in America. The pyrethrin content of *P. roseum* is about the same as that of *P. cinerariaefolium*.

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ALKALI METAL DERIVATIVES OF PHENYLATED METHANES AND ETHANES

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The fact that many of the colored organo-alkali compounds conduct the electric current in ether and in liquid ammonia solution,[3] and behave in other ways as salts, implies that the corresponding hydrides should exhibit an acidic character, albeit an exceedingly weak one. In fact, it has been shown that they may react with the ammono-base, potassium amide, in liquid ammonia solution to form the potassium salts. Thus triphenylmethane forms potassium triphenylmethide[4]

$$(C_6H_5)_3CH + KNH_2 \longrightarrow NH_3 + (C_6H_5)_3CK \qquad (1)$$

and potassium benzhydrolate yields dipotassium benzophenone[5]

$$(C_6H_5)_2CHOK + KNH_2 \longrightarrow (C_6H_5)_2CKOK + NH_3 \qquad (2)$$

This behavior indicates that these hydrides are ionized to a greater degree than the solvent ammonia, for otherwise reaction would be expected to proceed in the opposite direction corresponding to an ammonolysis of the salts. In the case of the alkali alkyls and alkali phenyls[6] such an ammonolysis does occur, demonstrating that the corresponding hydrocarbons are ionized to a less degree than ammonia.[7] Accordingly it is impossible to obtain organo-alkali compounds by the action of potassium amide upon these hydrocarbons.

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[2] A portion of this material was submitted by N. W. Mitchell in a thesis for the degree of Bachelor of Science at the Massachusetts Institute of Technology.

[3] (a) Schlenk and Marcus, *Ber.*, **47**, 1664–1678 (1914); (b) Kraus and Rosen, THIS JOURNAL, **47**, 2739–2740 (1925); (c) Wooster, "Dissertation," Brown University, **1927.**

[4] Kraus and Rosen, Ref. 3b, p. 2741.

[5] Wooster, THIS JOURNAL, **50,** 1389 (1928).

[6] (a) Kraus and White, *ibid.*, **45,** 777 (1923); (b) White, *ibid.*, **45,** 779 (1923).

[7] Strictly speaking the ionization of ammonia does not constitute a sharp line of demarcation between hydrocarbons whose salts are completely stable and those whose salts are completely ammonolyzed. Hydrocarbons whose ionization lies either closely above or below that of ammonia would be expected to yield salts whose ammonolysis would reach an equilibrium when appreciable amounts of both the salt and hydrocarbon were present. In all cases considered in this paper, however, the salt was either formed in very large proportions or else in amounts so minute as to escape detection. Thus it is permissible to conclude that the ionization of these hydrocarbons was either considerably above or considerably below that of the solvent.

It is not possible to apply the usual methods to determine the ionization constants of such very weak and sparingly soluble acids, but the facts just reviewed suggest the use of potassium amide in liquid ammonia to differentiate between those hydrides whose ionization is greater and those whose ionization is less than that of this solvent. The results of applying this test to a series of phenylated methanes and ethanes appear in Table I. The action of potassium metal upon the same hydrocarbons in liquid ammonia is also indicated.

TABLE I

THE ACTION OF POTASSIUM AND OF POTASSIUM AMIDE ON PHENYLATED METHANES AND ETHANES

No.	Hydrocarbon formula	Potassium	Potassium 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	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	$(C_6H_5)_2CHCH_2C_6H_5$	Reacts	Reacts
8	$(C_6H_5)_3CCH_3$	Reacts slightly	No action
9	$(C_6H_5)_2CHCH(C_6H_5)_2$	Reacts	Reacts
10	$(C_6H_5)_3CCH_2C_6H_5$	Reacts slightly	No action
11	$(C_6H_5)_3CC(C_6H_5)_3$	Adds	...

From these data it is apparent that the ability of potassium amide to replace with potassium a hydrogen atom in hydrocarbons of this class is confined to those compounds (Numbers 2, 3, 7 and 9 in Table I) 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 Numbers 4, 8 and 10), it is very likely that it is this hydrogen atom which is replaced. This circumstance may be of use as a principle for deciding the structure of hydrocarbons and organo-alkali compounds of these types.

In certain instances potassium metal is capable of reacting slightly with hydrocarbons on which the amide has no action. This may be due to addition to the carbon–carbon bond between the ethanic carbon atoms, for a similar action of sodium–potassium alloy and of 40% sodium amalgam has been reported by Ziegler and Thielmann and Conant and Garvey.[8] In this connection it is interesting to note that the metal is without action on tetraphenylmethane. This fact favors a negative answer to the question of the partial dissociation of this compound raised by Walden[9] in discussing the molecular weights obtained by Kraus and Kawamura.[10]

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[8] (a) Ziegler and Thielmann, *Ber.*, **56B**, 1740 (1923); (b) Conant and Garvey, THIS JOURNAL, **49**, 2599 (1927).

[9] Walden, "Chemie der freien Radikale," Leipzig, **1924**, p. 340.

[10] Kraus and Kawamura, THIS JOURNAL, **45**, 2756 (1923).

The Relative "Electronegativity" of Organic Radicals.—The ionization of toluene is apparently intermediate between that of diphenylmethane and those of benzene and aliphatic hydrocarbons, for although toluene does not react with potassium amide, benzyl bromide and potassium metal yield potassium benzylide 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. Under similar conditions the alkali phenyls and alkali alkyls are ammonolyzed too rapidly to show such reactions. Thus the ionization of methane (as hydrogen methide) appears to be progressively increased by the substitution of phenyl groups. This is in accordance with Lewis' idea as elaborated in his monograph and with the concepts of Lucas[11] but is the reverse of the series of radicals as arranged in the order of increasing "electronegativity" by Kharasch and Marker.

These authors criticize the conceptions of Lewis in the following terms[12]—"It seems to us, however, more logical that the phenyl radical would in virtue of its electronegativity attract the pair of electrons from the methyl carbon atom, become then negatively charged and repel other electrons from the methyl carbon atom, making the benzyl group much less electronegative than the methyl." In this logic they appear to have overlooked the fact that in attracting the electrons of the methyl carbon atom to a sufficient extent to become negatively charged, as they assume, the phenyl group must leave the former positively charged, with an increased ability to attract electrons, and thus, according to their own definitions more "electronegative."[13]

Moreover, it is difficult to reconcile their conclusions not only with the experimental results which appear in Table I, but also with such a fact as that the substitution of phenyl radicals in ethylene eventually renders the double bond inactive toward bromine but capable of readily adding the alkali metals.[14]

Also, in applying their concepts to the dissociation of free radicals these authors predict that the compound X_3C-CX_3 should be less stable and more highly dissociated than hexaphenylethane whenever the radical X is more "electronegative" than phenyl. This prediction is not supported

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[11] (a) Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph, The Chemical Catalog Co., New York, **1923**; (b) Lucas, THIS JOURNAL, **48**, 1828 (1926).

[12] Kharasch and Marker, *ibid.*, **48**, 3138 (1926).

[13] Since this paper was submitted for publication an article by Smyth [*ibid.*, **51**, 2386 (1929)] has appeared in which attention is called to the same error in connection with the postulates of Kharasch and Darkis [*Chem. Rev.*, **5**, 582 (1928)] regarding the influence of substitution on the polarity of the double bond.

[14] (a) Schlenk, Appendrot, Michael and Thal, *Ber.*, **47**, 473 (1914); (b) Schlenk and Bergmann, *Ann.*, **463**, 2–97 (1928).

by the behavior of dichlorotetraphenylethane,[15] $(C_6H_5)_2CClCCl(C_6H_5)_2$, dichlorotetrabiphenylethane,[16] hexanitroethane[17] and hexachloro-ethane,[18] none of which appear to be dissociated into free radicals. Accordingly, their view that ". . . . the weight or complexity of the radical is of no significance—it is the electronegativity of the radical attached to the methyl carbon atom that is of paramount importance" is a too narrow one.

Such marked discrepancies cast doubt upon the general applicability of Kharasch and Marker's table of the relative "electronegativity" of organic radicals based upon the reactions between mixed organic mercury compounds and hydrogen chloride. In our opinion it is somewhat premature to draw any general conclusions regarding "electronegativity" from the course of a single class of chemical reactions until due allowance has been made for the influence of such factors as temperature, concentration, nature of solvent and solubility.

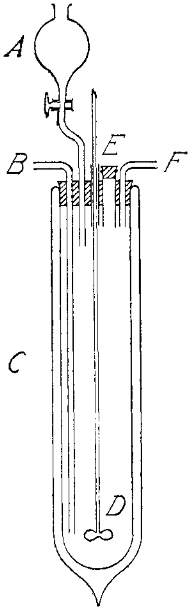

Fig. 1.—Apparatus for organic synthesis in liquid ammonia.

Experimental Part

Materials.—The toluene, diphenylmethane, triphenylmethane, ethylbenzene and dibenzyl were obtained from the Eastman Kodak Company and purified by crystallization or distillation. The other hydrocarbons were prepared by processes involving the use of liquid ammonia, as described below.

1,1,1-Triphenylethane was obtained by the action of methyl iodide on potassium triphenylmethide in liquid ammonia. This salt was prepared from potassium and triphenylmethane, the hydrocarbon being used in preference to a halide, in spite of its higher cost, because it could be more readily obtained in a very pure state. The reaction was carried out in the apparatus shown in Fig. 1, consisting of a large Dewar flask C of 1500-cc. capacity, a stirring screw D, operated by a stirring motor, and a rubber stopper fitted with an inlet B and an outlet F for ammonia gas, an opening E for the addition of solid reagents and a dropping funnel A for introducing liquids. The flask was filled two-thirds full of liquid ammonia, the stirrer started and a slow stream of ammonia gas blown through the liquid. The potassium was then introduced and the triphenylmethane (30 g.) slowly added in 5-g. portions at about half-hour intervals. Additional pieces of potassium were dropped in from time to time whenever the free metal had entirely reacted, as indicated by a change in color of the solution from opaque blue-black to transparent red. After all of the triphenylmethane had been added and had reacted, methyl iodide was dropped in until the solution became colorless. The equations for the principal reactions are

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[15] (a) Schmidlin, *Ber.*, **43**, 1153 (1910); (b) Norris, Thomas and Brown, *ibid.*, **43**, 2950 (1910).

[16] Schlenk and Racky, *Ann.*, **394**, 211, 215 (1912).

[17] Will, *Ber.*, **47**, 963 (1914).

[18] Beilstein, "Handbuch der organischen Chemie," [4] I, 87 (1918); Erstes Ergänzungswerk, [4] I, 26 (1928).

$$(C_6H_5)_3CH + K \longrightarrow (C_6H_5)_3CK + {}^1/_2H_2 \qquad (3)$$

$$(C_6H_5)_3CK + CH_3I \longrightarrow (C_6H_5)_3CCH_3 + KI \qquad (4)$$

and this type of synthesis is unique in that the preparation of a hydrocarbon from its next lower homolog is effected in a single process.

Although the liquid ammonia solution became colorless upon the addition of a slight excess of methyl iodide, part of the precipitate formed was light pink in color. This probably consisted of methylammonium triphenylmethide formed as a result of the reactions[19,20]

$$CH_3I + NH_3 \longrightarrow CH_3NH_3I \qquad (5)$$

$$CH_3NH_3I + (C_6H_5)_3CK \longrightarrow (C_6H_5)_3CNH_3CH_3 + KI \qquad (6)$$

By adding more potassium, continuing the stirring and then again adding a slight excess of methyl iodide, the major portion of this by-product was converted into the desired triphenylethane.

Most of the ammonia was allowed to evaporate. Water was then added to the residue and the aqueous solution filtered. The white solid on the filter paper was washed with water, dissolved in ether, the solution dried, filtered and evaporated and the product recrystallized from alcohol; yield, 85–94% of very pure product melting sharply at 95°.

1,1,1,2-Tetraphenylethane was prepared in a similar manner by the action of benzyl chloride on potassium triphenylmethide and a good yield of the hydrocarbon was obtained. The benzyl chloride was not very rapidly ammonolyzed so it was unnecessary to repeat the treatment with potassium as described in the preceding preparation.

1,1,2-Triphenylethane was obtained by reduction of triphenylethylene with sodium in liquid ammonia and decomposition of the resulting sodium addition product with ammonium chloride,

$$(C_6H_5)_2C{=}CHC_6H_5 + 2Na \longrightarrow (C_6H_5)_2C(Na){-}C(Na)HC_6H_5 \qquad (7)$$

$$(C_6H_5)_2C(Na){-}C(Na)HC_6H_5 + 2NH_4Cl \longrightarrow 2NaCl + 2NH_3 + (C_6H_5)_2CH{-}CH_2C_6H_5{}^{21} \qquad (8)$$

Sym.-**tetraphenylethane** was obtained from tetraphenylethylene by the method just described under 1,1,2-triphenylethane.

Tetraphenylmethane was prepared by the method of Kraus and Kawamura.[22]

Special Method of Purification.—Although the hydrocarbons prepared from triphenylmethane possessed sharp melting points and other attributes of a high degree of purity, they were always contaminated with exceedingly slight traces of triphenylmethane, just sufficient to interfere with the observation of their behavior with potassium and potassium amide. In the case of those hydrocarbons which react but slightly or not at all with potassium amide, the impurity may be removed by a thorough treatment of the product with this amide, which converts the triphenylmethane into its potassium salt. This salt may then be oxidized with a stream of dry air, forming triphenylmethyl peroxide, which is insoluble in ether and may thus be separated from the soluble hydrocarbons. (Tetraphenylmethane, which is itself almost insoluble in ether, may be freed from triphenylmethane by repeated crystallization from this solvent.)

The study of the hydrocarbons formed by attaching aliphatic radicals to the tri-

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[19] Compare White, Morrison and Anderson, THIS JOURNAL, **46,** 963 (1924).

[20] In a trial experiment this pink precipitate was found to decompose with loss of color upon warming to room temperature. The products are probably triphenylmethane and methylamine. This behavior is analogous to that of ammonium triphenylmethide (Ref. 10, p. 2758).

[21] Evidence that the disodium derivative is partly ammonolyzed to $(C_6H_5)_2C(Na)$-$CH_2C_6H_5$ will be presented in a forthcoming article.

[22] Kraus and Kawamura, Ref. 10, p. 2760.

phenylmethyl group which was made by Gomberg and Cone[23] was apparently rendered more difficult by the trouble of separating the product desired from the quantities of triphenylmethane also formed. The process just described promises to remove this difficulty satisfactorily.

The Action of Potassium and of Potassium Amide on the Hydrocarbons.—These reactions were carried out in a small reaction tube connected to an apparatus similar to that previously described.[24] Potassium metal was converted to the amide in liquid ammonia solution by the catalytic action of a piece of rusty iron. The hydrocarbon was then added to this pale yellow solution. In all cases but one[25] where reaction was observed, an intense red or orange-yellow coloration resulted in a very short time and most of the hydrocarbon was seen to dissolve. In all cases where no action was reported, no change in color was observed after the mixture had been stirred for at least thirty minutes and the hydrocarbon was recovered unchanged at the end of the experiment. In studying the action of the metal itself, a mixture of the hydrocarbon and the solution of potassium was stirred for thirty minutes, the iron oxide catalyst then added and the color observed after all of the free metal had been converted into the amide.

The Action of Alkali Metals on Benzyl Bromide.—In 1923, Kraus and White[26] observed a reaction between sodium and benzyl chloride in liquid ammonia, but did not characterize the products. This experiment was repeated with benzyl bromide, adding one equivalent to a solution of two equivalents of sodium in liquid ammonia. Reaction took place rapidly, but the solution remained blue in color and, therefore, contained free sodium. More of the bromide was added until the blue color was discharged and replaced by a deep, rich, red color which gradually faded until the solution became entirely colorless. A white precipitate was then visible. The solid product obtained by extraction of the residue with ether could not be readily purified by crystallization, but upon subjecting it to sublimation from an oil-bath, crystals were collected which melted at 52° and proved to be dibenzyl. A similar reaction was observed with potassium. The red color of the liquid ammonia solution indicated the presence of sodium benzylide, which reacted with excess benzyl bromide to form dibenzyl.

Thus far the action of sodium on alkyl or aryl monohalides in liquid ammonia has always followed one of two distinct courses. When the hydrocarbon residue has been unable to form a sodium salt which is stable in ammonia, the product has consisted of the hydrocarbon and amines corresponding to the halide used. This has been the case when alkyl or phenyl[27] halides were employed[6] and is expressed in the equation

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[23] Gomberg and Cone, *Ber.*, **39**, 2957 (1906).

[24] Wooster, This Journal, **51**, 1856 (1929).

[25] The reaction between *sym.*-tetraphenylethane and potassium amide in liquid ammonia proceeds slowly. This is doubtless due to the exceedingly low solubility of the hydrocarbon, since the addition of toluene promotes the reaction. The best result was obtained when a toluene solution of the hydrocarbon was added to the liquid ammonia solution of the amide. The stability of toluene and ethylbenzene toward potassium amide cannot be ascribed to solubility influences since these substances are more soluble in ammonia than those hydrocarbons which react readily with the amide [Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898)]. In all other instances where no action is reported the experiments were repeated using a toluene solution of each hydrocarbon but no difference in the results was observed.

[26] Kraus and White, Ref. 6a, p. 773.

[27] In this connection it must be noted that *traces* of biphenyl have been observed in a few instances.

$$2RCl + NH_3 + 2Na \longrightarrow RH + RNH_2 + 2NaCl \qquad (9)$$

although in practice, secondary and tertiary amines may also be formed.

On the other hand, when the hydrocarbon residue is capable of forming a sodium salt which is stable in ammonia, this salt results when the proportions of the reacting materials are correct.

$$RCl + 2Na \longrightarrow NaCl + RNa \qquad (10)$$

By further addition of the same or a different halide a synthesis of the Wurtz–Fittig type may be accomplished.

$$RNa + R'Cl \longrightarrow RR' + NaCl \qquad (11)$$

The reaction of benzyl bromide, therefore, presents an example of a new and intermediate case for although the sodium salt is unstable in ammonia, the reaction proceeds in such a manner that a synthesis of the Wurtz–Fittig type is possible. A further study of this reaction may yield considerable information regarding the mechanism of reduction by the alkali metals in liquid ammonia.

Summary

1. The acid character of hydrogen atoms in the side chains of aromatic hydrocarbons has been investigated. A table of the results has been prepared which illustrates the influence of the number and positions of the phenyl groups in the compound.

2. The influence of phenyl substitution upon the stability of certain organo-alkali compounds in ammonia is contrasted with the conclusions of Kharasch and Marker regarding the relative "electronegativity" of organic radicals.

3. Synthetic methods for the preparation of certain hydrocarbons in liquid ammonia solution are described.

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