mum value for the equilibrium constant for the reaction

$$NaR + H_2O = NaOH + {}^1/_2R + {}^1/_2RH_2$$

Since the sodium hydroxide is present as a solid we may express the equilibrium constant by the equation

$$K = (R)^{1/2}(RH_2)^{1/2}/(NaR)(H_2O)$$

If we assume, as a consequence of the complete destruction of the green color of the solution, that the reaction goes at least 99.9% to completion, then we obtain

$$K = 0.5 \times 999 \times 23/0.003 = 3.8 \times 10^6$$

referring the vapor pressure of water to that of pure liquid water as the standard state. This gives a value for ΔF of -9.0 kcal. These figures represent the minimum efficiency of sodium fluorenone as a drying agent. In any normal procedure a large excess of the drying agent would be used which would result in the removal of water until the pressure is at least as low as 10^{-7} mm.

CONTRIBUTION FROM THE
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The Vapor Density of Hexaphenylethane

BY H. E. BENT AND E. S. EBERS

In a recent publication the statement is made that hexaphenylethane probably does not dissociate in the vapor state.[1] In order to verify this statement an attempt was made to measure directly the vapor density of hexaphenylethane. This measurement combined with the previous data on the vapor pressure would give the molecular weight in the vapor state.

Since the vapor pressure of hexaphenylethane at 120° is only 0.004 mm. a very large volume would be necessary in order to produce a weighable amount of compound. For this purpose a ten-liter flask was attached to the fiber gage used in the previous research and to a capsule of hexaphenylethane. Ground joints controlled by electromagnets were so arranged as first to saturate the ten-liter flask with the ethane and then, closing the ethane capsule, condense the vapor in a small ampoule. The flask could then be saturated again and the vapor a second time condensed and in this way any desired amount of material obtained.

The method was checked by determining the vapor density and the molecular weight of triphenylmethane. The result was high by about 20% which we assume to be due to adsorption. As it was expected that difficulty would be encountered with hexaphenylethane on account of decomposition a procedure was adopted with triphenylmethane which would avoid this difficulty as far as possible. The ground joint to the pump was opened just enough to reduce the pressure to about three-fourths of the saturation pressure. After the pressure had become constant the valves to the pump and to the capsule of sample were closed simultaneously and the valve to the receiver opened for a time sufficiently long to condense about half of the total amount of material in the ten-liter flask. The valve to the receiver was then closed and the pressure again measured, the difference between the initial and the final pressure giving a measure of the amount of material condensed. This process was repeated about ten times and the flask then cooled and the receiver cracked off. The amount of material was determined by weight, both by difference and by evaporation of the solution of the compound to dryness in a crucible. This method of operating between three-fourths and three-eighths saturation would also be effective in avoiding condensation in the ten-liter flask or in removing adsorbed material from the surface of the glass during condensation.

When the method was applied to hexaphenylethane it was found that decomposition was too rapid to permit even an approximate determination of the vapor density. In a flask of such a large size decomposition was so great that even with the pump operating the pressure remained several times that of hexaphenylethane for a space of three hours at 120° (the valve to the solid remaining open). By this time apparently all of the ethane had decomposed for the pressure gradually decreased. However, the material in the flask was no longer hexaphenylethane but a decomposition product for on closing off the flask the pressure remained perfectly constant. Under these conditions hexaphenylethane decomposes rapidly enough to be measured easily. We concluded, therefore, that it is not possible to meas-

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(1) G. R. Cuthbertson and H. E. Bent, THIS JOURNAL, 58, 2000 (1936).

ure the vapor density of hexaphenylethane by this method on account of rapid decomposition.

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Relative Reactivities of Organometallic Compounds. XIV. Orientation in Metalation

BY HENRY GILMAN AND ROBERT H. KIRBY

Schlenk and Meyer[1] have shown that Abeljanz[2] did not obtain phenylpotassium from benzene and potassium. However, Schorigin[3a] very probably had phenylpotassium in hand, despite the confusion due to the paucity of experimental data.[4] We have found that carbonation of the products resulting from interaction of benzene, diethylmercury and potassium gives benzoic acid (45% yield) as well as phthalic and terephthalic acids. The same products, in different quantities, are obtained when sodium is used in place of potassium.

The organo-alkali compounds appear to arise largely as a consequence of metalation by ethylalkali compounds

$$C_6H_6 + C_2H_5K \longrightarrow C_6H_5K + C_2H_6$$

and not by the action of the alkali metals or their amalgams on benzene, for the evolved gas consists predominantly of ethane and contains only small quantities of ethylene and hydrogen.[5] The isolation of phthalic and terephthalic acids establishes the intermediate formation of *o*- and *p*-dialkalibenzenes, and indicates that phenylsodium (or potassium) orients subsequent metalation to the *ortho* and *para* positions. Mercuration may not follow such orientation.[6] It is noteworthy that isophthalic as well as terephthalic acid has been obtained from successive interaction of benzene, diamylmercury, sodium and carbon dioxide in the interesting studies by Morton and Hechenbleikner.[7]

The results are consistent with some of the earlier generalizations on relative reactivities of organometallic compounds,[8] particularly the increase in reactivity of RM compounds with increase in atomic weight of the alkali metal. For example, Mr. R. V. Young, in a study of organoalkali compounds, has shown that ethyl-lithium does not metalate benzene during a two-month period at room temperature;[3b] the over-all metalation of benzene by ethylsodium is less than that by ethylpotassium; and ethylpotassium gives much more of the dimetalated compounds than does ethylsodium.[9]

The metalations reported are merely special cases of general metalation which may be a direct metathesis, and, when RM compounds are used, a metathesis resulting in the formation of the salt of the stronger acid. Metalation of aromatic nuclei by RM compounds may involve preliminary addition, with subsequent elimination of RH.[10] Metalation by RM compounds is, of course, possible with all compounds, saturated as well as unsaturated, for all hydrogens are acidic to varying degrees from the viewpoint of metalation. A pertinent illustration is the metalation of saturated aliphatic hydrocarbons of the R_3CH type by ethylpotassium. In such cases, it is unlikely that unsaturated compounds are intermediates, even though it has been shown that RM compounds can act as dehydrogenating agents.[11]

Experimental Part

Metalation with Ethylpotassium.—To a suspension of 3.13 g. (0.08 g. atom) of potassium shavings in 35 cc. of benzene was added 5.17 g. (0.02 mole) of diethylmercury. Reaction set in at once as was evident by amalgamation of the potassium, evolution of gas and warming of the benzene. The mixture was stirred without heating for forty-eight hours, cooled to 7° and carbonated with carbon dioxide gas. The yields of products, based on diethylmercury, were 33% benzoic acid and 14% terephthalic acid (mixed melting point of dimethyl ester). The odor of propionic acid was noticeable, and a strong fluorescein test established the presence of phthalic acid. Isophthalic acid was not isolated, but may have been present in small quantities. The gas evolved contained 8 cc. of ethylene,

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(1) Schlenk and Meyer, *Ber.*, **46**, 4060 (1913).

(2) Abeljanz, *ibid.*, **9**, 10 (1876).

(3) (a) Schorigin, *ibid.*, **43**, 1938 (1910); (b) *ibid.*, **41**, 2723 (1908).

(4) Wooster, *Chem. Rev.*, **11**, 8 (1932). See, also, Schlenk and Holtz, *Ber.*, **50**, 262 (1917).

(5) There is a possibility of some di-alkali compound being formed by self-metalation of phenylalkali compound. Incidentally, it is likely that the spontaneous transformations of some of the more reactive alkylalkali compounds involve self-metalation to give polymetalated types culminating in carbides [see ref. 12].

(6) Gilman and Kirby, *J. Org. Chem.*, **1**, 146 (1936).

(7) Morton and Hechenbleikner, THIS JOURNAL, **58**, 1024 (1936). Dr. Morton and co-workers have shown, in some unpublished studies, that phthalic acids are obtained in this reaction when diamylmercury is replaced by amyl chloride.

Possibly the amylidene disodium of Morton may orient differently from ethylsodium. A pertinent illustration is the different orientation effects of the very closely related phenyl-calcium and phenyllithium compounds in metalations.

(8) Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

(9) The extent of metalation varies with the R group. A 77% yield of benzoic acid was obtained from benzene and *n*-butylsodium followed by carbonation.[6]

(10) Gilman and Breuer, THIS JOURNAL, **56**, 1123 (1934).

(11) An illustration is the study by C. W. Bradley on the conversion of 1,4-dihydrodibenzofuran by phenyl-lithium to 4-dibenzofuryl-lithium and dibenzofuran.