177. *Organometallic Compounds of the Alkali Metals. Part II.**
The Metallation and Dimetallation of Benzene.

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The metallation of benzene by alkylpotassium compounds has been studied by a new procedure in which solutions of alkyl-lithium compounds in benzene are caused to react with potassium; the resulting mixture of phenyl-potassium and phenylenedipotassium is treated with carbon dioxide to give potassium salts of benzoic acid and the phthalic acids in overall yields of up to 90%. Disubstitution is largely *meta-para*, but the ratios of the isomers vary somewhat with the nature of the alkyl group in the reagent. Small quantities of the corresponding alkylbenzenes are also occasionally formed. Metallation of benzene by ethylsodium at 20° gives phenylsodium together with an approximately 7 : 3 mixture of *p*- and *m*-phenylenedisodium. Under forced conditions, the metallation of phenyl-lithium by *n*-butyl-lithium gives *p*- and *m*-phenylenedilithium in the approximate ratio of 2 : 1. The present results cannot be accommodated by the dimetallation theory of Morton and his co-workers (*J. Amer. Chem. Soc.*, 1943, **65**, 1339; *Chem. Reviews*, 1944, **35**, 1).
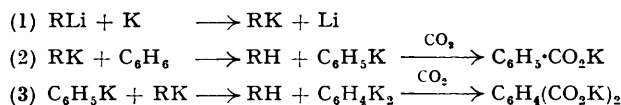
THE term " metallation " is commonly used to describe those reactions in which hydrogen atoms in organic compounds are replaced by metals (or groups containing metals, *e.g.*, $-MgBr$, $-HgOAc$). Some workers have used the term in a wider sense to cover the replacement of atoms other than hydrogen, *e.g.*, halogens (Braude and Coles, *J.*, 1951, 2078) ; but in this and subsequent papers the narrower definition will be adhered to.

The metallation of aromatic hydrocarbons, including benzene, was first demonstrated by Schorigin (*Ber.*, 1908, **41**, 2711, 2723 ; 1910, **43**, 1938) with the use of ethylsodium, prepared *in situ* from diethylmercury and sodium : ethylpotassium was stated to behave similarly, but no experimental details were given. Gilman and Kirby (*J. Amer. Chem. Soc.*, 1936, **58**, 2074) repeated this work and reported that reaction of ethylsodium and ethylpotassium with benzene led mainly to monometallation together with a little *ortho*- and *para*-dimetal-lation. Morton and Hechenbleikner (*ibid.*, 1936, **58**, 1024, 2599) and Morton and Fallwell (*ibid.*, 1938, **60**, 1426) used *n*-amylsodium and observed that dimetallation of benzene occurred at the *meta*- and *para*-positions in the approximate ratio of 4 : 1. Morton, Little, and Strong (*ibid.*, 1943, **65**, 1339) later described conditions for the dimetallation of benzene and toluene by *n*-amylsodium under which the second sodium atom was reported to enter the *meta*-positions exclusively. The latter results were used as a basis for a theor-etical interpretation of metallation reactions and the orientating influence of alkali metals; further elaboration was given by Morton (*Chem. Reviews*, 1944, **35**, 1).

As the evidence concerning the dimetallation of benzene appeared contradictory, we decided to investigate it in more detail. Conveniently rapid metallation of benzene only occurs with alkyl-sodium and -potassium compounds, for alkyl-lithium compounds do not react extensively even under forced conditions. Published procedures (see above references) for the preparation of alkyl-sodium and -potassium compounds are limited in scope and have certain other disadvantages : a satisfactory alternative has now been developed. Gilman and Young (*J. Org. Chem.*, 1936, **1**, 315) found that sodium–potassium alloy reacts with a solution of triphenylmethyl-lithium in ether to give the less soluble triphenylmethylpotassium : $CPh_3Li + K \longrightarrow CPh_3K + Li$. Initially, we attempted to extend this reaction to the direct preparation of alkylpotassium compounds by interaction of sodium–potassium alloy and solutions of alkyl-lithium compounds in paraffin hydro-carbons; reaction in such solvents was found to be negligible, but it occurs quite readily in the presence of aromatic hydrocarbons. Arylpotassium compounds are formed, fre-quently in very good yields, and are readily and almost quantitatively converted into the

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potassium salts of the corresponding carboxylic acids by treatment with solid carbon dioxide in ether.   Neither potassium metal nor alkyl-lithium compounds react individually with benzene under the conditions used in the metallation experiments, and it has been concluded that the reaction involves the following principal steps :

(1) $RLi + K \longrightarrow RK + Li$

(2) $RK + C_6H_6 \longrightarrow RH + C_6H_5K \xrightarrow{CO_2} C_6H_5 \cdot CO_2K$

(3) $C_6H_5K + RK \longrightarrow RH + C_6H_4K_2 \xrightarrow{CO_2} C_6H_4(CO_2K)_2$

Experiments have been carried out in which R = ethyl, *n*-propyl, *n*-butyl, *sec.*-butyl, *tert.*-butyl, and *n*-amyl.   The results are summarised in the Table and are discussed below. Reaction temperatures of 20° and 65° have been generally employed, potassium being used in the latter cases and the liquid 1 : 4 sodium–potassium alloy in the former.   Gilman and Young (*loc. cit.*) found that use of this alloy led to production of potassium compounds only ; we can confirm this.   Some alkyl-lithium compounds may be directly prepared in benzene solution from the corresponding halides and lithium metal (Ziegler and Colonius, *Annalen*, 1930, **479**, 135), but the reaction is rather slow and yields are not always satisfactory.   For the present purposes, it has been found preferable to employ *n*-pentane as a reaction medium as recommended by Gilman and his co-workers (*J. Amer. Chem. Soc.*, 1940, **62**, 2333 ; 1941, **63**, 2479).   Slight modifications have led to improved yields, except in the case of *tert.*-butyl-lithium.   Reactions with potassium have been carried out subsequent to the replacement of *n*-pentane by benzene.

From a reaction carried out at 65° using *sec.*-butyl-lithium, a little *sec.*-butylbenzene has been isolated.   Other alkyl-lithium compounds also appear to produce traces of the corresponding alkylbenzenes, although no alkylation has been found to occur at 20°.   The formation of alkylbenzenes during the metallation of benzene has not previously been observed.   It has been shown that little *sec.*-butylbenzene is formed by a reaction between *sec.*-butyl chloride and potassium in benzene at 65° : this has eliminated the possibility that *sec.*-butylbenzene isolated from the metallation experiment was derived from the presence of excess of *sec.*-butyl chloride in the preparation of *sec.*-butyl-lithium which was used.   The result suggests that the most reactive organometallic compounds can react with benzene in two ways, *viz.*, the metallation reaction (2) and an alkylation reaction which we tentatively express as $RK + C_6H_6 \longrightarrow C_6H_5R + KH$.   It is hoped that future work will show whether this alkylation occurs by direct elimination of a hydride ion, or whether the initial step is one of addition followed by loss of potassium hydride from the adduct. Reactions of the latter type are well known to occur between organolithium compounds and certain heterocyclic nuclei.   A third possibility, that alkylation occurs by reaction of a free *sec.*-butyl radical with benzene, is rendered unlikely by the absence of the olefinic dismutation products which would be expected to arise from such a radical.

For the sake of completeness, metallation experiments using sodium and lithium compounds have been carried out.   Ethyl-sodium was allowed to react with a moderate excess of benzene at 15—20°, and after a reaction with carbon dioxide there was obtained, in addition to benzoic acid, a mixture of terephthalic and *iso*phthalic acids in the approximate ratio of 7 : 3.   This ratio is of the same order as that found with ethylpotassium (see Table).   Morton (*loc. cit.*) mentioned that dimetallation of benzene by the insoluble *n*-amylsodium was exclusively *meta* only when exceptionally vigorous stirring was employed, and that otherwise some *para*-dimetallation occurred.   In order to exclude the possibility that *para*-attack is a consequence of inadequate mixing of the reagents, we have examined the metallation of phenyl-lithium by *n*-butyl-lithium in a one-phase reaction mixture.   Reaction occurred mainly at the *para*-position.

In the case of the potassium compounds, it is probable that equations (1), (2), and (3) represent a simplification of the true course of reactions.   This has been indicated by an experiment in which a solution containing an excess of *sec.*-butyl-lithium in benzene was caused to react with 1 g.-atom of potassium.   Equation (1) requires that 1 mole of *sec.*-butyl-lithium should be consumed : in fact, 1·4 moles were consumed (*i.e.*, converted into insoluble material).   This anomaly becomes less puzzling when it is considered that

alkyl-lithium compounds do not exist in solution as simple molecules. Ethyl-lithium in benzene solution is some six-fold associated (Hein, Petzchner, Wagler, and Segitz, *Z. anorg. Chem.*, 1924, **141**, 161) and it is probable that solutions of other organolithium compounds are similarly constituted. The initial reactions between such solutions and potassium may be pictured as involving the stepwise substitution of lithium by potassium in the associated complex, this giving rise to a series of compounds of progressively decreasing solubility. It is to be expected that as the solubility of the product becomes less, so also does the rate of reaction with potassium; and when an insufficiency of potassium is employed, the final production of sparingly soluble complexes of the type $(RLi)_x(C_6H_5K)_y$ may reasonably be postulated. Similar behaviour is observed in reactions between phenyllithium and potassium (Bryce-Smith, unpublished).

Dimetallation.—The present results indicate that orientation in dimetallation is very largely *meta-para*; *ortho*-positions are scarcely attacked, if at all. [Previous reports (see above) of *ortho*-dimetallation may probably be attributed to the use of the unsuitable " fluorescein test " to detect traces of phthalic acid (cf. Mulay and Mathur, *Current Sci.*, 1951, **20**, 206).] The *meta : para* ratio varies somewhat with the nature of the alkyl group in the reagent, but there is no obvious relation between this ratio and the length or degree of branching of the alkyl chain. For a given alkyl group, the effect of varying the metal does not appear to be great, although the *para : meta* ratio of 1·2 which we have found with *n*-amylpotassium is higher than that found by Morton and his co-workers (*loc. cit.*) with the use of *n*-amylsodium; but these workers' evidence for " exclusive " *meta*-dimetallation of benzene largely rested upon a melting point for di-*p*-bromophenacyl *iso*phthalate which we now find to have been some 11° low.

Interpretation of the present dimetallation results is rendered difficult by the fact that the reaction mixtures have of necessity been heterogeneous. In questions of the directing influence of substituents in aromatic systems, it is usually assumed that the entropy of activation is the same at each nuclear position, *i.e.*, that each position is equally available to the attacking reagent (except where the geometry of the molecule results in steric hindrance). It is unlikely that this assumption can be made in the case of dimetallation, for both reagents are highly insoluble in the reaction medium. With sodium and potassium compounds, the fact that dimetallation occurs at all under such unfavourable physical conditions strongly suggests that the reactions occur between adjacent molecules in a mixed crystal lattice. Geometric factors should therefore greatly influence the orientation in these reactions, and should depend in some measure upon the nature of the alkyl group in the reagent. If an intermolecular steric effect does indeed operate, it follows that the observed isomer ratios cannot properly reflect the activation energies for reactions at the corresponding nuclear positions : hence the comparison of alkali-metal substituents with other atoms or groups of known character may at present not be justified. These considerations also probably apply to dimetallation by the soluble organolithium compounds in view of their considerable association in benzene solution. The *overall* effect of a lithium substituent is evidently one of deactivation towards the metallation reaction, for even when two strongly *ortho*-directing groups such as methoxyl are present, only one lithium atom is introduced under the usual conditions (Wittig, Pockels, and Dröge, *Ber.*, 1938, **71**, 1903; Gilman, Willis, Cook, Webb, and Meals, *J. Amer. Chem. Soc.*, 1940, **62**, 667).

EXPERIMENTAL

M. p.s are corrected unless otherwise stated.

Purification of Materials.—" AnalaR " benzene was purified by fractional freezing : this process, repeated five times, gave material, n_D^{20} 1·5010, which solidified to a clear glass at 5°. *n*-Pentane was freed from unsaturated and aromatic compounds by several hours' shaking with 5% oleum, then washed, dried, and distilled over sodium. The fraction, b. p. 35—36°, was used. All alkyl halides had a b. p. range of <0·5°. *tert.*-Butyl chloride was prepared immediately before use, and all materials were thoroughly dried.

Experiments were conducted under an inert atmosphere : the vapour of the refluxing medium was used in preference to nitrogen, and the system was closed by a mercury seal. The stirrer was made gas-tight by a seal of " Portex " tubing which was effective under reduced

pressure when lubricated by liquid paraffin. Otherwise, hydrocarbon greases were avoided. The usual precautions were taken for the handling of substances spontaneously inflammable in air; the potassium compounds are particularly sensitive in this respect.

Preparation of Alkyl-lithium Compounds.—(a) *Ethyl-*, n-*propyl-*, n-*butyl-*, sec.-*butyl-*, *and* n-*amyl-lithium.* Lithium (2·0 g., 0·29 g.-atom) was extruded as wire of 0·5 mm. diam. from a " Nalik " press directly into *n*-pentane (40 c.c.). A mixture of the halide (0·12 mole of ethyl bromide, or *n*-propyl, *n*-butyl, *sec.*-butyl, or *n*-amyl chloride) with *n*-pentane (40 c.c.) was added continuously during 3—4 hours. Gentle refluxing was maintained by a warm water-bath and the mixture was vigorously stirred. Stirring under reflux was continued for 1 hour after addition of the halide solution. Yields were determined by the removal of 1-c.c. portions of clear solution, treatment with water, and titration with standard acid. Ethyl-lithium has a low solubility in *n*-pentane and in this case portions of the stirred suspension were removed for estimation. With each compound, yields of 93—98% were regularly obtained; but these were greatly reduced if the halide solution was added more rapidly or not steadily. It was found that the solubility of ethyl-lithium in *n*-pentane at 20° is 7·6 g./l. This low solubility doubtless explains the high yields which may be obtained with the use of ethyl bromide, for higher alkyl bromides under similar conditions furnish much poorer yields of the corresponding alkyl-lithium compounds.

(b) tert.-*Butyl-lithium.* When *tert.*-butyl chloride was employed in the above procedure, the highest yield of *tert.*-butyl-lithium was 5%. Tyler, Sommer, and Whitmore's method (*J. Amer. Chem. Soc.*, 1948, **70**, 2876) furnished a yield of 22% when carried out on the above scale : they reported yields averaging 66%.

General Procedure for Metallation by Alkylpotassium Compounds.—*n*-Pentane was distilled under reduced pressure and with vigorous stirring from a preparation which contained a known amount of an alkyl-lithium compound (free from lithium halide in some cases, but this was not essential). Benzene and potassium were then added (1 : 4 sodium–potassium alloy for those reactions to be carried out at 20°), and the mixture was vigorously stirred. Completion of the reaction was indicated when gas ceased to be evolved and was checked by titration of 1-c.c. portions of the clear supernatant liquid obtained by sedimentation. The whole product was quickly poured on a mixture of solid carbon dioxide and ether, and after a short time, alkali metals were destroyed by cautious addition of *tert.*-butyl alcohol containing *ca.* 20% of water. This alcohol was used in order to prevent any loss of acids by esterification during subsequent operations : the use of the pure alcohol led, in one instance, to a sudden over-vigorous reaction following a time lag. Separation of the mixture of mono- and di-carboxylic acids was effected in the following manner. The mixture was acidified to remove lithium carbonate and was then quickly basified with sodium hydroxide. The separated organic layer was examined for neutral reaction products, and the aqueous layer was boiled to remove *tert.*-butyl alcohol, saturated with salt, acidified, and extracted with sufficient benzene to dissolve the precipitated benzoic acid. Insoluble *iso*phthalic and terephthalic acids were obtained by centrifugation and were purified by reprecipitation and, if necessary, sublimation under reduced pressure. Benzoic acid obtained by evaporation of the benzene solution was usually perfectly pure without recrystallisation; but mixed m. p.s were always taken. The combined aqueous liquors were made alkaline and concentrated, and were then acidified and extracted with *cyclo*hexanone to furnish aliphatic acids and phthalic acid, if present. A further small quantity of benzoic and *iso*phthalic acids was generally obtained at this stage and these acids were combined with the main crops.

Separation of iso*Phthalic and Terephthalic Acids.*—(a) via *the dimethyl esters.* A mixture of the acids (0·6 g. of each) was heated under reflux for 10 hours with methyl alcohol (18 c.c.) and con-centrated sulphuric acid (2 c.c.). The clear solution was cooled to 5—10° and filtered. The crystals were quickly washed with methyl alcohol (2 c.c.) which had been cooled in solid carbon dioxide, and then with a little water to give dimethyl terephthalate (0·65 g., 93%), m. p. 140° (pure 141°). The filtrate was warmed under reduced pressure to remove methyl alcohol and treated with brine to precipitate dimethyl *iso*phthalate (0·65 g., 93%), m. p. 61—62° (pure 67°) : the m. p. could not be raised by recrystallisation from aqueous methyl alcohol or from light petroleum. Experiments with synthetic mixtures showed that the m. p. of pure dimethyl *iso*phthalate is depressed *ca.* 1° by each 1% of added dimethyl terephthalate up to at least 10%. Accordingly, the corrected yield of dimethyl terephthalate in the above separation was 98% and that of the *iso*-ester 88%. When only very small quantities of the mixture of acids were available, the esterification was conducted in a sealed tube (considerable pressure develops). Identities of esters were always confirmed by mixed m. p. determinations.

(b) via *the barium salts.* Separations were conducted essentially according to Smith's

method (*ibid.*, 1921, **43**, 1920), but were invariably imperfect, the recovery of terephthalic acid being sometimes as much as 10% low.

Yields (%) of products from the interaction of alkylpotassium compounds and benzene, after reaction with carbon dioxide.

Reagent	Temp.	Ph·CO₂H	C₆H₄(CO₂H)₂	*para/meta*	*ortho*	R·CO₂H	C₆H₅R
C₂H₅K	20°	25	0·3	*ca.* 2·5	—	—	—
C₂H₅K *	85	—	—	1·6	—	—	<1 †
n-C₃H₇K	65	53	7·5	0·55	—	—	<1 †
n-C₄H₉K	20	60	5	1·5	—	13	—
n-C₄H₉K	65	65	7·5	1·5	—	—	<1 †
sec.-C₄H₉K	20	(i) 48	3	0·7	—	—	—
		(ii) 57	9	0·7	trace †	—	—
sec.-C₄H₉K	65	56	8	1·2	—	—	4·5
tert.-C₄H₉K	20	46	3	*ca.* 2	—	—	—
n-C₅H₁₁K	65	86	4·5	1·2	—	—	<1 †

* Further data regarding this experiment are reserved for a future publication, since it was carried out under special conditions in connection with another problem.
† Not rigorously identified.

Metallation Reactions.—(*a*) *Ethylpotassium at* 20°. A solution of ethyl-lithium (0·084 mole) in benzene (120 c.c.) was vigorously stirred with an alloy of potassium (5·5 g., 0·14 g.-atom) and sodium (1·1 g.). Evolution of ethane commenced within a few minutes and the mixture became brown. The reaction was 93% complete after 52 hours. After a reaction with carbon dioxide there were obtained benzoic acid (2·5 g.) and a dicarboxylic acid (20 mg.). The latter furnished barium terephthalate (25 mg.) and a solid (4 mg.), m. p. 320—330° (uncorr.), which was probably crude *iso*phthalic acid. Neutral products were not investigated.

(*b*) n-*Propylpotassium at* 65°. The reaction between *n*-propyl-lithium (0·14 mole) and potassium (11 g., 0·28 g.-atom) in benzene (90 c.c.) was largely complete within 4¼ hours at 65°. The evolved gas was slightly unsaturated to bromine in carbon tetrachloride. Reaction with carbon dioxide gave benzoic acid (9·0 g.), *iso*phthalic acid (0·56 g.), and terephthalic acid (0·31 g.). The only definite neutral product was a liquid (0·1 g.), b. p. 155—165°, but the amount was insufficient to establish identity with *n*-propylbenzene (b. p. 159°). Diphenyl and phthalic acid were absent.

(*c*) n-*Butylpotassium at* 20°. The reaction between *n*-butyl-lithium (0·082 mole) and an alloy of potassium (6·2 g., 0·16 g.-atom) and sodium (1·5 g.) in benzene (50 c.c.) was 95% complete within 60 hours. Reaction with carbon dioxide gave benzoic acid (6·0 g.), *iso*phthalic acid (0·12 g.), terephthalic acid (0·18 g.), and *n*-valeric acid (1·05 g.), b. p. 184—186°. The bulk of the aliphatic acid was evidently derived from an insoluble organometallic species. No *n*-butylbenzene, diphenyl, benzophenone, or phthalic acid was detected.

(*d*) n-*Butylpotassium at* 65°. *n*-Butyl-lithium (0·07 mole) in benzene (45 c.c.) was heated to 80° to initiate a reaction with potassium (5·5 g., 0·14 g.-atom). The mixture was quickly cooled to 65° at which temperature the reaction was 73% complete after 4 hours. The evolved butane was slightly unsaturated to bromine in carbon tetrachloride. Reaction with carbon dioxide gave benzoic acid (4·1 g.), *iso*phthalic acid (0·18 g.), and terephthalic acid 0·26 g.). 0·2 G. of a colourless neutral liquid, b. p. 160—180°, was also obtained. This had an odour which resembled that of *n*-butylbenzene (b. p. 184°), but the amount was insufficient to confirm the identity. Diphenyl and phthalic acid were absent.

(*e*) sec.-*Butylpotassium at* 20°. The reaction between *sec.*-butyl-lithium (0·092 mole) and an alloy of potassium (6·6 g., 0·17 g.-atom) and sodium (1·65 g.) in benzene (55 c.c.) was 96% complete after 30 hours at 15—20°. (Estimation required the filtration of a measured portion of the brown suspension, for sedimentation was too slow for the usual method to be employed.) Reaction with carbon dioxide gave benzoic acid (5·1 g.), *iso*phthalic acid (0·11 g.), and terephthalic acid (0·075 g.). The presence of a trace of phthalic acid was indicated by a positive but weak " phenolphthalein test." *sec.*-Butylbenzene and diphenyl were absent.

(*f*) sec.-*Butylpotassium at* 65°. The reaction between *sec.*-butyl-lithium (0·0855 mole) and potassium (6·6 g., 0·17 g.-atom) in benzene (50 c.c.) was 95% complete after 1½ hours at 65°. *n*-Butane which was evolved had b. p. 0—2° (uncorr.) and was fully saturated to bromine in carbon tetrachloride. The reaction with carbon dioxide gave benzoic acid (5·5 g.), *iso*phthalic acid (0·23 g.), and terephthalic acid (0·275 g.); no phthalic acid was detected. A neutral liquid (1·5 g.) was obtained which distilled over the range 110—180° : only a trace of material of higher b. p. remained. This liquid was slightly unsaturated to bromine in carbon tetrachloride and was redistilled over a little sodium to give *sec.*-butylbenzene (0·5 g.), b. p. 170—173°/754 mm.,

3 L

n_D^{20} 1·4897. Forziati and Rossini (*J. Res. Nat. Bur. Stand.*, 1949, 473) record n_D^{20} 1·49020 (Found : C, 89·35; H, 10·65. Calc. for $C_{10}H_{14}$: C, 89·5; H, 10·5%). The *p*-sulphonamide had m. p. 78—79° (Found : N, 6·4. Calc. for $C_{10}H_{15}O_2NS$: N, 6·5%). Huntress and Autenrieth (*J. Amer. Chem. Soc.*, 1941, **63**, 3446) found m. p. 81·0—82·5°. It is possible that the present hydrocarbon was not isomerically pure, for a crop of material of lower m. p. which was obtained from the mother-liquors of the *p*-sulphonamide preparation also had N, 6·4%.

(*g*) An experiment similar to (*e*) was performed; but after the reaction with potassium was complete, the product was divided into two portions, one of which was treated directly with carbon dioxide, whereas the other was heated at 65° for 1½ hours before this step. The observed ratios of terephthalic to *iso*phthalic acid were the same to within the order of accuracy of the estimation. This demonstrated that no appreciable rearrangement or thermal decomposition of the dipotassium compounds occurs at 65°.

(*h*) *tert.-Butylpotassium at* 20°. The reaction between *tert.*-butyl-lithium (0·028 mole) and an alloy of potassium (1·75 g., 0·045 g.-atom) and sodium (0·45 g.) in benzene (35 c.c.) was 90% complete after 126 hours at 15—20°. Reaction of the product with carbon dioxide gave benzoic acid (1·35 g.), *iso*phthalic acid (0·02 g.), and terephthalic acid (0·04 g.). No phthalic acid was detected. Neutral reaction products were not investigated.

(*i*) n-*Amylpotassium at* 65°. The reaction between *n*-amyl-lithium (0·135 mole) and potassium (11 g., 0·28 g.-atom) in benzene (90 c.c.) was 95% complete after 4 hours at 63—65°. Reaction with carbon dioxide gave benzoic acid (13·3 g.), *iso*phthalic acid (0·23 g.), and terephthalic acid (0·27 g.). No phthalic acid was detected. A colourless neutral liquid (0·2 g.) was also obtained, of b. p. 178—210°; this when warmed with a little sodium had an odour similar to that of *n*-amylbenzene (b. p. 205°).

(*j*) *Reaction of potassium with excess of* sec.-*butyl-lithium in benzene.*—A solution of *sec.*-butyl-lithium (0·052 mole) in benzene (50 c.c.) was stirred with potassium (0·787 g., 0·0202 g.-atom) for 6 hours at 65° : lithium chloride was not present. By the usual titration procedure it was shown that 0·024 mole of soluble organometallic compound remained. Hence, 0·028 mole of *sec.*-butyl-lithium had reacted with 0·0202 g.-atom of potassium—a ratio of 1·39 : 1.

Non-reactivity of Alkyl-lithium Compounds towards Benzene.—It was desirable to show that alkyl-lithium compounds do not metallate benzene under the conditions of the previous experiments. Accordingly, solutions of *n*- and *sec.*-butyl-lithium in benzene were heated at 65° for 3 hours : also, a solution of *sec.*-butyl-lithium in benzene was kept at 15—20° for 8 days. The products from these experiments were treated with solid carbon dioxide and furnished specimens of the corresponding acids (*n*-valeric and *iso*valeric acids), which, without purification, were converted into the *p*-bromophenacyl esters. The " crude " esters had m. p.s and mixed m. p.s within 2° of the accepted values (64° and 55°, respectively). In no case did the neutral reaction products give a colour when warmed with sodium; the addition of 1% of benzophenone was readily detected in this manner. Benzophenone is always formed when phenyl-lithium reacts with carbon dioxide.

Metallation of Benzene by Ethylsodium.—A suspension of ethylsodium in *n*-pentane was prepared by addition of diethylmercury (4·8 g., 0·0186 mole) during 15 minutes to sodium wire (1·5 g., 0·065 g.-atom) in *n*-pentane (50 c.c.). Vigorous stirring was maintained for 130 minutes and the temperature was kept at 10—15° by cooling. To the black product was added benzene (4·5 g., 0·058 mole), and stirring was then continued at 15—20° for 6 days, by which time evolution of gas had become inappreciable. Reaction with solid carbon dioxide in ether gave benzoic acid (1·05 g., 23%), m. p. 118—119°, m. p. and mixed m. p. 121° after recrystallisation, together with a mixture of terephthalic and *iso*phthalic acids (0·0426 g., 1·5%). Separation *via* the dimethyl esters gave dimethyl terephthalate (0·0319 g.), m. p. 138—139° and mixed m. p. 139—140°, and dimethyl *iso*phthalate (0·0092 g.), m. p. 60—61° and mixed m. p. 63—64°. No phthalic acid was detected. Only insignificant traces of neutral reaction products were obtained and the characteristic odours of ethylbenzene and diphenyl were not detected.

Metallation of Phenyl-lithium by n-*Butyl-lithium.*—A solution of *n*-butyl-lithium in *n*-pentane (25 c.c. of 1·64N, 0·041 mole) was added to a solution of phenyl-lithium in benzene (45 c.c. of 1·89N, 0·085 mole). Both solutions were essentially free from lithium halides. The mixture was distilled until the liquid temperature reached 78° and was then kept under gentle reflux. The evolution of gas commenced after a few minutes and a pale brown solid slowly separated (LiH ?). Heating was continued for 20 hours, by which time the evolution of gas had ceased. Reaction with solid carbon dioxide in ether gave benzoic acid (5·0 g., 32%) together with a mixture of terephthalic and *iso*phthalic acids (0·18 g., 5%) which was separated *via* the dimethyl

esters. Dimethyl terephthalate had m. p. 140° and dimethyl *iso*phthalate m. p. 60—62° : their ratio was *ca.* 2 : 1. Tests for phthalic and formic acids were negative. From the neutral reaction products there was isolated triphenylmethanol (0·7 g.), m. p. and mixed m. p. 161°.

Reaction between sec.-*Butyl Chloride and Potassium in Benzene.*—*sec.*-Butyl chloride (20·5 g., 0·22 mole) was added during 30 minutes with vigorous stirring to potassium (7·8 g., 0·2 g.-atom) in benzene (100 c.c.) at 65°. The mixture became deep blue and gas was copiously evolved. Fractional distillation of the organic product obtained by addition of water gave *sec.*-butylbenzene (0·4 g., 3%), b. p. 173—175°. No diphenyl was formed.

Di-p-*bromophenacyl* iso*Phthalate.*—*m*-Toluic acid was recrystallised to constant m. p. and oxidised to *iso*phthalic acid by alkaline permanganate (90% yield). The di-*p*-bromophenacyl ester of this acid was prepared in the normal manner and recrystallised from alcohol–chloroform to constant m. p. 189·7° (Found : Br, 28·25. Calc. for $C_{24}H_{16}O_6Br_2$: Br, 28·5%). Kelly and Kleff (*J. Amer. Chem. Soc.*, 1932, **54**, 4444) recorded m. p. 179·1°; Morton, Little, and Strong (*loc. cit.*) recorded 179—179·5° : no analytical results were quoted in either case.

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