proportion of sodium for the salt of a dicarboxylic acid. This evidence might be taken to indicate the following structure,

$$(C_6H_5)_2CNa—CNa{=}C(C_6H_5)_2$$

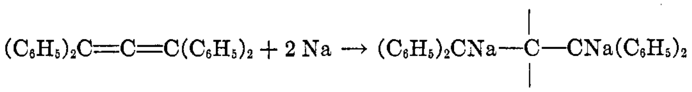
for the red disodium compound, but when the white reaction product is dissolved in water, reaction takes place and the salt of a monocarboxylic acid is formed. This acid has been shown to be 1,1,3,3-tetraphenylpropylene-2-carboxylic acid-1,

$$(C_6H_5)_2C(COOH)—CH{=}C(C_6H_5)_2$$

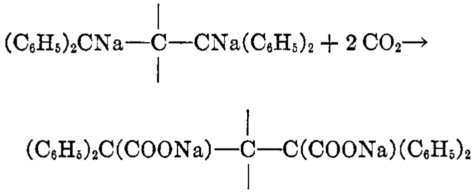
Schlenk and Bergmann contended that an acid of the structure,

$$(C_6H_5)_2C(COOH)—C(COOH){=}C(C_6H_5)_2$$

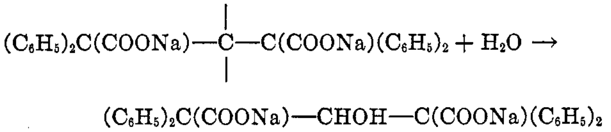
might form an anhydride but should otherwise be stable; they suggested the following equations for the reactions involved.



$$(C_6H_5)_2C{=}C{=}C(C_6H_5)_2 + 2\,Na \rightarrow (C_6H_5)_2CNa—\overset{|}{\underset{|}{C}}—CNa(C_6H_5)_2 \quad (149)$$



$$(C_6H_5)_2CNa—\overset{|}{\underset{|}{C}}—CNa(C_6H_5)_2 + 2\,CO_2 \rightarrow$$
$$(C_6H_5)_2C(COONa)—\overset{|}{\underset{|}{C}}—C(COONa)(C_6H_5)_2 \quad (150)$$



$$(C_6H_5)_2C(COONa)—\overset{|}{\underset{|}{C}}—C(COONa)(C_6H_5)_2 + H_2O \rightarrow$$
$$(C_6H_5)_2C(COONa)—CHOH—C(COONa)(C_6H_5)_2 \quad (151)$$

$$(C_6H_5)_2C(COONa)—CHOH—C(COONa)(C_6H_5)_2 \rightarrow NaHCO_3 +$$
$$(C_6H_5)_2C(COONa)—CH{=}C(C_6H_5)_2 \quad (152)$$

No evidence was presented to show that sodium bicarbonate was actually formed, and since the occurrence of the reaction expressed in equation 152 does not appear particularly more probable than the decomposition of the 1,2-dicarboxylic acid,

$$(C_6H_5)_2C(COOH)—C(COOH){=}C(C_6H_5)_2 \rightarrow CO_2 +$$
$$(C_6H_5)_2C(COOH)—CH{=}C(C_6H_5)_2 \quad (153)$$

it seems advisable to await further evidence before finally accepting these conclusions.

The other reactions of the disodium derivative of tetraphenylallene which are given in table 10 do suffice to show that its behavior is distinctly different from that of the 1,2 disodium addition compounds which have been previously investigated. Not only does mercury fail to react with the red salt, but dilute sodium amalgams react with tetraphenylallene to form the organo-alkali compound. Similar behavior has been observed only with triphenylmethyl and similar free radicals.

In order to establish the structures of the products listed in table 10, Schlenk and Bergmann carried out similar reactions with 1-sodium-1,1,3,3-tetraphenylpropylene-2, prepared according to equation 154.

TABLE 10

Reactions of the disodium derivative of tetraphenylallene

NO.	REAGENT	PRODUCT
1	CH_3I(room temperature)....	$(C_6H_5)_2C(CH_3)—CH=C(C_6H_5)_2$
2	CH_3I (below −20°)..........	$(C_6H_5)_2C=C=C(C_6H_5)_2$
3	$ClCH_2OCH_3$...............	$(C_6H_5)_2C(CH_2OCH_3)—CH=C(C_6H_5)_2$
4	$ClCOOCH_3$................	$(C_6H_5)_2C(COOCH_3)—CH=C(C_6H_5)_2$
5	C_2H_5NCS..................	$(C_6H_5)_2C[C(SNa){:}N \cdot C_2H_5]—CH=C_6H_5)_2$
6	$BrCH_2CH_2CH_2Br$...........	$(C_6H_5)_2C=C=C(C_6H_5)_2$
7	Iodine......................	$(C_6H_5)_2C=C=C(C_6H_5)_2$
8	Mercury....................	No action

TABLE 11

Reactions of sodiumtetraphenylpropylene, $(C_6H_5)_2CNa—CH=C(C_6H_5)_2$

NO.	REAGENT	PRODUCT
1	CO_2......................	$(C_6H_5)_2C(COONa)—CH=C(C_6H_5)_2$
2	CH_3I (at room temperature....................	$(C_6H_5)_2C(CH_3)—CH=C(C_6H_5)_2$
3	CH_3I (at −20°)...........	$(C_6H_5)_2C(CH_3)—CH=C(C_6H_5)_2$
4	$ClCH_2OCH_3$..............	$(C_6H_5)_2C(CH_2OCH_3)—CH=C(C_6H_5)_2$
5	C_2H_5NCS.................	$(C_6H_5)_2C[C(SNa){:}N \cdot C_2H_5]—CH=C(C_6H_5)_2$
6	$BrCH_2CH_2CH_2Br$.........	$(C_6H_5)_2C(CH_2CH_2CH_2Br)—CH=C(C_6H_5)_2$
7	Iodine.....................	A hydrocarbon, $C_{27}H_{22}$, of unknown structure

$$(C_6H_5)_2C(OC_2H_5)—CH=C(C_6H_5)_2 + 2\,Na \rightarrow NaOC_2H_5 + (C_6H_5)_2CNa—CH=C(C_6H_5)_2 \qquad (154)$$

The results which appear in table 11 are of interest for comparison with the data in table 10.

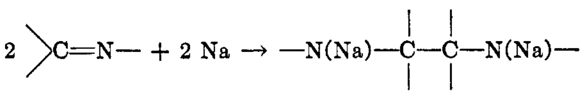
This investigation has inspired a renewed inquiry into the occurrence of free substituted methylenes as intermediates in a number of chemical reactions (19, 72, 87, 18). However, such work lies outside the scope of this review.

V. THE ADDITION OF ALKALI METALS TO MULTIPLE BONDS BETWEEN CARBON AND OTHER ELEMENTS

1. Alkali metal additions to carbon-nitrogen double bonds

Many compounds containing azomethine groups react with the alkali metals and, as in the case of ethylenic linkages, two types of reactions leading to normal and dimerized addition products are possible.

$$>C{=}N{-} + 2\ Na \rightarrow\ >C(Na){-}N(Na){-} \qquad (155)$$



$$2\ {>}C{=}N{-} + 2\ Na \rightarrow -N(Na){-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}N(Na){-} \qquad (156)$$

In some cases both types of addition reactions occur together. The results obtained with open chain compounds and with ring systems are similar. In table 12 are given the data furnished by a considerable number of experiments (147). The products were occasionally isolated in the form of molecular compounds with the parent substances as indicated. Some instances of the behavior of nitrogen-nitrogen double bonds toward alkali metals are also included.

Besides the two types of addition, it is evident that both substitution (table 12, nos. 14 and 20) and cleavage reactions (table 12, nos. 21, 22, and 23) also occur. In connection with the latter case it is interesting to note that the tendency toward cleavage of nitrogen-nitrogen single bonds is shown by the action of sodium on hydrazobenzene in liquid ammonia (198).

$$C_6H_5NH{-}NHC_6H_5 + 2\ Na \rightarrow 2\ C_6H_5NHNa \qquad (157)$$

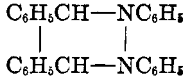
In fact, even the disodiumhydrazobenzene formed by the addition of sodium to azobenzene in liquid ammonia,

$$C_6H_5N{=}NC_6H_5 + 2\ Na \rightarrow C_6H_5N(Na){-}N(Na)C_6H_5 \qquad (158)$$

is further reduced by an excess of the metal.

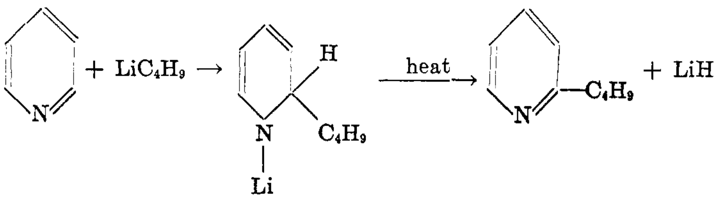
$$C_6H_5N(Na){-}N(Na)C_6H_5 + 2\,Na \rightarrow 2\,C_6H_5NNa_2 \qquad (159)$$

The two types of addition products yielded by azomethine groups show general differences in their chemical behavior similar to those which characterize the analogous derivatives of ethylenic linkages. Thus benzophenone-anil is regenerated from its typical 1,2 addition product (table 12, no. 1) by the action of mercury, methyl iodide, benzoyl chloride, phenyl benzoate, and phenyl isothiocyanate. On the other hand, substitution resulted from the action of methyl iodide and of phenyl isothiocyanate on the equally typical dimerized addition product derived from benzylidene aniline (table 12, no. 7). However, the reaction between this substance and benzophenone chloride gave rise to tetraphenylethylene, and treatment with ethyl benzoate or benzaldehyde led to the formation of a product containing no oxygen, which has been assumed to be



$$\begin{array}{l} C_6H_5CH{-}NC_6H_5 \\ \quad | \qquad\quad | \\ C_6H_5CH{-}NC_6H_5 \end{array}$$

Addition of organo-alkali compounds to azomethine groups may also occur, but thus far it has been definitely observed only between cyclic structures and lithium compounds, for although phenylisopropylpotassium reacts with equimolecular proportions of pyridine, the nature of the product is as yet unknown (231). Butyl- and phenyl-lithium form with pyridine addition products, which decompose on heating to 70–100° with loss of lithium hydride (231, 232).

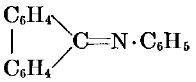
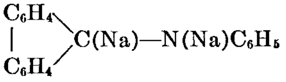
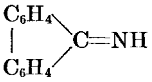
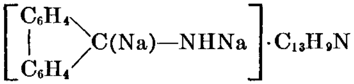
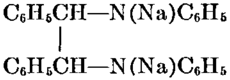
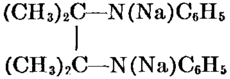
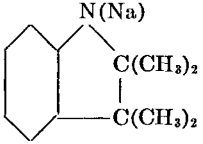


(160)

Phenyllithium reacts with quinoline and isoquinoline (14, 232). In the latter case hydrolysis of the resulting addition product is

TABLE 12

The addition of alkali metals to carbon-nitrogen and nitrogen-nitrogen double bonds

NO.	COMPOUND	PRODUCT
1	$(C_6H_5)_2C{=}N\cdot C_6H_5$ Benzophenone-anil	$(C_6H_5)_2C(Na)—N(Na)C_6H_5$
2	$(C_6H_5)(CH_3)C{=}N\cdot C_6H_5$ Acetophenone-anil	$(C_6H_5)(CH_3)C(Na)—N(Na)C_6H_5$
3	 Fluorenone-anil	
4	$C_6H_5CH{=}N\cdot C_2H_5$ Benzylidene-ethylamine	$C_6H_5CH(Na)—N(Na)C_2H_5$
5	$(C_6H_5)(CH_3)C{=}N\cdot CH_2C_6H_5$ Acetophenone-benzylimide	$(C_6H_5)(CH_3)C(Na)—N(Na)CH_2C_6H_5$
6	 Fluorenone-imine, $C_{13}H_9N$	
7	$C_6H_5CH{=}N\cdot C_6H_5$ Benzylidene-aniline	 $\begin{array}{l}C_6H_5CH—N(Na)C_6H_5\\ \quad\vert\\ C_6H_5CH—N(Na)C_6H_5\end{array}$
8	$(CH_3)_2C{=}N\cdot C_6H_5$ Acetone-anil	 $\begin{array}{l}(CH_3)_2C—N(Na)C_6H_5\\ \qquad\vert\\ (CH_3)_2C—N(Na)C_6H_5\end{array}$ and  + C_6H_5NHNa

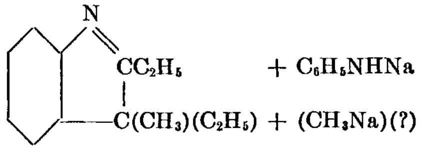
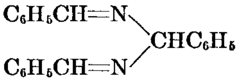
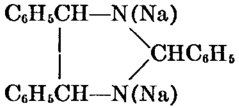
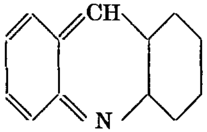
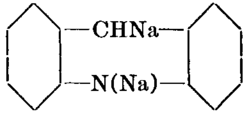
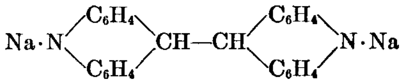
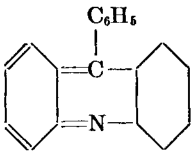
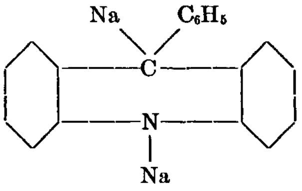
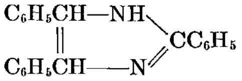
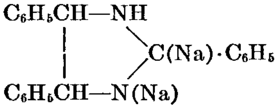
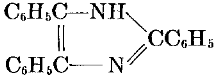
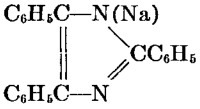
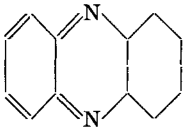
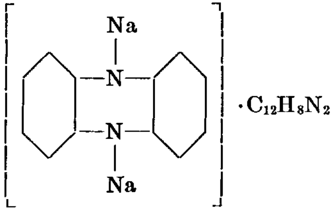
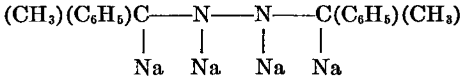
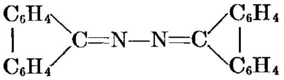
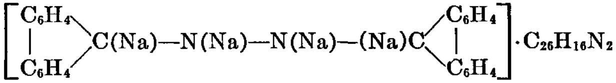
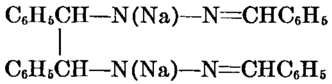
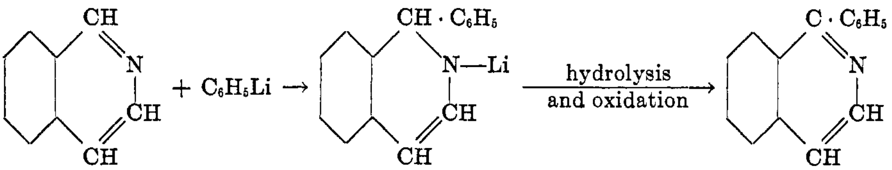
9	$(CH_3)(C_2H_5)C{=}N\cdot C_6H_5$ Methyl ethyl ketone-anil	Analogous to 8 and also 
10	$$\begin{matrix} C_6H_5CH{=}N \\ C_6H_5CH{=}N \end{matrix} \Big> CHC_6H_5$$ Hydrobenzamide	
11	 Acridine	 and 
12	 Phenylacridine	

TABLE 12—*Concluded*

NO.	COMPOUND	PRODUCT
13	 Amarine	
14	 Lophine	
15	 Phenazine, $C_{12}H_8N_2$	
16	$(CH_3)(C_6H_5)C{=}N{-}N{=}C(C_6H_5)(CH_3)$ Acetophenone-ketazine	 $(CH_3)(C_6H_5)\underset{\text{Na}}{C}{-}\underset{\text{Na}}{N}{-}\underset{\text{Na}}{N}{-}\underset{\text{Na}}{C}(C_6H_5)(CH_3)$
17	$(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$ Benzophenone-ketazine	$(C_6H_5)_2C(Na){-}N(Na){-}N(Na){-}C(Na)(C_6H_5)_2$
18	 Fluorenone-ketazine, $C_{26}H_{16}N_2$	

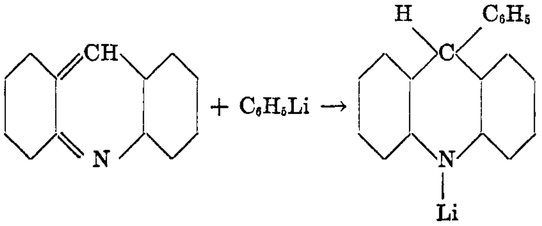
19	$C_6H_5CH{=}N{-}N{=}CHC_6H_5$ Benzalazine	 $C_6H_5CH{-}N(Na){-}N{=}CHC_6H_5$ $\vert$ $C_6H_5CH{-}N(Na){-}N{=}CHC_6H_5$
20	$(C_6H_5)_2C{=}N\cdot NH_2$ Benzophenone-hydrazone	$(C_6H_5)_2C{=}N\cdot NHNa$
21	$(C_6H_5)_2C{=}N\cdot N(C_6H_5)_2$ Benzophenone-diphenylhydrazone	$(C_6H_5)_2C(Na){-}NNa_2 + (C_6H_5)_2N\cdot Na$
22	$(C_6H_5)_2C{=}N\cdot NHC_6H_5$ Benzophenone-phenylhydrazone	$(C_6H_5)_2C(Na){-}NNa_2 + C_6H_5NHNa$
23	$(C_6H_5)_2C{=}N\cdot N(CH_3)(C_6H_5)$ Benzophenone-methylphenylhydrazone	$(C_6H_5)_2C(Na){-}NNa_2 + (C_6H_5)(CH_3)NNa$
24	$C_6H_5N{=}NC_6H_5$ Azobenzene, $C_{12}H_{10}N_2$	$[C_6H_5N(Na){-}N(Na)C_6H_5]\cdot C_{12}H_{10}N_2$
25	$CH_3N{=}NCH_3$ Azomethane	$CH_3N(Na){-}N(Na)CH_3$
26	$(C_6H_5)_2N{-}N{=}N{-}N(C_6H_5)_2$ Tetraphenyltetrazane	$2\ (C_6H_5)_2NNa + N_2$

accompanied by spontaneous oxidation to the arylated isoquinoline (14).



(161)

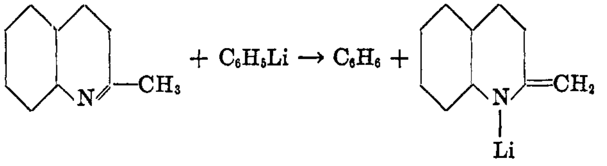
Phenyllithium also adds to acridine (14, 232),



(162)

and upon hydrolysis 9-phenyl-9,10-dihydroacridine is formed. The elimination of lithium hydride proceeds smoothly only with the pyridine derivatives.

With alkylated pyridines and quinolines substitution has been observed (232). Thus, the reaction between phenyllithium and quinaldine yields benzene and a lithium derivative of quinaldine.



(163)

Similar reactions have been observed by Bergstrom (25) who treated the alkylated pyridines and quinolines with alkali metal amides in liquid ammonia solution.

2. Alkali metal additions to carbon-oxygen double bonds

Non-enolizable aromatic ketones yield 1,2 addition products when treated with finely divided alkali metals in organic solvents (143, 150) or with the correct proportion of the alkali metal in liquid ammonia solution (168, 210). The same compounds may also be prepared by the action of alkali metal amides on suitably substituted carbinols in liquid ammonia (210).

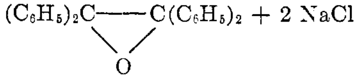
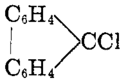
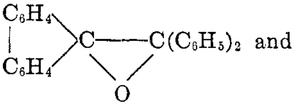
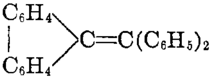
$$(C_6H_5)_2CHOH + KNH_2 \rightarrow (C_6H_5)_2CHOK + NH_3 \qquad (164)$$

$$(C_6H_5)_2CHOK + KNH_2 \rightarrow (C_6H_5)_2CKOK + NH_3 \qquad (165)$$

The first of these reactions is instantaneous, and on standing with excess potassium amide, the colorless solution of the carbinolate becomes intensely purple as the dipotassium derivative is formed.

TABLE 13

Reactions of disodiumbenzohydrol, $(C_6H_5)_2C(Na)ONa$

NO.	REAGENT	PRODUCTS
1	Water and other hydrolyzing agents	$(C_6H_5)_2CHOH + 2\ NaOH$
2	Carbon dioxide	$(C_6H_5)_2C(COONa)OCOONa$
3	Oxygen and iodine	$(C_6H_5)_2CO + Na_2O_2$ or $2\ NaI$
4	Benzyl chloride	$(C_6H_5)_2C(ONa)CH_2C_6H_5 + NaCl$
5	Benzophenone dichloride, $(C_6H_5)_2CCl_2$	
6	Fluorenone dichloride 	 

These substances show less tendency to regenerate the parent compounds in their reactions than do the other types of 1,2 addition products. This may be easily seen upon examination of table 13 (143, 150, 145, 88, 9, 89).

The action of ethyl bromide in liquid ammonia (210) leads to the intermediate formation of a product analogous to that obtained with benzyl chloride in ether,

$$(C_6H_5)_2C(Na)ONa + C_2H_5Br \rightarrow NaBr + (C_6H_5)_2C(ONa)C_2H_5 \qquad (166)$$

but the reaction proceeds further,

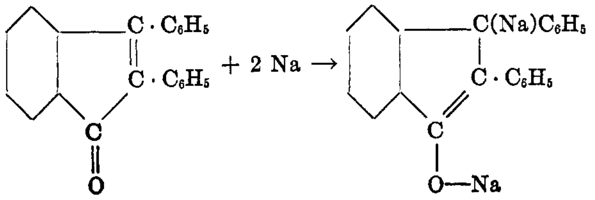
$$(C_6H_5)_2C(ONa)C_2H_5 + C_2H_5Br + NH_3 \rightarrow NaBr + C_2H_5NH_2 + (C_6H_5)_2C(OH)C_2H_5 \quad (167)$$

probably through the intermediate formation of ethylammonium bromide. The reaction observed with phenyl iodide in liquid ammonia is very odd.

$$(C_6H_5)_2C(Na)ONa + C_6H_5I + NH_3 \rightarrow NaI + C_6H_6 + (C_6H_5)_2C(NH_2)ONa \quad (168)$$

When disodiumphenylbiphenylcarbinol is treated with benzyl chloride there is obtained, in addition to phenylbiphenylbenzylcarbinol, a quantity of its benzyl ether and of triphenylethylene, which probably results from partial decomposition of the ether (150). The result obtained with methyl iodide is also interesting. Besides phenylbiphenylmethylcarbinol and its methyl ether (142), *p*-tolyl biphenyl ketone has been isolated after hydrolysis of the reaction product (150). No explanation has yet been offered for its formation.

Diphenylindone yields an unusual type of addition product with sodium (150).

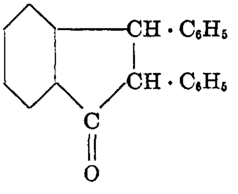


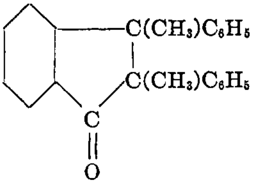
(169)

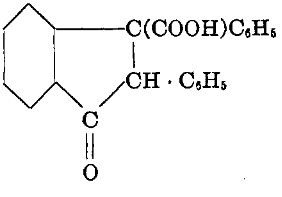
The reaction resembles in some respects the one which takes place with the diketone, benzil (181).

$$C_6H_5CO—COC_6H_5 + 2\ K \rightarrow C_6H_5C(OK)=C(OK)C_6H_5 \quad (170)$$

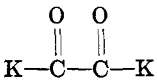
The products which are obtained when the sodium derivative of diphenylindone is treated with water, methyl iodide, and carbon dioxide (followed by hydrolysis), respectively, are indicated below.







The formation of a 1,2 addition product between sodium and benzaldehyde has been reported (28), and Joannis (82) obtained an addition product from the action of carbon monoxide on sodium and potassium, to which he assigned the constitution,

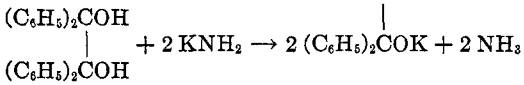


$$\mathrm{K{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}K}$$

In addition to the products just discussed, an entirely new type of compound may be obtained in many cases from the same ketones when they are treated with sticks of alkali metal in inert organic solvents (165, 164, 150, 135) or with a smaller proportion (one atom to one mole of ketone) of alkali metal in liquid ammonia (210).

$$(C_6H_5)_2C{=}O + Na \rightarrow (C_6H_5)_2\overset{|}{C}ONa \qquad (171)$$

The product prepared from potassium and phenyl biphenyl ketone has been shown to be monomolecular in solution, and since these substances may also be synthesized from the corresponding pinacols with the use of alkali metal alcoholates (164) or amides (209),



$$\begin{matrix}(C_6H_5)_2COH\\ |\\ (C_6H_5)_2COH\end{matrix} + 2\,KNH_2 \rightarrow 2\,(C_6H_5)_2\overset{|}{C}OK + 2\,NH_3 \qquad (172)$$

it has been suggested by Schlenk (164) that they are to be considered as a new type of free organic radicals having the general constitution, $RR'\overset{|}{C}{-}OM$ (M = alkali metal), and may be termed "metal ketyls."

3. The addition of alkali metals to carbon-sulfur double bonds

No definite addition compounds of this type are known. Schönberg (173) has found that colored products sensitive to air result from the action of alkali metals on certain thioketones.

VI. ORGANO-ALKALI COMPOUNDS AS INTERMEDIATES IN CHEMICAL REACTIONS

The study of organo-alkali compounds has awakened in some quarters a renewed interest in the mechanism of organic reactions involving the alkali metals, and the wider knowledge which has been obtained regarding the reactions and properties of the former substances has made possible a more thorough and penetrating investigation of such reaction mechanisms.

1. The polymerization of unsaturated hydrocarbons under the influence of alkali metals and organo-alkali compounds

Schlenk (143, 142) has shown that styrene and 1-phenylbutadiene are polymerized by the action of sodium powder in ether, and it is a well-known fact that this alkali metal promotes the polymerization of isoprene and butadiene to sodium rubber. Ziegler and Bähr (218) and later Ziegler and Kleiner (225) studied the action of organo-alkali compounds on these and similar hydrocarbons, observing that an addition reaction took place in some instances and in others polymerization ensued (see table 8). Since the addition products which might be formed in any case would themselves be organo-alkali compounds, it was evident that under favorable circumstances they, in turn, might add to other molecules of the unsaturated hydrocarbon. Such behavior would result in polymerization, and these investigators were led to suspect that the polymerization actually observed proceeded by such a mechanism,

$$CH_2{=}CHR + KR' \rightarrow R'CH_2{-}CHRK \qquad (173)$$

$$CH_2{=}CHR + R'CH_2{-}CHRK \rightarrow R'CH_2{\cdot}CHR{\cdot}CH_2{-}CHRK \qquad (174)$$

$$CH_2{=}CHR + R'CH_2{\cdot}CHR{\cdot}CH_2{-}CHRK \rightarrow$$
$$R'CH_2{\cdot}CHR{\cdot}CH_2{\cdot}CHR{\cdot}CH_2{-}CHRK \qquad (175)$$

and so on.

The previous systematic study of the addition of organo-alkali compounds to unsaturated hydrocarbons (section IV, 2) furnished some information about the influences governing the possible occurrence of such polymerization. It has been noted that whereas organo-alkali compounds of the type, $C_6H_5\overset{/}{\underset{\diagdown}{C}}—K$, were capable of addition reactions, those of the types, $(C_6H_5)_2\overset{/}{C}—K$, and $(C_6H_5)_3CK$, were not. Since the addition of RK to styrene yields a compound of the first type,

$$RK + C_6H_5CH{=}CH_2 \rightarrow C_6H_5CHK—CH_2R \qquad (176)$$

polymerization may be expected and does occur. On the other hand, the addition product formed with *asym*-diphenylethylene,

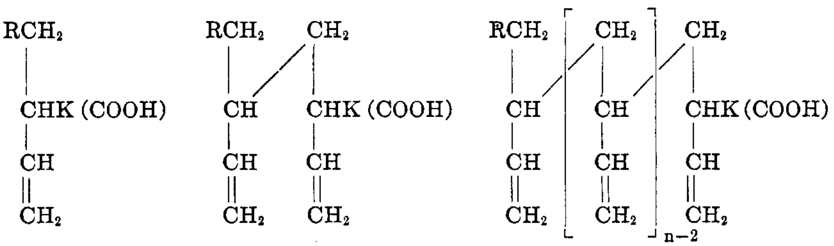
$$RK + (C_6H_5)_2C{=}CH_2 \rightarrow (C_6H_5)_2CK—CH_2R \qquad (177)$$

should be incapable of further addition and, in fact, no polymerization results. (Of course, polymerization could be expected only in the case of those unsaturated hydrocarbons capable of adding organo-alkali compounds and, furthermore, polymerization need not occur in all cases where the influences discussed are favorable.)

Ziegler and Kleiner undertook to test this hypothesis by treating phenylisopropylpotassium with butadiene-1,3 and isolating the addition products as carboxylic acids after treatment with carbon dioxide. The mean equivalent weight of the acid mixture could be obtained by determining the silver content of the silver salts, and a series of such experiments would show whether or not this value increased when the reaction time was lengthened.

However, the experiments were hindered by unsuspected complications. When phenylisopropylpotassium was treated with butadiene in excess (4 moles) the intense red color faded to a yellow as the reaction proceeded, but after a longer interval the color deepened again and finally became red once more. In order to obtain more information about the nature of the acid products, a quantitative determination of their unsaturation was made by hydrogenating them with the aid of a barium sulfate–palladium catalyst. Although the addition could occur in two different ways, the number of aliphatic double bonds per equivalent would in either case represent the number of butadiene residues in the molecule. This is evident from inspection of the formulas of the addition products which are given below. R equals $C_6H_5\overset{|}{C}(CH_3)_2$

1,2 Addition



Primary product 1 mole butadiene

2 moles butadiene

n moles butadiene

1,4 Addition

1 mole butadiene $RCH_2—CH=CH—CH_2K$ (COOH)

2 moles butadiene $RCH_2\cdot CH=CH\cdot CH_2\cdot CH_2\cdot CH=CH\cdot CH_2K$ (COOH)

n moles butadiene $RCH_2\cdot CH=CH\cdot CH_2\cdot [CH_2\cdot CH=CH\cdot CH_2]_{n-2}CH_2CH=CHCH_2K$ (COOH)

The results obtained in a study of the equivalent weights and unsaturation of the acid mixtures are given in table 14.

It can be seen that both the equivalent weights of the acids and the number of double bonds (or butadiene residues) per equivalent rapidly increase to a maximum and then slowly decrease. It is pertinent that the maximum values of these quantities also coincide with the minimum of color intensity. The explanation proposed is that the first process is polymerization via the mechanism already suggested, which is accompanied by a diminution in color due to the formation of weakly colored compounds in which the alkali metal is far removed from the aromatic radicals. The subsequent increase in color intensity and accompanying diminution in the tabulated quantities is attributed to re-formation of phenylisopropylpotassium by a reaction between the high molecular organo-alkali compound (R″K) and cumene (isopropylbenzene).

$$R''K + C_6H_5CH(CH_3)_2 \rightarrow R''H + C_6H_5CK(CH_3)_2 \qquad (178)$$

The cumene may result from the action of traces of moisture and of the solvent ether upon some of the phenylisopropylpotassium present during the earlier stages of the experiment.

$$C_6H_5CK(CH_3)_2 + (C_2H_5)_2O \rightarrow C_6H_5CH(CH_3)_2 + C_2H_4 + C_2H_5OK \qquad (179)$$

They were able to demonstrate the presence of regenerated phenylisopropylpotassium in the final reaction products by isolating phenylisobutyric acid, $C_6H_5(CH_3)_2CCOOH$, from the acid mixtures.

TABLE 14

Rate of polymerization of butadiene

(one mole of phenylisopropylpotassium and four moles of butadiene)

TIME	EQUIVALENT WEIGHTS	NUMBER OF DOUBLE BONDS PER EQUIVALENT
5 minutes	281	2.5
30 minutes	302	2.77
2 hours	261	2.45
4.5 hours	233	1.67
26 hours	237	1.74
2 days	216	1.62

TABLE 15

The polymerization of butadiene

BUTADIENE	AVERAGE EQUIVALENT WEIGHT OF ACIDS A	DOUBLE BONDS PER PER EQUIVALENT D	$A - 54\,D$
moles			
0	164	0	164
2	216	1.32	147
3	268	2.20	149
4	302	2.77	152
5	363	3.77	159
7	417	4.30	185
10	477	5.55	177
8	493	6.04	167

In the next series of experiments the alkali metal compounds were decomposed by carbon dioxide at the time of minimum color intensity and the influence of varying proportions of butadiene was studied. The results appear in table 15.

In agreement with the hypothesis of Ziegler and Kleiner the equivalent weights of the acids and the number of double bonds per equivalent increase when larger proportions of butadiene are used. A check on these quantities is provided by subtracting from the equivalent weight (A) the product of the number of double bonds (D) by 54, the molecular weight of butadiene. This difference ($A - 54D$) should equal the weight of the remainder of the molecule

$$C_6H_5\overset{|}{C}(CH_3)_2 + COOH = 164$$

and the correspondence is, in fact, reasonably close.

Of especial interest is the result obtained with eight molecules of butadiene and a very pure, freshly prepared sample of phenylisopropylpotassium which was, in consequence, relatively free from cumene. The values determined in this experiment are given in the last column of table 15. Both the equivalent weight of the acids and the number of butadiene residues in the molecule (6.04) are the highest obtained, and even the agreement between the check calculation, ($A - 52D$), and the theory is exceptionally good.

It may be noted that the number of butadiene residues in the acids is always less than the number of moles of butadiene used. Evidence was obtained to indicate that this fact was partly due to side reactions, in which phenylisopropylpotassium donated its alkali metal to butadiene, and partly to the fact that acids having a molecular weight much higher than 500–600 were lost in the process of separation because they are not soluble in alkali.

In spite of the fact that the molecular weight of the more complex acids falls within the range of caoutchouc fractions (129), they were relatively fluid oils. This result may, however, be ascribed to the presence of the "foreign" phenylisopropyl and carboxyl groups which constituted about 33 per cent of their molecular weight.

One experiment on the ozonization of an acid containing five butadiene residues yielded succinic aldehyde, succinic acid, and acetaldehyde, but very little formaldehyde. This suggests that the polymerization involved the 1,4 type of addition. The observation of Midgley and Henne (113) that 2-methylbutene-2 results from the action of sodium on isoprene in liquid ammonia is also interesting in this connection, for it shows that alkali metal addition to isoprene occurs in the 1,4 positions.

$$CH_2{=}C(CH_3)\cdot CH{=}CH_2 + 2\,Na \rightarrow CH_2Na\cdot C(CH_3){=}CH\cdot CH_2Na \qquad (180)$$

$$CH_2Na\cdot C(CH_3){=}CH\cdot CH_2Na + 2\,NH_3 \rightarrow 2\,NaNH_2 + (CH_3)_2C{=}CHCH_3 \qquad (181)$$

Reference may well be made here to the use of organo-alkali reactions in the study of polymerization by Bergmann and coworkers (22, 20).

2. The mechanism of the Wurtz-Fittig reaction

The coupling of two organic residues in the Wurtz-Fittig synthesis might be interpreted in two distinctly different ways. One interpretation involves the polymerization of free radicals,

$$2\,RX + 2\,Na \rightarrow 2\,NaX + 2\,R\text{—} \qquad (182)$$

$$2\,R\text{—} \rightarrow R_2 \qquad (183)$$

and the other assumes the intermediate formation of organo-alkali compounds.

$$RX + 2\,Na \rightarrow NaX + RNa \qquad (184)$$

$$RNa + RX \rightarrow R_2 + NaX \qquad (185)$$

Indirect evidence that organo-alkali compounds are actually formed in the reaction between organic halides and alkali metals under the conditions of the Wurtz-Fittig reaction has been obtained by many investigators. Shoruigin (174) has shown that the action of carbon dioxide on a reaction mixture of sodium and isobutyl bromide results in the formation of isovaleric acid.

$$(CH_3)_2CH\cdot CH_2Br + 2\,Na \rightarrow NaBr + (CH_3)_2CH\cdot CH_2Na \qquad (186)$$

$$(CH_3)_2CH\cdot CH_2Na + CO_2 \rightarrow (CH_3)_2CH\cdot CH_2COONa \qquad (187)$$

Analogous results with aryl halides have been recently reported by Morton and Stevens (117).

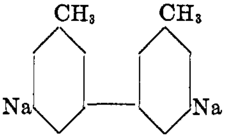
When a mixture of sodium, isoamyl bromide, and benzene was similarly treated, benzoic acid was obtained (174).

$$(CH_3)_2CH\cdot CH_2CH_2Br + 2\,Na \rightarrow NaBr + (CH_3)_2CH\cdot CH_2CH_2Na \quad (189)$$

$$(CH_3)_2CH\cdot CH_2CH_2Na + C_6H_6 \rightarrow (CH_3)_2CH\cdot CH_2CH_3 + C_6H_5Na \quad (190)$$

$$C_6H_5Na + CO_2 \rightarrow C_6H_5COONa \quad (191)$$

Fuchs and Metzl (56) found that hydrolysis of a reaction mixture obtained from sodium and 3,5-dibromotoluene yielded, among other products, *m*-ditolyl, which might have resulted from a sodium compound of the structure



Schlubach and Goes (170) employed carbon monoxide to detect the presence of sodium compounds in reaction mixtures of sodium with ethyl bromide and with bromobenzene. They were able to isolate ketones, tertiary alcohols, and acids, and concluded that the normal Wurtz-Fittig reaction involved organo-alkali compounds, whereas side reactions resulted from the formation of free radicals. Since the formation of phenylsodium might be expected to proceed more readily than that of ethylsodium, and the former would react more rapidly with ethyl bromide than with bromobenzene, they proposed these influences as the reason for the good yield of ethylbenzene obtainable from sodium, ethyl bromide, and bromobenzene.

Kirrmann (86) obtained large amounts of the corresponding hydrocarbon from the action of sodium on substituted vinyl halides,

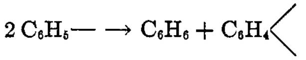
$$RCH{=}CHBr + 2\,Na \rightarrow NaBr + RCH{=}CHNa \quad (192)$$

$$RCH{=}CHNa + H_2O \rightarrow RCH{=}CH_2 + NaOH \quad (193)$$

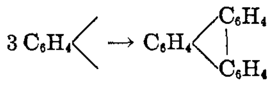
a result that might be correlated with the well-known fact that such halides show a relatively low reactivity. Goldschmidt and Schön (63) showed that the main reaction products obtained from sodium and 3-iodo-*o*-cresyl ethyl ether could be explained by reactions of the types expressed in equations 184, 185, and 190.

Direct evidence of the presence of organo-alkali compounds in such reaction mixtures has been obtained by Spencer and Price (179), Ziegler and Colonius (219), and W. Schlenk, Jr. (166). Since the simple lithium alkyls and aryls react very sluggishly with certain organic halides, these investigators were able in some instances to prepare lithium compounds directly by the reaction between lithium and suitable organic halides in ether and benzene solution (equation 4).

Evidence that free radicals are formed has also been obtained. For instance, Bachmann and Clarke (6) have isolated triphenylene from the numerous products of the reaction between sodium and chlorobenzene. They were unable to account for the formation of this substance except through the intermediate formation of phenyl radicals.



$$2\,C_6H_5— \rightarrow C_6H_6 + C_6H_4\Big\langle \tag{194}$$



$$3\,C_6H_4\Big\langle \rightarrow C_6H_4\left\langle\begin{array}{l}C_6H_4\\ \,|\\ C_6H_4\end{array}\right. \tag{195}$$

The use of solutions of alkali metals in liquid ammonia might be expected to be more favorable toward the formation of organo-alkali compounds. In fact, the reaction between sodium and triphenylchloromethane yields triphenylmethylsodium which is stable under these conditions (93). The intermediate formation of benzylsodium from sodium and benzyl halides in liquid ammonia has also been observed (95, 211, 37). Ethyl bromide and sodium react according to the equation

$$2\,C_2H_5Br + 2\,Na + NH_3 \rightarrow C_2H_6 + C_2H_5NH_2 + 2\,NaBr \tag{196}$$

which might be interpreted in terms of either hypothesis,

$$2\,C_2H_5Br + 2\,Na \rightarrow 2\,NaBr + 2\,C_2H_5— \tag{197}$$

$$2\,C_2H_5— + NH_3 \rightarrow C_2H_6 + C_2H_5NH_2 \tag{198}$$

or,

$$C_2H_5Br + 2\,Na \rightarrow NaBr + C_2H_5Na \qquad (199)$$

$$C_2H_5Na + NH_3 \rightarrow C_2H_6 + NaNH_2 \qquad (200)$$

$$C_2H_5Br + NaNH_2 \rightarrow C_2H_5NH_2 + NaBr \qquad (201)$$

However, when the ethyl bromide is added to a concentrated solution of excess sodium (209) the number of molecules of ethane evolved at first equals the number of molecules of ethyl bromide used, showing that the ethane and ethylamine result from independent reactions (equations 200 and 201) and are not formed simultaneously in a single process (equation 198).

On the other hand, a similar explanation of the reaction between sodium and chlorobenzene in ammonia is not valid. The products are benzene, diphenylamine, triphenylamine, and a little aniline (197). The formation of diphenylamine, for instance, might conceivably be represented by equations 202 to 206,

$$2\,C_6H_5Cl + 4\,Na \rightarrow 2\,NaCl + 2\,C_6H_5Na \qquad (202)$$

$$2\,C_6H_5Na + 2\,NH_3 \rightarrow 2\,C_6H_6 + 2\,NaNH_2 \qquad (203)$$

$$C_6H_5Cl + NaNH_2 \rightarrow C_6H_5NH_2 + NaCl \qquad (204)$$

$$C_6H_5NH_2 + NaNH_2 \rightarrow NH_3 + C_6H_5NHNa \qquad (205)$$

$$C_6H_5NHNa + C_6H_5Cl \rightarrow (C_6H_5)_2NH + NaCl \qquad (206)$$

but it has been found that reactions of the type expressed in equation 206 do not occur in liquid ammonia under such conditions (199, 51).

The evidence available strongly suggests that both organo-alkali compounds and free radicals are formed in these reactions. A question of the order of formation remains. Some investigators (170, 6) have considered the free radicals as the primary products (equation 182) from which the organo-alkali compounds were subsequently derived by addition. The fact that Ziegler and Colonius (219) and Gilman and Zoellner (61) were able to obtain as much as 80 to 95 per cent yields of phenyllithium from lithium and bromobenzene in ether indicates that the organo-alkali compounds may be the primary products. It is not difficult to imagine the occurrence of a reaction of this type (equation 184) in liquid ammonia, where the alkali metal may be used at very appreciable concentrations, but in such a heterogeneous system as is represented by the usual conditions of the Wurtz-Fittig synthesis, the simultaneous reaction of two atoms of alkali metal requires explanation.

Ziegler and Schäfer (227) have offered an interesting answer to this problem. They pointed out that the distances between the atoms in the solid alkali metals were of the same order of magnitude as those between carbon and halogen in organic halides. Thus, when the halogen atom of an organic halide came into contact with an atom on an alkali metal surface, the attached carbon atom would not be far from another atom on the same metal surface. These considerations readily suggest a reasonable mechanism for the occurrence of reactions of the type expressed in equation 184 under the conditions of the Wurtz-Fittig synthesis.

3. The mechanism of hydrogenation with alkali metals and their amalgams

Willstätter, Seitz, and Bumm (202) have recently made a careful and critical study of the process of reducing organic compounds with sodium amalgam and water. The original theory of this reaction, proposed by Kekulé (85), Kolbe (78), von Baeyer (7), and others, attributed the reducing effect to nascent hydrogen liberated by the action of water on the amalgam. However, the classical researches "Über die Konstitution des Benzols" and the later literature (203) have shown that amalgam reductions often lead to seemingly paradoxical results. Thus the permanganate stable acids of the benzene series are readily reduced, whereas the "olefinic" di- and tetra-hydro acids which are easily oxidized by permanganate, are reduced by amalgam and water only with difficulty, if at all. A striking contrast to this behavior is presented by catalytic hydrogenation of the same substances, which yields no intermediate unsaturated products and proceeds more readily with the "olefinic" compounds than with the benzene derivatives.

Willstätter and his coworkers (202) have made a quantitative investigation by carrying out the reduction process in an inert atmosphere, calculating the total amount of nascent hydrogen formed from the titre of the alkaline aqueous solution, and determining the evolved hydrogen gas as water after oxidation. They soon learned that even the nature of the reduction products, as well as the activity of the amalgam, was dependent on its purity. Furthermore, they were able to demonstrate the remarkable fact that, although sufficiently pure amalgam acts very rapidly on many aromatic and olefinic compounds with a reducing efficiency greater than 90 per cent, *it does not react appreciably with pure water.*

The improbability that 90 per cent of the nascent hydrogen would react with organic molecules before combining with itself to form molecular hydrogen, and the antiparallel influence of purification on the reducing action of the amalgam and on its reactivity toward water are difficult to reconcile with the older theory. Accordingly, Willstätter and his coworkers have suggested that the reduction takes place through the intermediate addition of sodium to the organic molecule, followed by hydrolysis of the resulting organo-alkali compound. Thus direct decomposition of the amalgam by water is a side reaction, and the factors which favor this reaction, such as impurities in the amalgam, decrease its reducing efficiency. Furthermore, the discrepancy between the results of catalytic hydrogenation and amalgam reduction may be explained by differences in the influences governing the addition of hydrogen and sodium. This hypothesis also furnishes a clear reason why every other hydrogen-liberating metal may not be substituted for sodium with similar results.

The influence of pH on the course of amalgam reductions was also studied, and the results were traced in some instances to an influence on the mode of addition and in others to an effect upon the hydrolysis of the organo-alkali compounds.

In a series of investigations, Lebeau and Picon (97, 98, 101) showed that certain hydrocarbons were hydrogenated by the action of sodium in liquid ammonia at room temperature. It is interesting to note that most of the compounds which were reduced in this way (anthracene, biphenyl, naphthalene, phenanthrene, phenylethylene, and stilbene) have also been found to yield addition products with the alkali metals or with organo-alkali compounds (145, 144, 222), whereas the compounds which were unaffected (103) (amylene, benzene, toluene, cymene, terpinene, terpinoline, carvine, terebene, α-pinene, and menthene) have not as yet been found capable of adding the alkali metals, although several have been specially investigated with this point in view (209). This coincidence suggests that these reductions may also involve the intermediate formation of alkali metal addition products, and a more detailed study of the reduction of naphthalene in liquid ammonia has been made to test this possibility (213).

Since the product of the reduction was a tetrahydronaphthalene (101), the process may be expressed by equations 207 and 208 if the formation of an organo-alkali compound is assumed,

$$C_{10}H_8 + 4\,Na \rightarrow C_{10}H_8Na_4 \tag{207}$$

$$C_{10}H_8Na_4 + 4\,NH_3 \rightarrow C_{10}H_{12} + 4\,NaNH_2 \tag{208}$$

or by equations 209 and 210, if the reduction is attributed to nascent hydrogen.

$$4\,Na + 4\,NH_3 \rightarrow 4\,NaNH_2 + 4\,(H) \tag{209}$$

$$4\,(H) + C_{10}H_8 \rightarrow C_{10}H_{12} \tag{210}$$

Investigation of the reaction at the boiling point of liquid ammonia (−33.5°) showed that only four atoms of sodium per molecule of naphthalene reacted, regardless of the quantity of excess metal present and (within reasonable limits) of the time elapsed (213). This is in agreement with equations 207 and 208, but is contrary to the hypothesis that the reduction of naphthalene and the consumption of sodium are the result of *independent* reactions (equations 209 and 210). Other evidence confirming the presence of an organo-alkali compound was furnished by the red color of the liquid ammonia solution and the amounts of sodium peroxide obtained on oxidation of the reaction mixture. At −33.5° the 1,2,3,4-tetrasodium-1,2,3,4-tetrahydronaphthalene originally formed is approximately three-fourths ammonolyzed; at room temperature the results of Lebeau and Picon indicate that the ammonolysis is practically complete.

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