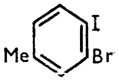
948. *The Reaction of 3-Bromo-4-iodotoluene with Magnesium and Lithium.*

By Roy C. Hinton, Frederick G. Mann, and Ian T. Millar.

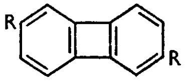
The reaction of 3-bromo-4-iodotoluene with magnesium and lithium has been studied with particular reference to the neutral products. The action of magnesium gives a crude product which contains 2 : 6-dimethyldiphenylene and on carboxylation affords 2 : 7-dimethylfluorenone. The product from the action of lithium contains 2 : 6 : 11-trimethyltriphenylene, and on hydrolysis also furnishes 4 : 4′-dimethyldiphenyl.

The probable mechanisms by which these compounds are formed are discussed.

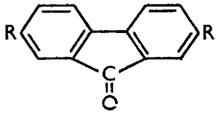
Magnesium reacts with *o*-di-iodobenzene,[1] *o*-bromoiodobenzene,[2] and 3-bromo-4-iodotoluene[3] (I) to give diphenyl, diphenylene (II; R = H), and 2 : 6-dimethyldiphenylene (II; R = Me) respectively, in addition to other products in each case. Diphenyl is also undoubtedly formed in this reaction with *o*-bromoiodobenzene, but it co-distils with diphenylene, and consequently in the above experiments the reaction product was treated with carbon dioxide, whereby fluorenone (III; R = H) was formed and was readily separated from the diphenylene. Lithium reacts with *o*-di-iodobenzene and *o*-bromoiodobenzene to give triphenylene (IV; R = H). The probable mechanisms of the reactions producing these compounds, particularly those from *o*-bromoiodobenzene, have been discussed.[2, 3]



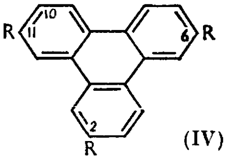
(I)



(II)



(III)



(IV)

We now record a brief investigation of the neutral compounds formed by the action of these metals on 3-bromo-4-iodotoluene (I), particularly as in the earlier experiments 2 : 6-dimethyldiphenylene (II; R = Me) arose incidentally in the synthesis of 4-methyl-*o*-phenylenebis(diethylphosphine)[3] and consequently was initially highly impure: the action of carbon dioxide on the crude reaction mixtures has not been studied except as an aid to the isolation of the neutral products.

When 3-bromo-4-iodotoluene (I) was brought into reaction with magnesium in ether, initially with cooling and finally with boiling under reflux, and the chilled product then carboxylated, the usual working up gave a neutral fraction which furnished 2 : 6-dimethyldiphenylene (II; R = Me) and 2 : 7-dimethylfluorenone (III; R = Me).

The acidic fraction furnished *p*-toluic acid, 2-bromo-4-methylbenzoic acid, a trace of 2-iodo-5-methylbenzoic acid, and a gummy residue the components of which could not be satisfactorily isolated but which were almost certainly substituted diphenic acids.

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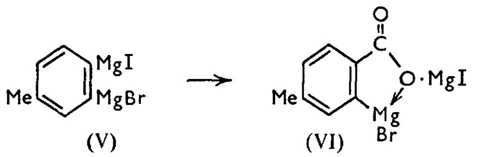
[1] Heaney, Mann, and Millar, *J.*, 1956, 1.

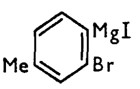
[2] *Idem*, *J.*, 1957, 3930.

[3] Hart and Mann, *J.*, 1957, 3939.

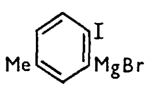
The formation of these three identified acids shows that the magnesium has reacted with 3-bromo-4-iodotoluene (I) to give the di-Grignard reagent (V), and the mono-Grignard



(V) (VI)



(VII)

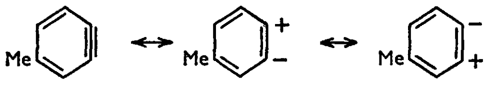


(VIII)

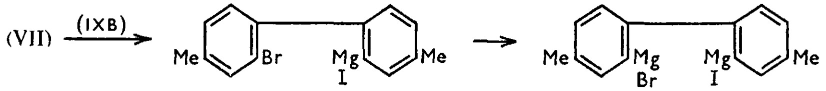
reagents (VII) and (VIII), the last however in very small proportion. The formation of the di-Grignard reagent (V) has already been proved by its conversion into the above diphosphine:[3] complete carboxylation of this reagent is undoubtedly prevented by the formation of the comparatively stable chelated intermediate (VI),[1] which on hydrolysis furnishes the *p*-toluic acid.

3-Bromo-4-iodotoluene (I) reacted with lithium in cold ether to give 2 : 6 : 11-trimethyltriphenylene (IV; R = Me), m. p. 128·5—129·5° after purification by conversion into its orange picrate, m. p. 191—192°, and also, after hydrolysis of the crude reaction mixture, 4 : 4′-dimethyldiphenyl. The identity of the hydrocarbon (IV; R = Me) is based on the following evidence. (*a*) Analysis, molecular-weight determination, and its absorption spectrum show the hydrocarbon to be a trimethyltriphenyl. (*b*) The only other isomer having one methyl group substituted in each benzene ring in other than the *ortho* positions is 2 : 6 : 10-trimethyltriphenylene, which Barker, Emmerson, and Periam[4] have prepared by an unambiguous synthesis and which has m. p. 190° and gives an orange picrate, m. p. 221—222°. We are greatly indebted to Dr. C. C. Barker for a specimen of this hydrocarbon for comparison with our 2 : 7 : 10-isomer.

The formation of these neutral compounds by the action of magnesium and lithium is of great interest and provides strong support for the mechanisms suggested for the reactions of *o*-bromoiodobenzene with these metals.[2] It is clear that the reagent (VII) is the chief mononuclear Grignard reagent formed, and that it could, by loss of magnesium dihalide, generate in solution the highly reactive transient 4-methylbenzyne, of which (IXA, B, and C) are canononical forms.



(IXA) (IXB) (IXC)



(X) (XI)

The dimerisation of either of the polar forms (IXB) or (IXC)—originally suggested by Lüttringhaus and Schubert[5] for benzyne itself—would give 2 : 6-dimethyldiphenylene (II; R = Me), and only a cross-dimerisation of (IXB) and (IXC) would provide the 2 : 7-isomer. The product obtained in our present experiments was readily purified, and no indication of an isomer could be obtained.

The interaction of the 4-methylbenzyne (IXB) with the ionised Grignard reagent (VII) would give the diphenyl derivative (X), which could then react with more magnesium to give the di-Grignard reagent (XI): carboxylation of this reagent (XI) would give 2 : 7-dimethylfluorenone (III; R = Me).

It is noteworthy that a similar interaction of the 4-methylbenzyne (IXC) with the reagent (VII) would have given 2 : 6-dimethylfluorenone, which was not detected.

A similar selective action apparently operates with the lithio-derivatives. Reaction

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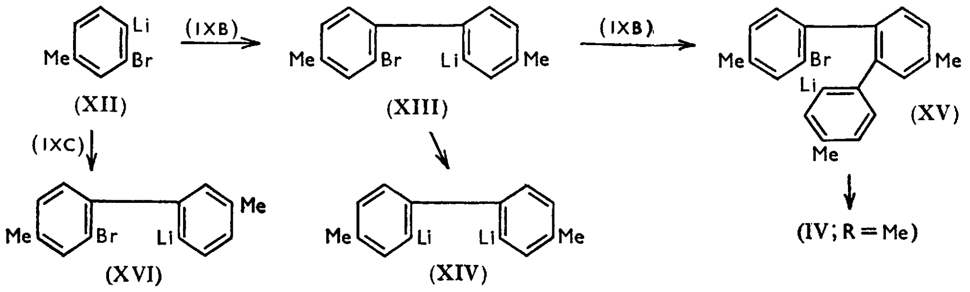
[4] Barker, Emmerson, and Periam, *J.*, 1958, 1077.

[5] Lüttringhaus and Schubert, *Naturwiss.*, 1955, **42**, 17.

of the lithio-derivative (XII) with the 4-methylbenzyne (IXB) will give the lithiodiphenyl derivative (XIII). A portion of this compound may undergo further lithiation to (XIV) which on subsequent hydrolysis forms the 4 : 4′-dimethyldiphenyl. A further portion of this compound (XIII) may react again with the 4-methylbenzyne (IXB) to give the



lithio-derivative (XV), which by loss of lithium bromide forms 2 : 6 : 11-trimethyltriphenylene (IV; R = Me): the latter would also be formed if the compound (XIII) reacted similarly with the 4-methylbenzyne (IXC).

It is noteworthy that if the initial reaction of the lithio-derivative (XII) occurred with the 4-methylbenzyne (IXC), the product (XVI) on further lithiation and hydrolysis would furnish 3 : 4′-dimethyldiphenyl: furthermore, this product (XVI), if it reacted again with the 4-methylbenzyne (IXC) would give 2 : 6 : 10-trimethyltriphenylene, but reaction with the 4-methylbenzyne (IXB) would furnish the 2 : 6 : 11-isomer.

Although there can be little doubt regarding the general mechanism by which the above neutral products are formed, decisive evidence for the specifically selective initial operation of the 4-methylbenzyne in the form (IXB), which is necessary for the production of the compounds (III; R = Me), (IV; R = Me), and 4 : 4′-dimethyldiphenyl, is dependent on the absence of isomers of each of these compounds. The probability that isomeric forms were discarded during the separation and purification of the components of the crude mixtures, which were always obtained in small quantity, must be assessed.

In the magnesium experiments, the 2 : 6-dimethyldiphenylene (II; R = Me) was readily purified by steam-distillation, and therefore the 2 : 7-isomer, which is also volatile in steam,[6] was absent. The residue furnished 2 : 7-dimethylfluorenone (III; R = Me) on recrystallisation, but the rise in m. p. without significant change in composition indicated the possible presence of an isomer in small quantity. In the lithium experiments, the crude mixture of 4 : 4′-dimethyldiphenyl and 2 : 6 : 11-trimethyltriphenylene (IV; R = Me) gave on distillation an initial semicrystalline fraction: the crystals were the pure 4 : 4′-dimethyldiphenyl but the fraction may have been a mixture of this compound with an isomer or with the triphenylene (IV; R = Me). Addition of picric acid to a solution of the undistilled residue deposited the almost pure picrate of 2 : 6 : 11-trimethyltriphenylene: the picrate of the 2 : 6 : 10-isomer has a closely similar solubility, and this hydrocarbon was almost certainly absent. The evidence indicates therefore that initial reaction of the 4-methylbenzyne (IXB) with the reagents (VII) and (XII) must constitute the dominant, if not the exclusive, reaction of the methylbenzyne in these series of changes.

EXPERIMENTAL

Reaction with Magnesium.—A solution of 3-bromo-4-iodotoluene (I) (93 g.) in ether (250 c.c.) was added dropwise with stirring to magnesium (18 g., 2·2 atomic equivalents) in a nitrogen atmosphere, the reaction being initially controlled by ice-cooling. The complete mixture was boiled under reflux for 3 hr., cooled, and filtered directly on to crushed solid carbon dioxide (1 kg.), leaving unchanged magnesium (7·8 g., 0·9 atomic equivalent). The mixed product was allowed to attain room temperature, and was then hydrolysed with dilute sulphuric acid and

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[6] Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187.

thoroughly extracted with ether. The united ethereal extracts were extracted with 10% aqueous sodium hydroxide.

Evaporation of the ethereal solution gave a brown liquid, from which steam-distillation gave 2 : 6-dimethyldiphenylene (II; R = Me) as a yellow distillate which solidified, and from aqueous ethanol furnished pale yellow crystals (0·12 g., 0·4%), m. p. 138—140° (lit.,[3] 139—141°) (Found: C, 93·1; H, 6·6. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%). A benzene or toluene solution when mixed with methanolic picric acid deposited a red crystalline picrate, too unstable for isolation.

The brown solid residue from the distillation, when twice recrystallised from ethanol, gave bright yellow 2 : 7-dimethylfluorenone (III; R = Me), m. p. 142—145° (Found: C, 86·4; H, 6·1. Calc. for $C_{15}H_{12}O$: C, 86·5; H, 5·8%), and after a third recrystallisation (0·3 g., 0·9%) m. p. 150—151° (lit.,[7] m. p. 157°) (Found: C, 86·7; H, 6·2%): it gave a red 2 : 4-*dinitrophenylhydrazone*, m. p. 259—260° (decomp.) (from dioxan) (Found: C, 65·0; H, 4·4; N, 14·5. $C_{21}H_{16}O_4N_4$ requires C, 64·9; H, 4·2; N, 14·4%). The nuclear magnetic resonance spectrum of the fluorenone (III; R = Me) gave strong evidence for a symmetrical distribution of the methyl groups. The only other symmetric isomer which could have been formed is 3 : 6-dimethylfluorenone, which has m. p. 118°.[8]

The sodium hydroxide extract gave, on acidification, a gum which could not be readily recrystallised. It was therefore treated in ethereal solution with an excess of diazomethane; the mixture of methyl esters on distillation gave the fractions, (1) b. p. 100—112°/15 mm. (2·9 g.), (2) b. p. 112—175°/15 mm. (8·7 g.), and (3) 97—215°/0·2 mm. (8·0 g.). Fraction (1) was methyl *p*-toluate (Found: C, 72·1; H, 6·9. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%); hydrolysis gave *p*-toluic acid, m. p. 177—179° (lit.,[9] 179°), characterised as its anilide, m. p. 144—145° (lit.,[10] 144—145°) (Found: C, 79·3; H, 6·6; N, 6·8. Calc. for $C_{14}H_{13}ON$: C, 79·6; H, 6·1; N, 6·6%), with unchanged mixed m. p.s for each compound.

Fraction (2) on redistillation gave (*a*) a major fraction, b. p. 152—159°/15 mm. (7·1 g.), and (*b*) a very small higher fraction, b. p. 95—195°/0·1 mm. Fraction (*a*) was methyl 2-bromo-4-methylbenzoate (Found: C, 46·8; H, 4·2. Calc. for $C_9H_9O_2Br$: C, 47·2; H, 4·0%): aqueous alkaline hydrolysis furnished the acid, from which traces of *p*-toluic acid were removed by steam-distillation, but repeated recrystallisation from light petroleum (b. p. 60—80°) was required to obtain the pure 2-bromo-4-methylbenzoic acid, m. p. 138·5—139·5° (lit.,[11] 140°) (Found: C, 44·6; H, 3·2. Calc. for $C_8H_7O_2Br$: C, 44·7; H, 3·3%). Fraction (*b*) on distillation gave a fraction, b. p. 110—156°/0·5 mm., which on hydrolysis furnished undoubtedly 2-iodo-5-methylbenzoic acid, m. p. 126·5—129° after repeated recrystallisation as before from light petroleum—it was still contaminated with the previous acid (Found: C, 37·4; H, 2·9. Calc. for $C_8H_7O_2I$: C, 36·7; H, 2·7%).

Reaction with Lithium.—A solution of 3-bromo-4-iodotoluene (15·4 g.) in ether (80 c.c.) was added dropwise to a stirred mixture of fine lithium foil (1·7 g., 4·6 atomic equivalents) in ether (80 c.c.) under nitrogen, a moderate reaction occurring after *ca.* 15 min. Benzene (100 c.c.) was then added and the mixture stirred at room temperature for 3 hr., cooled, and filtered on to crushed ice: unchanged lithium (0·9 g., 2·4 equivalents) was collected. The organic layer was separated, and on removal of the ether afforded a brown oil consisting of 4 : 4′-dimethyldiphenyl and 2 : 6 : 11-trimethyltriphenylene (IV; R = Me). A reasonably sharp separation of these components by distillation was not possible, because although the diphenyl began to distil first, co-distillation of the two components steadily increased. An early and incomplete fraction of 4 : 4′-dimethyldiphenyl was collected at 80—140°/0·3 mm., and formed a semi-crystalline mass: the crystals, when sublimed or recrystallised from ethanol gave the pure compound (Found: C, 91·9; H, 8·0. Calc. for $C_{14}H_{14}$: C, 92·25; H, 7·7%), m. p. 118·5—120°, unaffected by admixture with an authentic sample (lit.,[12] 122°).

The residue, in ether, was passed through an alumina column, the ether then removed, and the residue extracted with boiling ethanol. A benzene solution of the final residue, when treated with ethanolic picric acid, deposited 2 : 6 : 11-*trimethyltriphenylene picrate*, which, on

[7] Bergmann, Berthier, Hirschberg, Loewenthal, Pullman, and Pullman, *Bull. Soc. chim. France*, 1951, 669.

[8] Chardonnens and Würmli, *Helv. Chim. Acta*, 1946, **29**, 922.

[9] Gattermann, *Annalen*, 1888, **244**, 51.

[10] Hantzsch, *Ber.*, 1891, **24**, 58.

[11] Claus, *J. prakt. Chem.*, 1889, **39**, 486.

[12] Ullmann and Meyer, *Annalen*, 1904, **332**, 44.

crystallisation from ethanol containing a small proportion of benzene, gave orange crystals (0·95 g., 11%), m. p. 191—192° (decomp.) (Found: C, 65·3; H, 4·3; N, 8·3. $C_{21}H_{18},C_6H_3O_7N_3$ requires C, 64·9; H, 4·2; N, 8·4%). The picrate when added to boiling water deposited very pale brown 2 : 6 : 11-*trimethyltriphenylene*, m. p. 128·5—129·5° [from light petroleum (b. p. 60—80°)] (Found: C, 93·4; H, 6·8%; *M*, in freezing benzene, 268. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%; *M*, 270·4). It deposited a yellow 1 : 3 : 5-trinitrobenzene addition product, m. p. 219—222° (decomp.), from benzene solution.

The experimental data regarding 2 : 6 : 10-trimethyltriphenylene were omitted by an oversight in ref. 4, but Dr. C. C. Barker states in a personal communication: " Self-condensation of 4-methyl*cyclo*hexanone gave the sparingly soluble dodecahydro-2 : 6 : 10-trimethyltriphenylene, m. p. 195°, and this compound was readily dehydrogenated with palladium–charcoal to give 2 : 6 : 10-*trimethyltriphenylene*, m. p. 190° (Found: C, 93·3; H, 6·7. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%)." This hydrocarbon gave an orange *picrate*, m. p. 221—222°, prepared and recrystallised as the former picrate (Found: C, 64·6; H, 4·3; N, 8·5. $C_{21}H_{18},C_6H_3O_7N_3$ requires C, 64·9; H, 4·2; N, 8·4%).

(A) $\lambda_{max.}$ (mμ)	254	263	278	289	333	340	349
$\log_{10}\varepsilon$	4·95	5·20	4·32	4·25	2·93	2·72	2·81
(B) $\lambda_{max.}$ (mμ)	249	258	273	285	315	327	333
$\log_{10}\varepsilon$	4·95	5·2	4·3	4·25	3·2	3·0	3·15
(C) $\lambda_{max.}$ (mμ)	253·5	262·5	277·5	288·5			
$\log_{10}\varepsilon$	4·94	5·18	4·30	4·23			

The annexed Table gives the ultraviolet absorption spectra, in 95% ethanol, of (A) 2 : 6 : 11-trimethyltriphenylene, (B) triphenylene, for which Heaney, Mann, and Millar's values [1] are given, (C) 2 : 6 : 10-trimethyltriphenylene, these being the only values given by Barker *et al.*[4]

In a similar experiment, the reaction mixture was carboxylated, but no acidic products were isolated; the crude neutral components were not examined in detail, but in solution gave 2 : 7-dimethylfluorenone 2 : 4-dinitrophenylhydrazone (1·4%), m. p. and mixed m. p. 256—257° (from dioxan).

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