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

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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 phenyl-lithium 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.

2.5 cc. of hydrogen and 535 cc. of ethane, all volumes being corrected.

In a second experiment, using 75 cc. of benzene, reaction started slowly and four hours elapsed before an appreciable quantity of mercury separated. The yields were: 45% of benzoic acid and 17% of terephthalic acid.

From a third experiment, which differed from the second only in limiting the time of reaction to twenty hours, the yield of benzoic acid was 33% and the yield of terephthalic acid was 11%. Positive fluorescein tests were also obtained in the second and third experiments.

Metalation with Ethylsodium.—The procedure was identical with the first experiment with ethylpotassium, 1.84 g. (0.08 g. atom) of sodium being used. Reaction set in immediately. The products identified were: 41% of benzoic acid; a small quantity of terephthalic acid (mixed melting point with dimethyl ester); and phthalic acid (as indicated by a positive fluorescein test). The gas evolved contained 12 cc. of ethylene, 10 cc. of hydrogen and 420 cc. of ethane. Incidentally, the limited evolution of ethylene and hydrogen belies any considerable metalation by alkali hydride which arises from the thermal decomposition of ethylalkali compound.[12]

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(12) Carothers and Coffman, This Journal, **51**, 588 (1929).

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Comparison of the Total Nitrogen in Wheat Seeds by the Gunning (Modified Kjeldahl) and the Dumas Combustion Methods

BY W. Z. HASSID

Smyth and Wilson[1] analyzed peas for total nitrogen before and after germination in distilled water, in salt solution media and in alkaloids. The peas showed an increase of 0.2 to 0.3% nitrogen in the dry residue after germination.

In the opinion of these authors, the increase in nitrogen was not the result of atmospheric nitrogen assimilation, but was due to the inadequacy of the Kjeldahl method to measure the total nitrogen in the ungerminated peas. By the official Kjeldahl procedure only 90% of the total nitrogen as compared with the Dumas combustion method could be obtained, and this varied with different modifications of the official procedure. On the basis of these results, Smyth and Wilson concluded that in the process of germination the nitrogen of the seeds was converted into compounds which were more easily determinable by the Kjeldahl method than those in the dry seeds.

Since Smyth and Wilson's results cast doubt on the validity of the conclusions drawn by Lipman and Taylor[2] and others who obtained similar results relative to the power of green plants to fix atmospheric nitrogen, it seemed desirable to make a study of the modified Gunning method and the Dumas combustion method as a means of determining the nitrogen in seeds and seedlings. To this end, wheat seeds of the "little club" variety were subjected to analysis for total nitrogen by both the modified Gunning and Dumas combustion methods.

TABLE I

N ANALYSIS OF 12 SAMPLES OF WHEAT SEEDS BY THE MODIFIED GUNNING METHOD

Sample no.	Sample wt.	% N	
1	1.0000	2.27	Average 2.25%
2	1.0000	2.20	
3	1.0920	2.18	
4	1.4060	2.25	
5	1.4060	2.25	
6	1.4040	2.27	
7	1.4000	2.25	
8	1.4000	2.25	
9	1.4026	2.25	
10	1.4000	2.20	
11	1.4010	2.30	
12	1.4020	2.31	

N ANALYSIS OF 6 SAMPLES OF WHEAT SEEDS BY THE DUMAS METHOD (COMBUSTION)

Sample no.	Sample wt.	% N	
1	1.0205	2.25	Average 2.28%
2	1.1100	2.27	
3	1.0000	2.28	
4	1.0344	2.31	
5	1.0000	2.30	
6	1.0000	2.29	

A study of the table makes it clear that the modified Gunning method as used in this experiment yields as much nitrogen as the Dumas method for the wheat seeds analyzed. It appears, therefore, that such results as were obtained by Lipman and Taylor and by others who claimed to have shown nitrogen fixation by wheat plants cannot be invalidated on the basis of the results and conclusions of Smyth and Wilson, cited above.

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(1) E. M. Smyth and P. W. Wilson, *Biochem. Z.*, **282**, 1 (1935).

(2) C. B. Lipman and J. K. Taylor, *J. Franklin Inst.*, 475–506 (1924).