[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

An Addition-Metalation Reaction of Benzene with Phenylpotassium[1]

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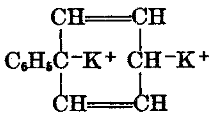
Phenylpotassium, but not phenylsodium, appears to add to benzene. The addition was accompanied by metalation so that the final product was dihydrobiphenyldipotassium. The product was similar to that which was obtained by the addition of potassium to biphenyl under the same experimental conditions. A continuation of the addition-metalation process, accompanied probably by elimination of potassium hydride, produced a cross-linked insoluble infusible polymer. In the light of the present work it is reasonable to assume that Abeljanz in 1872 had obtained phenylpotassium as an intermediate in the reaction of potassium with benzene.

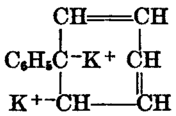
For many years alkali metal amides[2] and organoalkali metal compounds[3] have been known to add to pyridine but not to benzene. This paper reports that phenylpotassium probably adds to benzene. Metalation follows immediately to give dihydrobiphenyldipotassium. Equation 1 shows

$$C_6H_5K + C_6H_6 \longrightarrow C_6H_5{-}C_6H_6{-}K \xrightarrow{C_6H_5K} C_6H_5{-}C_6H_5K_2 \quad (1)$$

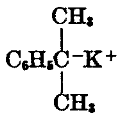
these steps. The final organodipotassium product absorbed strongly at 1165 cm.$^{-1}$, which is characteristic for the benzyl type ion[4] and is identical with that shown by phenylisopropylpotassium.[4] Therefore one anion center must be at the alpha carbon as shown in (*a*) or (*b*) just as it is in phenylisopropylpotassium shown in (*c*). The second anion center is possibly at the para position as in (*a*) rather than at the ortho position as in (*b*) because attachment of two potassium ions to distant carbon atoms seems more favored than to adjacent carbons. Other evidence to be described later supports that opinion. There may be also a general delocalization of electrons over both rings as in $[C_6H_5C_6H_5]^{--}K_2^{+}$ with which this paper is not concerned.



(*a*)



(*b*)



(*c*)

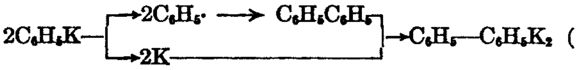
The reaction is probably a true addition of phenylpotassium to benzene rather than a union of two phenylpotassium compounds as in Equation 2

$$2C_6H_5K \longrightarrow C_6H_5{-}C_6H_5K_2 \quad (2)$$

because benzene was necessary. In petroleum which was freed from benzene, the infrared absorption at 1205 cm.$^{-1}$, characteristic for the phenyl ion,[4] changed very little during a month of aging. In the presence of benzene, however, absorption at that wave length disappeared during weeks at room temperature or hours at 70° while absorption appeared and increased at 1165 cm.$^{-1}$ characteristic for the anion center at the alpha carbon atom.

The biphenyl-type character of the product was demonstrated by pyrolysis under vacuum at 150° whereby biphenyl was recovered in about 30% yield. The same treatment applied to the starting material, phenylpotassium, yielded benzene as the volatile product. Furthermore potassium metal reacted with biphenyl in heptane under the conditions employed in the reaction of phenylpotassium with benzene. The infrared absorption of this addition product was essentially identical with that of the addition-metalation product from phenylpotassium and benzene, notably at 1165 cm.$^{-1}$ Also it yielded biphenyl when pyrolyzed at 150° under reduced pressure.

For a while the presence of a little biphenyl in the non-acid portion from the product of the addition-metalation reaction of phenylpotassium with benzene and the knowledge that potassium metal could add to biphenyl under those same conditions suggested that the course of the addition-metalation reaction might, instead, have been through decomposition of phenylpotassium to biphenyl and potassium followed by recombination, as in Equation 3. The need for benzene in the process and the



$$2C_6H_5K \begin{cases} \rightarrow 2C_6H_5\cdot \longrightarrow C_6H_5C_6H_5 \\ \rightarrow 2K \end{cases} \rightarrow C_6H_5{-}C_6H_5K_2 \quad (3)$$

failure to get biphenyl from the pyrolysis of phenylpotassium made this possibility seem less reasonable than the process according to Equation 1.

Identification of the product by carbonation was only partially satisfactory because separation of a pure diacid and determination of the structure were not easy. The comparatively high melting dihydrobiphenyldicarboxylic acid had the same neutralization equivalent as benzoic acid but the molecular weight of the dimethyl ester was a little over twice that of methyl benzoate. The diacid was somewhat sensitive to air oxidation as might have been expected. Previously some difficulty with a

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[1] This work was performed as part of a research project sponsored by the National Science Foundation.

[2] A. E. Chichibabin and O. A. Zeide, *J. Russ. Phys. Chem. Soc.*, **46**, 1216 (1914).

[3] K. Zeigler and H. Zeiser, *Ann.*, **485**, 174 (1921).

[4] A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958).

structure of this type had been experienced by Schlenk and Bergmann[5] and by Hückel and Bretschneider[6] who worked with the material obtained by hydrolysis of the addition product of alkali metal with biphenyl. Three facts about the diacid, however, accord with the view that the second anion center in the addition-metalation product is para to the first as represented in (*a*); first because vacuum distillation of the diacid over copper yielded a small amount of crystalline *p*-phenylbenzoic acid, second because an attempt to prepare a crystalline anhydride (such as an ortho dicarboxylic acid should yield) by heating in acetic anhydride and distilling yielded only a thick polymer-like mass and third because the ultraviolet absorption of the dicarboxylic acid showed no double bond conjugated with another double bond or with a carboxyl group.

Phenylpotassium, but not phenylsodium, reacted with benzene. The difference between the two salts is not surprising. Already the potassium ion has shown a preference for a lateral position. For instance potassium metal and sodium oxide metalated alkylaryl hydrocarbons at the alpha carbon atom,[7] potassium hydroxide metalated fluorene[8] in spite of the greater acidity of water over fluorene, amylpotassium metalated cumene predominantly in the lateral position[4] whereas amylsodium attacked the nucleus, and phenylpotassium surprisingly metalated cumene at the alpha carbon in disregard of the accepted difference in acidity between the hydrogen atoms of the side chain and the nucleus. Therefore the addition-metalation process (Equation 1) would have been favored by a change of a potassium ion from the nucleus in phenylpotassium to the alpha carbon as in structure (a) or to the distant para carbon atom which is connected to the alpha position through a pair of vinyl groups.

Presumably the process of addition-metalation should continue until high molecular weight products are obtained. For instance the initial product (*a*) from Equation 1 would lose potassium hydride (Equation 4) to give biphenylpotassium. This

$$C_6H_5C_6H_5K_2 \longrightarrow KH + C_6H_5C_6H_5K \qquad (4)$$

compound, however, has a potassium ion attached to the nucleus just as does phenylpotassium. Therefore it should add to another aromatic ring. A continuation of this unusual addition type of polymerization should lead to high molecular weight products. Something of this type seemed to occur because the residue after pyrolysis at 150° under vacuum was an infusible insoluble cross-linked mass. The infrared absorption showed the presence of some aromatic rings. In other words the residue was not a burnt carbonaceous mass but seemed to be the result of a mixture of orderly processes which increased the molecular size.

This work throws considerable light on an early claim by Abeljanz[9](1872,1876) that he had prepared phenylpotassium. He had observed that Berthelot[10] had been able to prepare naphthalenedipotassium, $C_{10}H_8K_2$, by fusing potassium metal with naphthalene, and he sought to carry out a similar reaction with benzene. In a closed tube, reaction set in at 150–190° but the mixture was kept for 7 hr. at 230–250°. Decomposition of the bluish black apparently crystalline mixture with ethyl bromide or water yielded biphenyl and *p*-terphenyl. He attributed these products to phenylpotassium and phenylene dipotassium. thirty-six years later (1913) Schlenk and Meyer[11] maintained that Abeljanz had only coated metal with carbon. They advocated striking the reference from the literature. The current results suggest that both laboratories had made phenylpotassium, but as an intermediate rather than an end product. If potassium metal added to benzene as per Equation 5 the

$$2K + C_6H_6 \longrightarrow KC_6H_6K \longrightarrow KH + C_6H_5K \qquad (5)$$

dihydrophenyldipotassium product should be unstable at that temperature and lose potassium hydride to form phenylpotassium. From that point the steps would be as described in this paper. Diphenyl, *p*-terphenyl, and "carbon" should be formed. Both laboratories had obtained all of the products[12] which the present work, carried out at lower temperatures, would suggest.

Mention should be made also of the preparation of phenylpotassium by shaking potassium-sodium alloy and diphenyl ether in benzene as carried out by Müller and Benge.[13] Equation 6 shows that the

$$2K + C_6H_5OC_6H_5 \longrightarrow C_6H_5K + KOC_6H_5 \qquad (6)$$

process is essentially the same as the preparation from anisole in this laboratory[4] and might, indeed, be preferable because of the formation of potassium phenoxide instead of methoxide. Müller and Benge, however, happened to carry out the reaction in benzene which should react with phenylpotassium. Hence they found only a 33% yield of benzoic acid after carbonation whereas their analysis of phenol showed 95% cleavage. Much of the phenylpotassium must have reacted with benzene during the ten days shaking of the mixture, and the separation of some high melting (185–200°)

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(5) W. Schlenk and E. Bergmann, *Ann.*, **463**, 90 (1928).

(6) W. Hückel and H. Bretschneider, *Ann.*, **540**, 157 (1930).

(7) C. E. Claff, Jr., and A. A. Morton, *J. Org. Chem.*, **20**, 981 (1955).

(8) A. A. Morton, C. E. Claff, Jr., and H. P. Kagan, *J. Am. Chem. Soc.*, **76**, 4556 (1954).

(9) H. Abeljanz, *Ber.*, **5**, 1027 (1872); **9**, 10 (1876).

(10) M. Berthelot, *Ann.*, **143**, 97 (1867).

(11) W. Schlenk and H. Meyer, *Ber.*, **46**, 4060 (1913).

(12) H. Podall and W. E. Foster, *J. Org. Chem.*, **23**, 401 (1958), noted the formation of some biphenyl during the alkylation of benzene over potassium graphite at 200°. It might have formed from a reaction of potassium with benzene as observed by Abeljanz and by Schlenk and Mayer.

(13) E. Müller and Benge, *Ber.*, **69**, 2171 (1936).

acid supports that idea. Lüttringhaus and Schubert[14] used a similar preparation of phenylpotassium *in situ* for their study of the metalation of diphenyl ether. In that case, however, the metal ion moved promptly from phenyl to diphenyl ether.

The reactions of phenylpotassium with a few other compounds were tested. The reagent metalated anisole in the ortho position and carbonation produced *o*-anisic acid. When this *o*-potassionisole was heated to 70°, cleavage to potassium phenoxide took place just as had occurred with the corresponding sodium reagent.[15] The large amount of tar formed simultaneously suggested that this arylpotassium compound, $o\text{-}KC_6H_4OCH_3$, may have undergone some addition with itself similar to Equation 2 or otherwise reacted to yield high molecular weight material. Addition of phenylpotassium to butadiene gave a polymer with a ratio of *trans*-1,4- to 1,2-structure equal to 0.71. The same product was obtained regardless of whether the phenylpotassium was in the presence of potassium chloride or methoxide, that is, whether the reagent had been prepared from amyl chloride and benzene or from anisole.[4] Also the addition-metalation product from phenylpotassium and benzene produced the same ratio of 1,4- and 1,2-structures in polybutadiene. This ratio is higher than the value (0.35) found in this laboratory for polymerization by the usual type of sodium reagent but is much lower than found for polybutadiene made with the Alfin reagent.[16] No addition took place with *t*-butylbenzene; the infrared absorption remained strong at 1210 cm.$^{-1}$ while standing a week. The metalation of cumene by phenylpotassium has been reported in a separate paper.[4]

EXPERIMENTS

Infrared absorption by the potassium compounds. The method of measurement of the infrared absorption of the organoalkali reagents and the value of these measurements have been described in another paper.[4]

Preparation of phenylpotassium. The method of preparing this reagent from amyl chloride, benzene, and potassium was described in the previous paper.[4] Benzoic acid was obtained by carbonation as described previously. A suspension of the potassium reagent was centrifuged and the solvent was replaced by dry heptane. This operation was repeated twice. Thereafter the absorption at 1205 cm.$^{-1}$ remained approximately the same for a month (the duration of the test). The benzene-heptane solvent was similarly replaced by *t*-butylbenzene which had been dried over sodium hydride. The absorption at 1205 cm.$^{-1}$ showed no change during a week. Under similar conditions, but in benzene, a noticeable change in intensity of that band took place and a new band began to appear at 1165 cm.$^{-1}$

Reaction of phenylpotassium with benzene. Examination of a preparation of phenylpotassium which happened to have stood for six months at room temperature showed that absorption at 1205 cm.$^{-1}$ had disappeared and a new band at 1165 cm.$^{-1}$ had appeared. Accordingly a portion of the preparation was carbonated by addition to solid carbon dioxide. The carboxylic acid melted at 270–280° but had a neutralization equivalent of 127, similar to benzoic acid. The crude mixture was digested several times in hot water but did not dissolve easily as would benzoic acid. The dissolved and undissolved portions showed atom ratios of carbon to hydrogen equal to 1.09 and 1.12, respectively. The calculated value for either benzoic acid or 1,4-dihydrobiphenyldicarboxylic acid is 1.17. Distillation of the undissolved portion in a 20 × 2 cm. short-path still gave a yellow appearing product on the finger tip condenser and a white powdery material on the wall. The melting point, percentage oxygen (by difference) and the atom ratio of carbon to hydrogen were 270–280°, 24.7, and 1.12 for the former and >325°, 25.1 and 1.07 for the latter. The percentage oxygen in benzoic acid is 26.2. The slightly lower value for oxygen in these products can be attributed to a small loss of potassium hydride from the mixture of organopotassium compounds present from the reaction.

A portion of the undissolved acid was esterified by methanol and acid and the ether solution of the ester was separated from traces of acid by extraction with sodium carbonate solution. The residue left by evaporation of the ether had a molecular weight of 301 in camphor. [$C_{12}H_{10}(CO_2CH_3)_2$ requires 272.] Also the ester distilled at 150°/1 mm. Both facts agree with the view that the product was largely the mono adduct from phenylpotassium and benzene followed by metalation as per Equation 1.

Distillation of 1 g. of the dissolved acid with 5 g. of copper powder at 150°/1 mm. gave a white crystalline material which melted at 220–225° after being recrystallized from heptane. The acid chloride melted at 112–114° and the amide melted at 226–228°. The corresponding values recorded[17] for *p*-phenylbenzoic acid and its chloride are 228° and 114–115°. The infrared absorption of the acid was identical with that from a previous preparation in this laboratory.

From another preparation which had been made by stirring phenylpotassium with benzene at 70° for 12 hr., the yellow-white mixture of carboxylic acids was steam distilled in order to remove benzoic acid (4.3 g.) which was present because of some phenylpotassium which had not yet reacted with benzene. The residue of high molecular weight acid became yellow-brown because of aerial oxidation. This sensitivity to air generally hampered efforts to get pure compounds from the mixture.

Repeated crystallization from ethanol-water and from heptane eventually yielded minute crystals which melted with decomposition at 325° (another lot at 335–350°) and had a neutralization equivalent of 150. The analysis of carbon and hydrogen, however, corresponded to no simple product. Bromine yielded no simple product which showed a specific composition.

The mixture of carboxylic acids was heated in acetic anhydride for several hours but no crystalline product was obtained from the solution or from the mixture which was obtained therefrom by precipitation with a hydrocarbon. An attempt to sublime an anhydride from this product at 150°/1 mm. in a short path still yielded no crystalline material.

The ultraviolet absorption in ethanol showed that the diacid had a maximum absorption at 368 mμ and a molar extinction coefficient of 670. No conjugated system seemed to be present.

The non-acid portion from one of the preparations was

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[14] A. Lüttringhaus and K. Schubert, *Naturwissenschaften*, **42**, 17 (1955).

[15] A. A. Morton and A. E. Brachman, *J. Am. Chem. Soc.*, **76**, 2973 (1954).

[16] A. A. Morton, I. Nelidow, and E. Schoenberg, Proc. 3rd Rubber Tech. Conf. (1954), 108; A. A. Morton, *Advances in Catalysis IX*, 743 (1957), Academic Press Inc., New York.

[17] I. Heilbrom, *Dict. of Organic Chemistry*, Oxford Univ. Press, New York, N. Y., 1950, Vol. II, p. 608.

distilled to remove the solvent. A small amount of biphenyl (0.1 g.) was recovered. It melted at 69–71° and showed no depression when mixed with an authentic sample.

Thermal decomposition of the potassium compounds. A suspension (50 ml.), containing 28.2 milliequiv. of phenylpotassium in heptane-benzene, was centrifuged and washed with pentane in order to remove all trace of benzene or biphenyl. Then the pentane was removed by vacuum distillation and the phenylpotassium was subjected to heat at 150°/1 mm. for 9 hr. The solid collected in the cold trap melted to a liquid with the odor of benzene. The yield was 1.06 g. (50%); n^{25}_{D} 1.4960. The residue from this decomposition was decomposed with methanol. The product was infusible and insoluble in common organic solvents. An analysis showed 87.03% carbon and 4.85% hydrogen with some ash. The atomic ratio of 1.5 carbon for each hydrogen atom suggests that a condensed aromatic system was present. The infrared absorption made on a sodium bromide pellet was pronounced at 1600 cm.$^{-1}$ and at 695 to 810 cm.$^{-1}$, characteristic for substituted benzene rings.

A similar decomposition was carried out on the reaction product of phenylpotassium with benzene. An aged suspension (50 ml.) containing 41.7 milliequiv. of phenylpotassium or its equivalent was centrifuged and washed with pentane. From this material 1 g. (30% yield) of a white powder was collected at 150°/1 mm. It was identified as biphenyl by its melting point (70°) and mixed melting point with an authentic sample. The residue was not soluble in benzene and common solvents and appeared similar to that obtained from phenylpotassium itself.

Potassium metal with biphenyl. Biphenyl (78 g., 0.5 mole) was stirred with 39 g. (1 atom) of potassium sand in 500 ml. of heptane at 70° for 6 hr. The infrared absorption bands of this suspension were identical with those from a fully aged preparation of phenylpotassium with benzene. After carbonation 61 g. (50%) of carboxylic acids was recovered which melted at 240–250°. The infrared absorption of these acids was the same as for the acids derived from the reaction of phenylpotassium with benzene. The melting point was lower than for some of the fractions obtained from the phenylpotassium-benzene preparation but that fact is understandable because of the numerous variations from isomers and secondary changes. Attempts to separate crystalline carboxylic acids from this material proved as difficult as with the material prepared from phenylpotassium-benzene.

Phenylsodium with benzene. A preparation of phenylsodium made from amyl chloride (61 ml., 0.5 mole) and sodium (23 g., 1 atom) in benzene which had stood for 24 months showed a strong absorption at 1205 cm.$^{-1}$ and only very weak absorption in the region of 1165 cm.$^{-1}$

Phenylpotassium and anisole. A suspension of 50 ml. (28 milliequiv.) of phenylpotassium (from amyl chloride, benzene, and potassium) in heptane was allowed to react with 27 g. (0.25 mole) of anisole at room temperature for one week. Carbonation and separation of the carboxylic acid gave 2.7 g. (60%) of a beautifully crystalline (from heptane) material which melted at 102–103°, did not depress the melting point of an authentic sample of *o*-anisic acid, and showed infrared absorption identical with that sample.

A sample of *o*-potassioanisole prepared as described above was heated at 75° for 20 hr. Carbonation yielded 26 g. of phenol which was identified by the melting point of the tribromo derivative (89–92°). The large residue of tarry product which accompanied the phenol suggested that this arylpotassium compound might have undergone some change comparable to that written for phenylpotassium in Equations 2 or 3.

Butadiene and potassium reagents. Phillips research grade of butadiene (30 ml.) was polymerized in 200 ml. of pentane by 10 ml. of (a) a suspension of phenylpotassium made from either amyl chloride, benzene, and potassium or from anisole and potassium or (b) a suspension of phenylpotassium in benzene which had aged and therefore had changed to the biphenyl type product. In each case polymerization was allowed to take place for 1 hr. Then the mixture was decomposed with methanol and the solvent and excess butadiene removed by evaporation at reduced pressure. The infrared absorptions in carbon disulfide solution showed ratios of trans 1,4- to 1,2-structures (absorption at 10.34 and 10.98 microns, respectively) of 0.71.

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A Study of the Preparation of Ketones from Mixed Aldoketene Dimers

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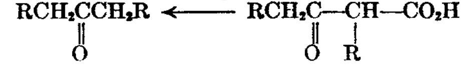
Several pairs of acid chlorides have been dehydrohalogenated by means of triethylamine, under differing conditions, to mixtures of ketene dimers. The latter have been hydrolyzed in poor yields to mixtures of symmetrical and unsymmetrical ketones. In addition, considerable amounts of acids have been obtained in most cases, which suggests that variations exist in the rates of formation and dimerization of the aldoketenes.

Sauer[2] has shown that the procedure which involves the dehydrochlorination of acid chlorides by tertiary amines to ketene dimers, followed by hydrolysis of the latter, affords symmetrical ketones in high yields. The dehydrohalogenation of a mixture of two acid chlorides would be expected to lead to four ketene dimers. Sauer[2] has demonstrated in the case of acetyl and lauroyl chlorides the formation of the two simple dimers, and one of the



$$\mathrm{RCH_2COCl} \xrightarrow{\mathrm{R_3N}} \mathrm{RCH{=}C{=}O} \longrightarrow \text{Aldoketene dimer} \xrightarrow{\mathrm{H_2O,\ H^+}} \mathrm{RCH_2\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle R}{|}}{CH}{-}CO_2H} \xrightarrow{-\mathrm{CO_2}} \mathrm{RCH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_2R}$$

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[1] Abstracted in part from the Ph. D. thesis of H. M. Molotsky, 1953.

[2] J. C. Sauer, *J. Am. Chem. Soc.*, 69, 2444 (1947).