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1. *The Reaction of o-Di-iodobenzene with Magnesium, Lithium, and n-Butyl-lithium.*

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The reaction of *o*-di-iodobenzene with the above reagents, followed by carboxylation of the product, has been investigated. The main product isolated with magnesium is diphenyl, and with lithium is tri-*o*-phenylene. *n*-Butyl-lithium affords a mixture of 2 : 2'-di-(*o*-carboxyphenyl)diphenyl and 2 : 2'-di-(*o*-*n*-butylphenyl)diphenyl. The origin of these products is briefly discussed.

p-DIBROMOBENZENE with magnesium under suitable conditions gives a mono- or a di-magnesium derivative (Ziegler and Tiemann, *Ber.*, 1922, **55**, 3406; Gilman, Beaber, and Jones, *Rec. Trav. chim.*, 1929, **48**, 597; von Braun, Irmisch, and Nelles, *Ber.*, 1933, **66**, 1471): 1 : 4-dibromonaphthalene behaves similarly (Zalkind, *Ber.*, 1934, **67**, 1031). *p*-Dibromobenzene can also be converted into *p*-bromophenyl-lithium by the action of *n*-butyl-lithium (Gilman and Melvin, *J. Amer. Chem. Soc.*, 1950, **72**, 995).

The preparation of *o*-phenylenebis(magnesium halide) or of *o*-phenylenedilithium would be of great value, particularly for the synthesis of cyclic systems, and we have therefore studied the action of magnesium, lithium, and *n*-butyl-lithium on *o*-di-iodobenzene in particular.

The reaction of magnesium with the three di-iodobenzenes, first noted by Votoček and Kohler (*Ber.*, 1914, **47**, 1219), was further investigated by Bruhat and Thomas (*Compt. rend.*, 1926, **183**, 297) who found that all three di-iodobenzenes react with substantially more than one equivalent of magnesium, and that the product from the *meta*- and the *para*-compound on carboxylation gave *isophthalic* and *terephthalic* acid in 15 and 50% yield respectively, whereas that from the *ortho*-compound gave only benzoic acid in unspecified yield. They concluded that all the di-iodobenzenes give the corresponding phenylenebis-(magnesium iodide), and confirmed this process for the *ortho*-derivative by treating the product with benzonitrile and with benzophenone, subsequently isolating the expected diketone and glycol respectively, in low yield.

We found that *o*-di-iodobenzene in ether reacted readily with 1 equivalent of magnesium, and the product, when carboxylated in the usual way, afforded *o*-iodobenzoic acid (29%), unchanged di-iodobenzene (25%), and a trace of benzoic acid. The use of 2 equivalents of magnesium also gave a vigorous reaction, but even after prolonged digestion only 1.5 equivalents had reacted: carboxylation then gave benzoic acid (5.5% after purification), no other acid being detected, while the ether layer afforded diphenyl (17%).

These results, we suggest, indicate that some *o*-phenylenebis(magnesium iodide) is formed, but that it reacts with carbon dioxide to give the complex (I), which resists further carboxylation and on hydrolysis forms benzoic acid. The major reaction arises almost undoubtedly by an initial Fittig condensation, giving 2 : 2'-di-iododiphenyl, which then forms the bis(magnesium iodide) derivative (II), hydrolysis of which gives the diphenyl. This mechanism is supported by the fact that under the conditions employed by us and by Bruhat and Thomas (*loc. cit.*), the *o*-di-iodobenzene could not be induced to react with more than 1.5—1.6 equivalents of magnesium. The lack of reactivity of the derivative (II) with carbon dioxide may be due partly to steric hindrance, but also to the very low solubility

(*Monatsh.*, 1893, **14**, 323) obtained by the action of sodium in similar conditions. *o*-Dibromobenzene with *n*-butyl-lithium gave a small quantity of the hydrocarbon (V; R = Buⁿ) and, as the main product, a colourless amorphous solid, melting above 350° and insoluble in all common solvents; this solid was not further investigated.

Although an intensive investigation of the above reactions, with considerable variation in the many factors involved, might well reveal a change in the yield and even the nature of the products, it is clear that the preparation of an *o*-phenylenebis(magnesium halide) or of *o*-phenylene-dilithium as a synthetic reagent is not practicable under the conditions described above.

EXPERIMENTAL

Experiments with metals and with *n*-butyl-lithium were performed in a nitrogen atmosphere. Carboxylation was carried out by pouring the reaction solution into a slurry of solid carbon dioxide and ether. In all experiments the non-acidic product was carefully examined for the presence of 2:2'-di-iododiphenyl, and also (except in experiments involving benzene as a solvent) benzene: neither compound was detected.

Reactions with Magnesium.—(a) A solution of *o*-di-iodobenzene (9.9 g.) in ether (50 c.c.) was added dropwise to a stirred mixture of magnesium (0.73 g., 1 atom) and ether (10 c.c.), which reacted readily, external cooling being required. The mixture was then stirred at room temperature for 2 hr., and the clear yellow solution, containing no free magnesium, was carboxylated. The product was extracted with aqueous sodium hydroxide, which when acidified deposited a crude crystalline acid: distillation of this acid in steam gave a trace of benzoic acid; the remainder, when recrystallised from water, afforded *o*-iodobenzoic acid (2.2 g., 29%; m. p. 160°; *p*-bromophenacyl ester, m. p. 110°). The ether layer on evaporation gave *o*-di-iodobenzene, b. p. 78—82°/0.05 mm. (2.5 g., 25%).

(b) The above experiment was repeated but with magnesium (1.46 g., 2 atoms), the ethereal *o*-di-iodobenzene being added at such a rate that the mixture did not boil. The Grignard reagent separated as a heavy amber-coloured oil. The mixture was stirred for 3 hr. at room temperature, filtered to remove unchanged magnesium (0.37 g., 0.5 atom), and carboxylated. The mixture was acidified with dilute hydrochloric acid, then basified and extracted with aqueous sodium hydroxide. The latter when acidified deposited a crude acid, m. p. 114°, which when recrystallised thrice from light petroleum (b. p. 60—80°) and twice from water afforded benzoic acid (0.2 g., 5.5%), m. p. alone and mixed, 120°. The ethereal layer, when dried and distilled, gave diphenyl, b. p. 140—160°/15 mm., m. p. alone and mixed, 67° after recrystallisation from methanol (0.4 g., 17%).

(c) A Grignard reagent was prepared from *o*-di-iodobenzene (16.5 g.) in ether (70 c.c.) and magnesium (1.95 g., 1.6 atoms), benzene (20 c.c.) being then added to give a homogeneous solution with only a trace of undissolved magnesium. The solution was stirred for 2 hr., and then cooled in ice-water whilst iododimethylarsine (18.6 g., 1.6 mols.) in benzene (30 c.c.) was slowly added. The clear yellow solution was boiled under reflux for 2 hr., cooled in ice, and hydrolysed with aqueous ammonium chloride. The organic layer, when dried and distilled, gave iododimethylarsine, b. p. 30—50°/0.3 mm. (3 g., 16%), and 2-diphenyldimethylarsine, b. p. 98—110°/0.3 mm. (6.5 g.). The latter product on treatment with methyl iodide gave 2-diphenyltrimethylarsonium iodide (4.6 g., 58%), m. p. 259—260° (from ethanol) (Found: C, 44.8; H, 5.0. C₁₅H₁₈IAs requires C, 45.0; H, 4.55%).

To confirm the identity of the tertiary arsine, a Grignard reagent was prepared under nitrogen from 2-iododiphenyl (14 g.) and magnesium (1.3 g., 1.06 atoms) in ether (70 c.c.), into which, after 90 minutes' stirring at room temperature, a solution of iododimethylarsine (11.6 g., 1 mol.) in benzene (40 c.c.) was added during 15 min. The mixture was boiled under reflux for 2 hr., cooled in ice, and hydrolysed as before. The organic layer, when dried and distilled, gave 2-diphenyldimethylarsine, b. p. 104—106°/0.3 mm. (6 g., 46%). This gave a methiodide, which, after crystallisation from ethanol, had m. p. 259—260°, undepressed by admixture with the above iodide. The arsine, prepared in this way, gives high carbon values on analysis, owing to contamination with diphenyl, with which it co-distils. The methiodide was therefore decomposed by being heated under nitrogen at 280°/0.15 mm.; the distillate on refractionation gave the pure *arsine*, b. p. 114°/0.5 mm. (Found: C, 65.1; H, 5.9%). C₁₄H₁₅As requires C, 65.1; H, 5.9%).

It is noteworthy that a repetition of experiment (c), but with chlorodiphenylarsine, gave a product from which only iododiphenylarsine, b. p. 137—139°/0.4 mm., was isolated.

Reaction with Lithium.—A solution of *o*-di-iodobenzene (6.6 g.) in ether (20 c.c.) was added dropwise to a stirred mixture of fine lithium foil (0.6 g., 4.1 atoms) in ether during 3 hr., reaction readily occurring. Benzene (25 c.c.) was then added and the mixture boiled under reflux for 3 hr. Carboxylation of the cooled product gave no trace of an organic acid. The organic layer, when dried and evaporated, gave a dark solid residue, which after crystallisation from ethanol (charcoal) followed by sublimation at 160—180°/0.4 mm., afforded tri-*o*-phenylene (IV) (0.45 g., 30%), m. p. 191—192° (Found: C, 95.0; H, 5.6. Calc. for C₁₈H₁₂: C, 94.7; H, 5.3%). The identity of this hydrocarbon was confirmed by its ultraviolet absorption spectrum in ethanol, which gave the characteristic maxima (with log₁₀ ε values in parentheses): 249 (4.95), 258 (5.2), 273 (4.3), 285 (4.25), 315 (3.2), 327 (3.0), 333 mμ (3.15): these values accord closely with those given by Clar and Lombardi (*Ber.*, 1932, **65**, 1411; cf. also Rapson, Schwartz, and Stewart, *J.*, 1944, 73).

In an experiment similar to the above but with *o*-dibromobenzene, the boiling under reflux was continued for 12 hr. before the lithium was extensively attacked. Carboxylation gave no trace of acid, and no triphenylene was detected in the ethereal layer. The latter on evaporation gave a dark non-volatile residue which was extracted with cold benzene. Dilution of the extract with ethanol gave a yellow-brown amorphous precipitate, m. p. 280—285° after three reprecipitations. In view of the nature of the product and its difficult purification, it was not further investigated.

Reaction with n-Butyl-lithium.—A solution of *o*-di-iodobenzene (6.6 g.) in benzene (50 c.c.) and light petroleum (b. p. 40—60°) (100 c.c.) was added to a stirred 1.9*N*-solution of *n*-butyl-lithium (26 c.c., 2.4 mols. of solute) in the above petroleum, a vigorous exothermic reaction rapidly developing. The mixture was boiled under reflux for 3 hr., and then carboxylated. Working up in the usual way gave an acid (0.6 g.) and a hydrocarbon (0.15 g.), both colourless crystalline compounds.

Recrystallisation of the acid from ethanolic petroleum or from aqueous ethanol gave 2 : 2'-*di*-(*o*-carboxyphenyl)diphenyl (V; R = CO₂H) (0.35 g., 17%), which retained ethanol even after drying at 80°/0.2 mm. for 6 hr. (Found: C, 78.4; H, 5.0. C₂₈H₁₈O₄.0.25C₂H₆O requires C, 78.4; H, 4.85%), but which on sublimation at 200—220°/0.1 mm. gave the pure acid, m. p. 244—245° (Found: C, 79.0; H, 4.8%; *M*, ebullioscopic in ethanol, 408. C₂H₁₈₈O₄ requires C, 79.15; H, 4.6%; *M*, 394). A methanolic solution of the acid, when saturated with hydrogen chloride and boiled for 1 hr., gave the *dimethyl ester*, m. p. 147—148°, after crystallisation from light petroleum (b. p. 60—80°) (Found: C, 79.75; H, 5.1. C₂₈H₂₂O₄ requires C, 79.6; H, 5.25%). The infrared spectrum of the acid (V; R = CO₂H), determined in a hexachlorobutadiene mull, showed bands at 6.24, 6.35, 13.30, and 13.40 μ, assigned to the *o*-phenylene groups, and at 5.92 and 10.7 μ, assigned to the CO₂H groups.

The hydrocarbon, recrystallised from ethanolic benzene, gave 2 : 2'-*di*-(*o*-*n*-butylphenyl)diphenyl (V; R = Buⁿ) (0.10 g., 5%), m. p. 228—230° raised to 229—231° by sublimation at 260—270°/0.1 mm. (Found: C, 92.0; H, 7.6%; *M*, ebullioscopic in carbon tetrachloride, 413. C₃₂H₃₄ requires C, 91.8; H, 8.2%; *M*, 419). The infrared spectrum, determined as above, showed bands at 6.25, 13.28, and 13.41 μ due to the *o*-phenylene groups, at 3.43 and 3.51 μ due to the CH₂ groups, and at 7.27 μ assigned to the •C•Me group. The ultraviolet spectrum (solution in light petroleum, b. p. 60—80°) showed no maximum or minimum over the range 200—300 mμ. The identity of the hydrocarbon is confirmed by the very close similarity of this spectrum with that of 2 : 2'-diphenyldiphenyl (V; R = H) in ethanol and *n*-hexane determined by Rapson, Schwartz, and Stewart (*loc. cit.*): the following values for this compound have been measured from the very small curve given by these authors.

(V; R = Bu ⁿ)	λ (mμ)	210	245	250	257	270
	log ₁₀ ε	4.35	4.00	3.93	3.85	3.70
(V; R = H)	λ (mμ)	210	245	250	257	270
	log ₁₀ ε	4.6	4.3	4.25	4.1	3.75

o-Di-iodobenzene was also treated with *n*-butyl-lithium (1 mol.) in the petroleum solution at 0° for 1 min., and the product was then carboxylated; working up as before gave the acid (V; R = CO₂H) in lower yield, with a trace of benzoic acid and some unchanged *o*-di-iodobenzene.

o-Dibromobenzene, when similarly treated with *n*-butyl-lithium (2.4 mols.), gave as the main product a colourless solid, which was insoluble in all common organic solvents and did not melt below 350°; the crude material, when extracted with boiling ethanol, gave the hydrocarbon (V; R = Buⁿ) in very low yield. No acid could be isolated from the products of

carboxylation. *o*-Dibromobenzene, when treated with *n*-butyl-lithium (1 mol.) in the petroleum at 0° for 5 min. and then carboxylated, gave the same products, *o*-dibromobenzene (75%) being recovered unchanged.

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