781. *The Reaction of* o-*Bromoiodobenzene with Magnesium and Lithium.*

By Harry Heaney, Frederick G. Mann, and Ian T. Millar.

o-Bromoiodobenzene with magnesium (one equivalent) forms mainly o-bromophenylmagnesium iodide, but with two equivalents forms, in addition, o-phenylenedimagnesium bromide iodide and diphenylene. These Grignard reagents were identified by carboxylation, and by interaction with iododimethylarsine, which gave the corresponding dimethylarsino-derivatives. In addition, three tertiary arsines, 2-diphenylyldimethylarsine, 2 : 2'-diphenylylenebisdimethylarsine, and o-terphenyl-2 : 2''-ylenebisdimethylarsine, were formed in small amounts.

o-Bromoiodobenzene with lithium gives diphenyl and triphenylene, and this affords the best synthetic route to triphenylene.

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

We have recently described the action of magnesium, lithium, and *n*-butyl-lithium on *o*-di-iodobenzene, and shown that the major products are diphenyl, tri-*o*-phenylene (I), and 2 : 2'-di-(*o*-lithiophenyl)diphenyl (II) respectively.[1] We have described also the action of magnesium on *o*-dibromobenzene to form *o*-bromophenylmagnesium bromide (III) in 26—30% yield.[2] The bromide (III) has been prepared also by Wittig and Pohmer,[3] who adduce evidence that it readily loses magnesium bromide to form benzyne (IV) as a highly reactive intermediate product, readily undergoing addition reactions.

In view of these results, we investigated the action of magnesium and of lithium on *o*-bromoiodobenzene. Magnesium (one equivalent) reacts with ethereal *o*-bromoiodobenzene chiefly to form *o*-bromophenylmagnesium iodide, the presence of which is shown

[1] Heaney, Mann, and Millar, *J.*, 1956, 1.
[2] *Idem, J.*, 1956, 4692.
[3] Wittig and Pohmer, *Chem. Ber.*, 1956, **89**, 1334.

(*a*) by hydrolysis, which gives bromobenzene in 34% yield, and (*b*) by reaction with iodo-dimethylarsine, Me_2AsI, which affords o-bromophenyldimethylarsine in 52% yield. (The value of the iodoarsine for detection and estimation of Grignard reagents has been described earlier.[1]) o-Bromophenyl derivatives prepared in this way are apt to be contaminated by traces of the o-iodophenyl analogues, presumably from o-iodophenylmagnesium bromide formed simultaneously with the isomeric Grignard reagent.

(I)   (II)   (III)
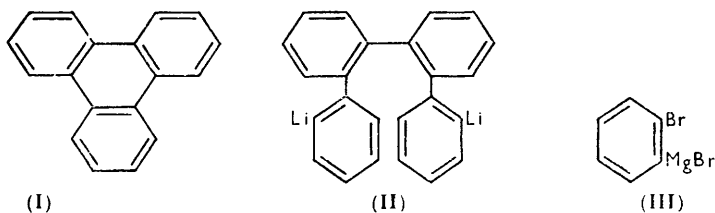
When, however, ethereal o-bromoiodobenzene reacts at 0° with an excess (2·2 equivalents) of magnesium, the chief products are (*a*) o-bromophenylmagnesium iodide (V), (*b*) o-phenylenedimagnesium bromide iodide, o-$C_6H_4(MgBr)\cdot MgI$, and (*c*) diphenylene (VI) in 3·5% yield based on the dihalide.

The presence of o-bromophenylmagnesium iodide was shown by the iodoarsine, which again afforded o-bromophenyldimethylarsine, and by carboxylation, which furnished o-bromobenzoic acid (26% yield after purification). The presence of the di-Grignard compound was shown by reaction with the iodoarsine, which also gave o-phenylenebisdi-methylarsine, o-$C_6H_4(AsMe_2)_2$, in 8% yield, and by the carboxylation, which also furnished benzoic acid (17% yield after purification). The latter probably arises by combination of carbon dioxide with one magnesium halide unit in the di-Grignard compound, which is rendered inactive then by internal chelation;[1] consequently hydrolysis subsequently removes the second unit, forming benzoic acid (cf. p. 3932). Carboxylation also gave fluorenone (VII) in 2·5% yield after distillation and crystallisation.

The use of iododimethylarsine gave, in addition, in small yield a number of other tertiary arsines, which are discussed below.
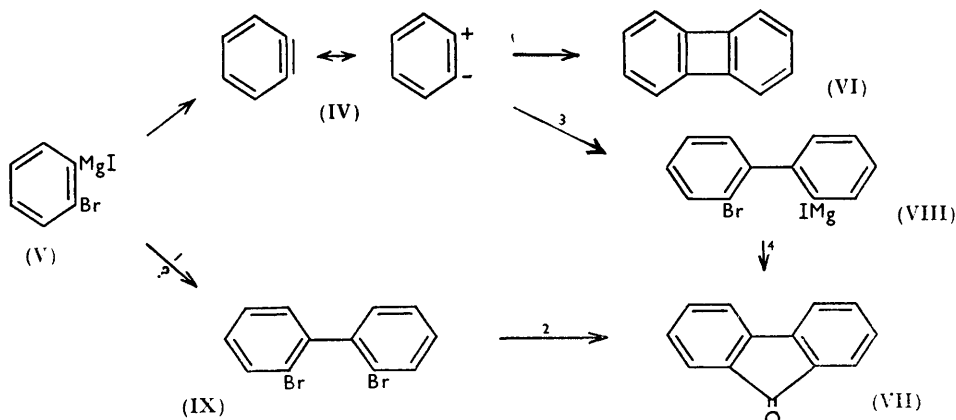
Reagents: 1, C_6H_4BrI; 2, (*a*) 2Mg, (*b*) CO_2; 3, $Br\cdot C_6H_4\cdot MgI$; 4, (*a*) Mg, (*b*) CO_2.

The mechanism whereby diphenylene is formed in the above reactions is of considerable interest. It is possible that the magnesium brings about a Fittig reaction to a small extent with o-bromoiodobenzene to form 2 : 2′-dibromodiphenyl (IX), which then undergoes an intramolecular Fittig reaction to form diphenylene. It is highly improbable, however, that 2 : 2′-dibromodiphenyl is an intermediate, for Rapson, Shuttleworth, and

van Niekerk[4] have shown that this compound in ether reacts very incompletely with magnesium even on prolonged heating, and that the Grignard compound so formed, when heated with cupric chloride (Krizewski–Turner reaction), yielded diphenylene (4% based on the magnesium reacted), tetraphenylene (16%), and diphenyl. The yields of these hydrocarbons, calculated on the total dihalide employed, are of course exceedingly small.

Our reaction occurred in the absence of an added catalyst, and neither 2 : 2'-dibromodiphenyl nor tetraphenylene could be detected in the products.

It is more probable that the *o*-bromophenylmagnesium iodide (V) lost magnesium halide to form benzyne (IV), which could readily dimerise to diphenylene (VI), as Lüttringhaus and Schubert have suggested.[5] The highly reactive benzyne (IV) is probably a transient intermediate in the formation of fluorenone (VII), for it could react also with the ionised *o*-bromophenylmagnesium iodide (V) to form 2'-bromo-2-diphenylylmagnesium iodide (VIII) which by further reaction with magnesium followed by carboxylation would furnish fluorenone (VII). These conversions, from (V) ⟶ (IV) ⟶ (VIII), closely follow those suggested by Gilman and Gorsich[6] for *o*-bromophenyl-lithium, analogous to (V). The alternative route, whereby the iodide (V) reacts with *o*-bromoiodobenzene to form 2 : 2'-dibromodiphenyl (IX), which then similarly gives fluorenone, is highly improbable for the reasons stated above. Both routes involve the formation of 2 : 2'-diphenylylenedimagnesium dihalide, which, in spite of its apparent low solubility in ether and consequent low reactivity,[1] has the two ·MgX groups in positions which would favour strongly cyclic ketone formation after initial reaction with one equivalent of carbon dioxide.

In these experiments, carboxylation of the reaction product was preferred to direct hydrolysis, which would probably have given diphenyl, which is difficult to separate from diphenylene.

The reaction mixture produced by the interaction of *o*-bromoiodobenzene and magnesium (3 equivalents) at 0°, when treated with iododimethylarsine, gave rise to dimethylphenylarsine, $PhAsMe_2$, in 7% yield, and also to small quantities of three other tertiary arsines, 2-diphenylyldimethylarsine (X), 2 : 2'-diphenylylenebisdimethylarsine (XI) and *o*-terphenyl-2 : 2''-ylenebisdimethylarsine (XII).

The arsine (X) was formed also when *o*-di-iodobenzene was treated similarly,[1] and it was suggested that 2 : 2'-di-iododiphenyl was initially formed and then gave rise to a di-Grignard reagent of type (XIII), which in turn with iododimethylarsine gave an internal chelated compound (XIV), the latter on hydrolysis furnishing the arsine (X).

It should be noted, however, that, if the bonds to the arsenic atom in the cyclic compound (XIV) are tetrahedrally disposed, a scale model giving maximum relief of strain by rotating the planes of the *o*-phenylene groups to an angle of *ca.* 35° to one another, shows that the C–Mg–As angle is *ca.* 65°, whereas if the magnesium in addition remains co-ordinated to a molecule of ether, and thus has sp^3 tetrahedral configuration, this angle should be *ca.* 110°.

An alternative route to the arsine (X) is possible. Weldon and Wilson[7] have suggested that *p*-phenylenebis(magnesium bromide), $C_6H_4(MgBr)_2$, as a result of the powerful inductive effect of the bromomagnesium groups, may undergo partial dissociation in ethereal solution to give ·MgBr and ·C_6H_4·MgBr radicals, and that the latter abstract hydrogen from the solvent to give phenylmagnesium bromide. It is, therefore, not improbable that the di-Grignard compound (XIII), formed from the mono-Grignard compound (VIII), similarly gives some proportion of the radical (XV), which then affords 2-diphenylylmagnesium halide (XVI), reaction of which with iododimethylarsine gives the arsine (X).

[4] Rapson, Shuttleworth, and van Niekerk, *J.*, 1943, 326.
[5] Lüttringhaus and Schubert, *Naturwiss.*, 1955, **42**, 17.
[6] Gilman and Gorsich, *J. Amer. Chem. Soc.*, 1956, **78**, 2217.
[7] Weldon and Wilson, *J.*, 1946, 235.

Furthermore, if *o*-phenylenedimagnesium bromide iodide, $C_6H_4(MgBr)\cdot MgI$, underwent a similar free-radical dissociation, it would explain the formation of dimethylphenylarsine on treatment with iododimethylarsine. The formation of benzoic acid on carboxylation

Reagent: 5, Me₂AsI.
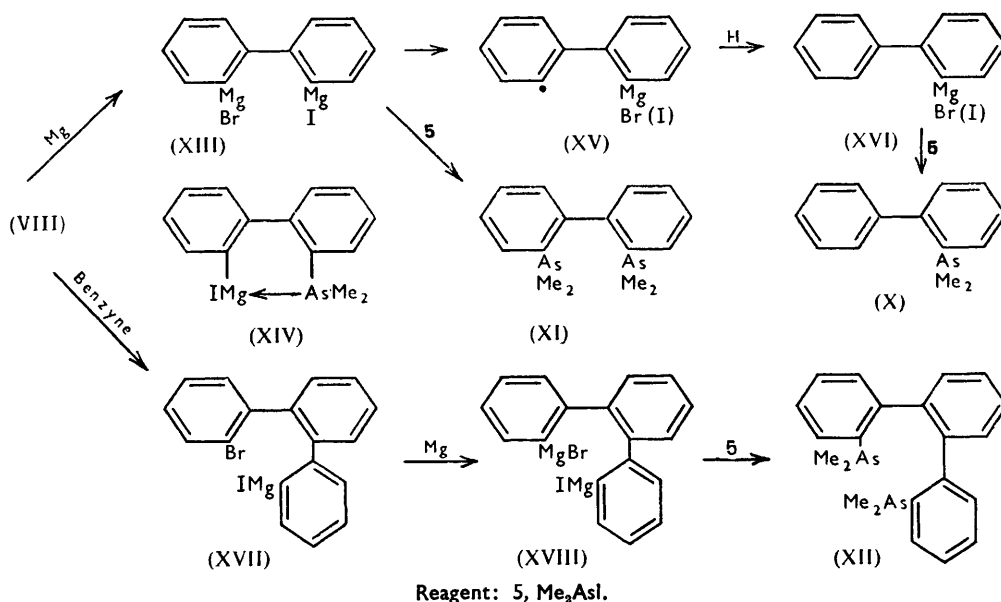
also is explicable on the basis of this dissociation, but the *complete* absence of phthalic acid, in contrast to the formation of some *o*-phenylenebisdimethylarsine with iododimethylarsine, strongly indicates the formation of a chelated complex as previously suggested,[1] in this carboxylation reaction.

The diarsine (XI) could clearly arise from direct reaction of a small proportion of the di-Grignard compound (XIII) with iododimethylarsine.

There are a number of possible routes whereby the diarsine (XII) could arise, and very little evidence regarding the nature of the intermediate compounds. We suggest that the mono-Grignard compound (VIII) reacts also to some extent with benzyne to give the Grignard reagent (XVII), which by further reaction with magnesium to give the compound (XVIII), followed by interaction with iododimethylarsine, would yield the diarsine (XII). An internal Fittig reaction occurring in the Grignard reagent (XVII) would account for the trace of triphenylene detected when the initial reaction mixture was carboxylated instead of being treated with the iodoarsine.

In assessing the probability of the above reaction routes, it must be emphasised that the three tertiary arsines (X), (XI), and (XII) must result from a series of competing reactions, all of which only occur to a very small extent.

The diarsines (XI) and (XII) were identified by analysis and molecular-weight determinations, by preparation of dimethiodides, and in particular by formation of cyclic derivatives. Thus the diarsine (XI) readily underwent diquaternisation with ethylene dibromide to give the tricyclic diarsonium dibromide (XIX), and the diarsine (XII) with potassium palladobromide furnished the cyclic covalent palladium derivative (XX).

The Grignard solution from the interaction of *o*-bromoiodobenzene and magnesium (2 equivalents) at 0° was also treated with chlorodiethylphosphine, Et_2PCl. After hydrolysis, the crude product on distillation gave the fractions (*a*) crude tetraethyldiphosphine $Et_2P\cdot PEt_2$, (*b*) *o*-bromophenyldiethylphosphine contaminated with the *o*-iodo-analogue, (*c*) diphenylene, and (*d*) a number of smaller, higher, indeterminate fractions

which gave no crystalline derivatives. In view of the results of Hart and Mann,[8] this part of the investigation was not pursued further.

o-Bromoiodobenzene, when slowly added in ether to fine lithium foil, underwent a vigorous reaction: the temperature was at once reduced to *ca.* 10° until this stage was complete, and the mixture was then diluted with benzene and boiled. After hydrolysis, the
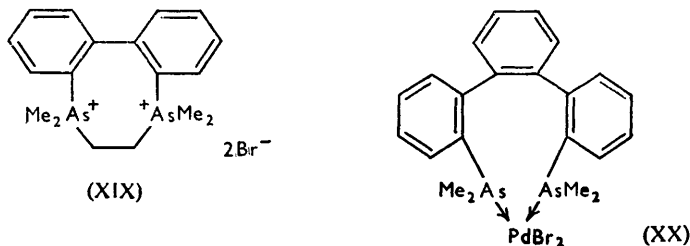
organic layer yielded diphenyl (12%) and triphenylene (I) (55%). When in a similar experiment the mixture was carboxylated before hydrolysis, the acidic fraction gave an unidentified oil, and the organic layer furnished diphenyl (2·8%) and triphenylene (48%). The formation of triphenylene in 55% yield provides the best known synthesis of this hydrocarbon.

It was suggested earlier[1] that the production of triphenylene in 29% yield by the action of lithium on *o*-di-iodobenzene arose from the intermediate formation of 2 : 2'-di-iododiphenyl. An analogous route for the production of triphenylene from *o*-bromoiodobenzene is, however, improbable. The first product of the action of lithium on *o*-bromoiodobenzene would undoubtedly be *o*-bromophenyl-lithium (XXI), which could react with the bromoiodobenzene to give 2 : 2'-dibromodiphenyl. It is known, however, that 2 : 2'-dibromodiphenyl, when treated with phenyl-lithium (a more forcing reagent than metallic lithium for replacement of halogen), gives triphenylene in only 8% yield.[9]

An alternative reaction scheme appears more probable. It is known that *o*-bromophenyl-lithium (XXI) is highly reactive,[6] and it readily loses lithium bromide to give in good yield products apparently derived from benzyne, such as the adduct of benzyne with furan. In our experiments, the highly reactive benzyne thus formed could unite with another molecule of *o*-bromophenyl-lithium (XXI) to give 2'-bromo-2-diphenylyl-lithium (XXII), which by further addition to benzyne could give the *o*-terphenyl derivative (XXIII) and thus, by loss of lithium bromide, the triphenylene (I). It may be objected
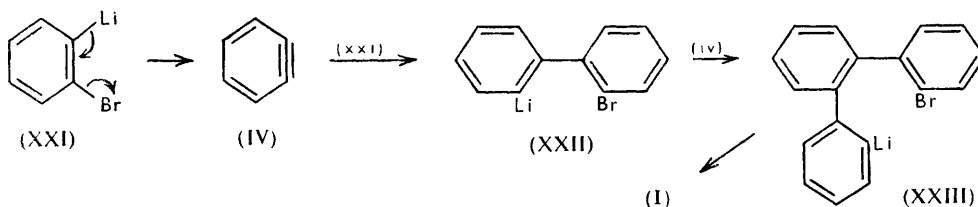
that the production of triphenylene in high yield is being postulated from the lithio-derivative (XXII), whereas in similar circumstances the analogous magnesium iodide derivative (VIII) gave only a trace of this hydrocarbon. The chemical properties of lithio-derivatives are frequently different from those of the corresponding Grignard derivatives, owing (apart from other factors) to differences of polarity of the carbon–metal bond, and to the facts that the ·MgX unit remains almost certainly co-ordinated to the ether, whereas the lithium

[8] Hart and Mann, following paper.
[9] Barton and McOmie, *J.*, 1956, 796.

is free from such co-ordination: consequently a difference in reactivity between the compounds (XXII) and (VIII), particularly to reagents such as benzyne, is not unexpected.

The above experiments, combined with those recorded earlier,[1] show clearly that the reaction of magnesium or of lithium on o-bromoiodobenzene or o-di-iodobenzene, followed by interaction with a chloro-arsine or -phosphine, does not afford a practicable route for the synthesis of o-phenylenebis-arsines or -phosphines of type $C_6H_4(AsR_2)_2$ and $C_6H_4(PR_2)_2$. The effect of nuclear methyl groups is discussed in the following paper.[8]

Wittig and Bickelhaupt,[10] in a recent brief preliminary note, have claimed that lithium reacts with di-(o-phenylene)dimercury to give o-dilithiobenzene in 80% yield, the identity of the dilithium compound being confirmed by carboxylation, which furnished phthalic acid in 70% yield. This dilithium compound should provide a new synthetic route to the o-phenylenebis-arsines and -phosphines.

We are investigating the chemical properties of cyclic diarsonium dihalides such as (XIX) and similar salts obtained with other alkylene dihalides, and the analogous salts prepared from the diarsine (XII).

EXPERIMENTAL

Compounds are colourless unless otherwise described. All reactions with magnesium and lithium were carried out under nitrogen. Carboxylation was carried out by pouring the reaction mixture on a slurry of solid carbon dioxide and ether, which was allowed slowly to evaporate. M. p.s were determined on a Kofler stage, except where " I.T." indicates immersion in a previously heated block.

Interaction of o-*Bromoiodobenzene and Magnesium* (*One Equivalent*).—(A) A solution of o-bromoiodobenzene (17·4 g.) in ether (50 c.c.) was added dropwise to a stirred mixture of magnesium (1·65 g., 1·0 atom-equiv.) and ether (10 c.c.), which reacted readily, external cooling being required. The mixture was stirred at room temperature for 1 hr. before the clear yellow solution was hydrolysed with aqueous ammonium chloride. The organic layer, when dried (Na₂SO₄) and distilled, gave bromobenzene, b. p. 149—153°/753 mm. (3·3 g., 34%), and o-bromo-iodobenzene, b. p. 117—119°/13 mm. (5·3 g., 29%).

In a similar experiment the product was carboxylated, but the acidic fraction gave an oil which did not crystallise and was not investigated further. The o-bromophenylmagnesium iodide was therefore characterised by the use of iododimethylarsine in the following experiment.

(B) A reaction mixture, similarly prepared from o-bromoiodobenzene (4·50 g.) in ether (20 c.c.) and magnesium (0·4 g., 1·0 atom-equiv.) in ether (20 c.c.), was stirred at room temperature for 1 hr., then cooled in ice-water, and a solution of iododimethylarsine (3·72 g., 1 mol.) in benzene (20 c.c.) added. The mixture was stirred at room temperature for 30 min. and then boiled under reflux for 1 hr. before finally being cooled in ice and hydrolysed with saturated aqueous ammonium chloride.

The organic layer when dried (Na₂SO₄) and distilled in nitrogen gave iododimethylarsine, b. p. 50—70°/13 mm. (0·8 g., 21·5% recovery), and o-bromophenyldimethylarsine, b. p. 125—135°/13 mm. (2·2 g., 52%). The latter fraction when treated with an excess of methyl iodide deposited o-bromophenyltrimethylarsonium iodide, which, once recrystallised from methanol, decomposed without melting at ca. 240° (2·8 g., 45%). Treatment of the iodide with methanolic sodium picrate gave the corresponding methopicrate, m. p. and mixed m. p. 181—182°, after crystallisation from methanol (lit.,[2] m. p. 181—182°).

In an experiment in which the o-bromophenylmagnesium iodide was prepared at 0°, followed by treatment with iododimethylarsine as above, the yield of o-bromophenyltrimethylarsonium iodide fell to 34·5%.

Interaction with Magnesium (2—3 *Equivalents*).—(A) A solution of o-bromoiodobenzene (14·15 g.) in ether (100 c.c.) was added dropwise to a stirred mixture of magnesium (2·67 g., 2·2 equivs.) and ether (75 c.c.). When the reaction had started, the mixture was cooled in ice-water and the remaining dihalide added during 1 hr. Benzene (75 c.c.) was added and the mixture stirred at 0° for a further 2 hr., and then at room temperature for 2 hr., and finally boiled under reflux for 1 hr., and cooled. The mixture was decanted from excess of magnesium (0·65 g., 24% recovery) and carboxylated.

The product was hydrolysed with dilute aqueous hydrochloric acid, basified, and extracted

¹⁰ Wittig and Bickelhaupt, *Angew. Chem.*, 1957, **69**, 93.

with aqueous sodium hydroxide, which when acidified deposited a crude semicrystalline acid (4·8 g.). Fractional sublimation gave first, at 95—100°/13 mm., a crude acid, m. p. 102—105°, which when resublimed afforded benzoic acid, m. p. 115—117° (1·05 g., 17%), increased to 118—119° (mixed and unmixed) (0·81 g., 14%) by recrystallisation from light petroleum (b. p. 80—100°). Raising the temperature to 130—135°/13 mm. then gave a sublimate of *o*-bromobenzoic acid, m. p. 143—145° (2·8 g., 26%), which when recrystallised twice from light petroleum (b. p. 80—100°) had m. p. and mixed m. p. 150°.

The neutral ethereal solution was evaporated and the residue distilled in steam. The crude crystalline diphenylene (VI) which distilled had m. p. 98—106°, increased to 107—109° by recrystallisation from methanol, and to 110·5—111·5° by sublimation at 100°/13 mm. (Found: C, 94·5; H, 5·7. Calc. for $C_{12}H_8$: C, 94·7; H, 5·3%) (lit.,[11] m. p. 110—111°). The identity of this hydrocarbon was confirmed by the formation of the scarlet picrate, m. p. 122—123°, from ethanolic picric acid (lit.,[4] m. p. 122—123°). The ultraviolet absorption spectrum in ethanol was in good accord with that reported by Baker, Boarland, and McOmie:[12]

Observed:

$\lambda_{max.}$ (mμ)	240	248	327	330	339	343	348	358	$\lambda_{min.}$ (mμ)	280	352
$\log_{10} \varepsilon$	4·77	5·05	3·45	3·46	3·79	3·73	3·54	3·94	$\log_{10} \varepsilon$	2·34	3·51

Reported:

$\lambda_{max.}$ (mμ)	239	248	326	330	339	343	348	358	$\lambda_{min.}$ (mμ)	280 *	352 *
$\log_{10} \varepsilon$	4·77	5·05	3·47	3·49	3·79	3·76	3·58	3·97	$\log_{10} \varepsilon$	2·3	3·5

* Exact values not given: these are taken from the graph given by Baker *et al.*[12]

A further quantity of diphenylene (0·013 g.) (total, 0·134 g., 3·5% based on the amount of dihalogeno-compound employed) was obtained by sublimation of the residue from the recrystallisation liquors, after removal of solvent and a trace of *o*-bromoiodobenzene by distillation.

The residue from this last sublimation, on short-path distillation at 145°/0·1 mm., gave fluorenone (VII), yellow crystals, m. p. 79—80° (from aqueous ethanol) (Found: C, 86·5; H, 4·3. Calc. for $C_{13}H_8O$: C, 86·75; H, 4·5%) (yield of purified product, 0·118 g., 2·5%). It was further identified by means of its ultraviolet spectrum, its 2 : 4-dinitrophenylhydrazone, m. p. 283°, and *p*-nitrophenylhydrazone, m. p. 268°.

The neutral residue, non-volatile in steam, on sublimation at 175—180°/0·1 mm. gave triphenylene (0·001 g.), m. p. and mixed m. p., 191—192°. A trace of dark solid (*ca.* 0·005 g.) remained, representing the whole of the non-acidic product not identified as described above.

(*B*) A solution of *o*-bromoiodobenzene (56·6 g.) in ether (200 c.c.) was added to magnesium (14·58 g., 3 equivs.) in ether (100 c.c.) as described in Expt. (*A*). Benzene (100 c.c.) was then added and the mixture stirred at 0° for a further 2 hr. before addition of iododimethylarsine (92·8 g., 4 mols.) in benzene (100 c.c.) during 1 hr. The mixture was stirred at room temperature for 1 hr., and then boiled under reflux for 1 hr. before being cooled in ice and hydrolysed with saturated aqueous ammonium chloride.

The organic layer when dried and distilled under nitrogen gave the following fractions: (i) Iododimethylarsine, b. p. 50—70°/13 mm. (11·4 g., 12%); (ii) dimethylphenylarsine, b. p. 95—110°/13 mm. (3·4 g.), which, treated with an excess of methyl iodide, deposited crystalline trimethylphenylarsonium iodide (4·4 g., 6·8%), m. p. and mixed m. p. 243—244° (I.T. 220°) (from ethanol) (lit.,[13] m. p. 244°). Treatment of this methiodide in ethanol with iodoform also in ethanol gave the stable iodoform adduct, m. p. 140—141°, from ethanol (Found: C, 16·1; H, 1·9. Calc. for $C_9H_{14}AsI,CHI_3$: C, 16·5; H, 2·2%) (lit.,[14] m. p. 143—145°).

(iii) *o*-Bromophenyldimethylarsine, b. p. 132—138°/13 mm. (5·4 g.), when treated with an excess of methyl iodide deposited crystalline *o*-bromophenyltrimethylarsonium iodide, which decomposed at *ca.* 240° (yield of purified salt, 8·1 g., 10%). The methiodide as before gave the yellow methopicrate, m. p. and mixed m. p. 181—182°, from methanol. An ethanolic solution of the arsine when boiled with aqueous-ethanolic potassium palladobromide deposited orange *dibromobis-*(*o-bromophenyldimethylarsine*)*palladium*, m. p. 183—185° when thrice recrystallised from acetone (Found: C, 24·5; H, 2·8. $C_{16}H_{20}Br_4As_2Pd$ requires C, 24·3; H, 2·5%).

[11] Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187.
[12] Baker, Boarland, and McOmie, *J.*, 1954, 1476.
[13] Michaelis and Link, *Annalen*, 1881, **207**, 205.
[14] Steinkopf and Schwen, *Ber.*, 1921, **54**, 2969.

(iv) A fraction, b. p. 145—180°/13 mm. (15·9 g.), which on refractionation gave: (*a*) o-Bromophenyldimethylarsine, b. p. 76—83°/0·2 mm. (6·3 g., 14%) (total yield, 24%), identified as before.

(*b*) o-Phenylenebisdimethylarsine, b. p. 90—96°/0·2 mm. (4·1 g., 8%), identified by the following derivatives:

Treatment of the diarsine with methyl iodide at room temperature gave o-phenylenebisdimethylarsine monomethiodide, m. p. 224—226° after crystallisation from ethanol (lit.,[15] m. p. 226—228°).

Treatment of the base with ethylene dibromide (1 mol.) at 100° for 3 hr. gave *AsAsAs'As'*-tetramethylethylene-o-phenylenediarsonium dibromide, m. p. 255° (from methanol) (lit.,[16] m. p. 255°). An aqueous solution of this dibromide, treated with aqueous sodium picrate, deposited the corresponding dipicrate, yellow crystals, m. p. 234—235°, from water (lit.,[16] m. p. 234—235°).

The diarsine (0·157 g.) in ethanol when treated with potassium palladobromide (0·281 g., 1 mol.) deposited a chocolate-brown almost insoluble compound, probably the salt $[(C_6H_4As_2Me_4)_2Pd][PdBr_4]$ which when heated with a mixture of ethanol (20 c.c.) and hydrobromic acid (5 c.c.; *d* 1·50) under reflux gave orange dibromo-o-*phenylenebis(dimethylarsine)*-*palladium*, m. p. 310—312° (decomp.) (Found: C, 21·8; H, 3·1. $C_{10}H_{16}Br_2As_2Pd$ requires C, 21·8; H, 2·9%).

(*c*) 2-Diphenylyldimethylarsine (X), b. p. 106—114°/0·2 mm. (4·2 g., 8·5%). A portion of this arsine, when treated with an excess of methyl iodide, deposited crystals of 2-diphenylyltrimethylarsonium iodide, which when recrystallised from methanol had m. p. and mixed m. p. 259—260°. This iodide, treated with sodium picrate, both in methanol, deposited yellow 2-*diphenylyltrimethylarsonium picrate*, m. p. 138—139° (from methanol or ethanol) (Found: C, 49·8; H, 3·8; N, 8·5. $C_{21}H_{20}O_7N_3As$ requires C, 49·5; H, 3·55; N, 8·65%).

2-Diphenylyldimethylarsine in hot ethanol, when boiled with aqueous-ethanolic potassium palladobromide, deposited *dibromobis(2-diphenylyldimethylarsine)palladium*, orange crystals, m. p. 223—224° from acetone (Found: C, 42·7; H, 4·1. $C_{28}H_{30}Br_2As_2Pd$ requires C, 42·95; H, 3·9%).

(*d*) A fraction, b. p. 116—128°/0·2 mm. (0·6 g.). A portion, when heated with an excess of methyl iodide, deposited the crystalline 2 : 2'-*diphenylylenebis(trimethylarsonium iodide)*, m. p. 286—288° after four crystallisations from methanol (Found: C, 33·8; H, 3·8. $C_{18}H_{26}I_2As_2$ requires C, 33·5; H, 4·0%).

A second portion, treated with methyl bromide at room temperature for 6 hr., gave the highly deliquescent 2 : 2'-*diphenylylenebis(trimethylarsonium bromide) dihydrate*, m. p. 292—294° after crystallisation from ethanol–light petroleum (b. p. 60—80°) (Found: C, 37·1; H, 5·6. $C_{18}H_{26}Br_2As_2,2H_2O$ requires C, 36·8; H, 5·2%). This salt, treated in ethanol with sodium iodide, deposited the above dimethiodide, m. p. and mixed m. p. 286—288°.

The 2 : 2'-diphenylylenebis(trimethylarsonium iodide), when heated at 0·05 mm. in an air bath at 260°, decomposed smoothly to give 2 : 2'-*diphenylylenebisdimethylarsine* (XI) as a colourless viscous distillate, which, after redistillation in nitrogen (b. p. 110°/0·05 mm.), formed crystals, m. p. 46—46·5° (Found: C, 52·95; H, 5·4. $C_{16}H_{20}As_2$ requires C, 53·05; H, 5·6%).

An ethanolic solution of the diarsine when boiled with aqueous ethanolic potassium palladobromide deposited *dibromo-(2 : 2'-diphenylylenebisdimethylarsine)palladium*, highly insoluble orange crystals which, after being washed with water and ethanol, decomposed at *ca.* 270° (Found: C, 30·9; H, 3·7. $C_{16}H_{20}Br_2As_2Pd$ requires C, 30·55; H, 3·2%).

A portion of the diarsine (XI) was heated with ethylene dibromide (1 mol.) in a sealed tube at 100° for 6 hr. The crystalline product, thrice recrystallised from ethanol–light petroleum (b. p. 60—80°), gave AsAsAs'As'-*tetramethyl-AsAs'-ethylene-AsAs'-2 : 2'-diphenylylenediarsonium dibromide* (XIX), m. p. 211—213° (decomp.) (Found: C, 37·35; H, 5·1. $C_{18}H_{24}Br_2As_2,1\frac{1}{2}H_2O$ requires C, 37·45; H, 4·7%).

This salt, treated with sodium picrate, both in ethanol, gave the yellow *dipicrate*, m. p. 250—252° when thrice recrystallised from water or acetone (Found: C, 42·1; H, 3·15; N, 9·7. $C_{30}H_{28}O_{14}N_6As_2$ requires C, 42·5; H, 3·35; N, 9·95%).

(v) The undistilled residue, when treated with an excess of methyl iodide and a trace of methanol, deposited a crystalline methiodide, which when washed with methanol and then extracted with ethanol [to remove 2 : 2'-diphenylylenebis(trimethylarsonium iodide)] and

[15] Mann and Baker, *J.*, 1952, 4142.
[16] Glauert and Mann, *J.*, 1950, 682.

finally recrystallised from a large volume of ethanol, gave o-*terphenyl*-2 : 2″-*ylenebis(trimethyl-arsonium iodide) dihydrate*, m. p. 283—285° (3·2 g., 6%). (Found: C, 38·05; H, 4·6. $C_{24}H_{30}I_2As_2,2H_2O$ requires C, 38·0; H, 4·5%). Recrystallisation from methanol gave the anhydrous *di-iodide*, m. p. 308—310° (I.T. 260°), 315° (I. T. 300°) (both with decomp.) (Found : C, 40·0; H, 4·4. $C_{24}H_{30}I_2As_2$ requires C, 39·9; H, 4·2%). This salt decomposed smoothly at 235—245°/0·2 mm., to give the diarsine as a syrup which crystallised from ethanol, and when then recrystallised twice from aqueous ethanol gave o-*terphenyl*-2 : 2″-*ylenebisdimethylarsine* (XII) m. p. 92·5—93·5° (Found: C, 60·2; H, 5·2%; M, in boiling ethanol, 430. $C_{22}H_{24}As_2$ requires C, 60·3; H, 5·5%; M, 438).

An ethanolic solution of the diarsine when boiled with aqueous ethanolic potassium pallado-bromide deposited *dibromo-o-terphenyl*-2 : 2″-*ylenebis(dimethylarsine)palladium* (XX), orange crystals from dioxan or ethanol, which decomposed above 350° (Found: C, 37·45; H, 3·85%; M, in boiling chloroform, 690. $C_{22}H_{24}Br_2As_2Pd$ requires C, 37·5; H, 3·45%; M, 704·5). When an aqueous solution of the diarsine and chloroauric acid was gently boiled, *dichloro-(o-terphenyl*-2 : 2″-*ylenebisdimethylarsine)digold* was deposited as nearly colourless crystals, m. p. 180° (Found: Au, 43·75. $C_{22}H_{24}Cl_2As_2Au_2$ requires Au, 43·65%). Carbon values were low and inconsistent). This compound was unstable, readily depositing gold from ethanolic solution or in the solid form. This instability is general for many tertiary arsine–aurous halide complexes.[17]

(C) In another experiment a Grignard solution was prepared as in (B), but with o-bromo-iodobenzene and magnesium (2 equivs.), and was then treated with chlorodiethylphosphine (2 mols.) as described for the reaction with iododimethylarsine. After hydrolysis with aqueous ammonium chloride and drying of the organic layer, the solvents were removed and the residue distilled under reduced pressure, giving the fractions, b. p. 55—70°/0·5 mm. (probably crude tetraethyldiphosphine) and 70—82°/0·1 mm. The latter gave a methiodide, m. p. 195—196° after four recrystallisations from ethanol, probably o-bromophenyldiethylmethylphosphonium iodide, contaminated with diethyl-o-iodophenylmethylphosphonium iodide (Found: C, 32·4; H, 4·5. Calc. for $C_{11}H_{17}BrIP$: C, 34·1; H, 4·4. Calc. for $C_{11}H_{17}I_2P$: C, 31·9; H, 4·1%). Extensive fractionation of the material boiling above 82°/0·1 mm. gave a large number of fractions, all of which failed to give crystalline derivatives with methyl and ethyl iodide, potassium palladobromide, or chloroauric acid. Diphenylene (VI) separated in crude crystalline form from all the lower-boiling fractions thus obtained, and when recrystallised from aqueous methanol and sublimed at 100°/13 mm. had m. p. and mixed m. p. 110·5—111·5°.

Repetition of this experiment on a larger scale gave a similar result.

Interaction of o-*Bromoiodobenzene and Lithium.*—A solution of o-bromoiodobenzene (14·15 g.) in ether (75 c.c.) was added dropwise to a stirred mixture of fine lithium foil (1·42 g., 4 atomic equivs.) and ether (75 c.c.) during 1 hr. After an induction period of 10 min., a vigorous reaction started and the mixture was then cooled in ice-water while the remainder of the dihalide was added, the temperature of the mixture being kept at 10°. Benzene (100 c.c.) was then added and the mixture stirred at 10° for 1 hr. and finally at room temperature for 1 hr. The mixture was filtered to remove unchanged lithium (0·55 g., 38%) and hydrolysed by pouring it on ice. The organic layer was evaporated and the semi-crystalline residue distilled in steam. The steam-distillate was extracted with ether, the extract evaporated, and the crystalline residue recrystallised from aqueous methanol, to give diphenyl, m. p. and mixed m. p. 69—70° (yield of purified product, 0·456 g., 12%). The non-volatile residue was extracted with ether and dried ($MgSO_4$) and the solution percolated through alumina. The crystalline material obtained by evaporation of the solution, when sublimed at 175—180°/0·1 mm., afforded triphenylene (I), m. p. and mixed m. p. 191—192° (2·132 g., 54·5%).

In a similar experiment the reaction mixture was carboxylated. The acidic fraction was an oil. Diphenyl was isolated in lower yield (2·75%) and the main product was again triphenylene (48%).

[17] Mann, Wells, and Purdie, *J.*, 1937, 1828.