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ARYNE CHEMISTRY—II[1]

SYNTHESES OF SOME SUBSTITUTED TRIPHENYLENES VIA ORGANOMETALLIC REAGENTS DERIVED FROM 4,4'-DIMETHYL-2-FLUORO-2'-IODOBIPHENYL

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Abstract—Several possible mechanisms are considered for the formation of triphenylene and substituted triphenylenes in aryne reactions involving organometallic compounds. A stepwise rather than a concerted mechanism is favoured both from previous evidence and from present work. In particular, we have synthesized 2,7-dimethyl-; 1,6,11- and 2,6,11-trimethyl-; 1,3,6,11- and 2,3,6,11-tetramethyl-; and 6,11-dimethyl-2-methoxytriphenylene by way of a biphenyl intermediate.

Triphenylene and substituted triphenylenes have been isolated in a number of reactions of *o*-dihaloaromatic compounds with metals. These reactions have been interpreted as involving aryne intermediates.[2] Dimerization and trimerization of benzyne have been suggested as accounting for the formation of biphenylene and triphenylene respectively.[3]

Energetically, a concerted trimerization is extremely improbable. Dimerization of aryne intermediates would be expected to occur only if the aryne was generated in high concentration and in the absence of other highly reactive species. Such idealized conditions are found in the flash photolysis of benzenediazonium-2-carboxylate, where biphenylene is the major product, together with a very low yield of triphenylene.[4] Similar results are obtained by the action of lead tetracetate on 1-aminobenzotriazole, in the absence of trapping agents.[5] In aryne reactions involving organometallic compounds, the above conditions are difficult to attain; but a 24% yield of biphenylene has been reported, together with 3% of triphenylene, in the reaction of *o*-fluorobromobenzene with lithium amalgam.[6]

These results suggest that the triphenylene might arise by Diels-Alder addition of benzyne to biphenylene. An analogous mechanism has been postulated to account for the formation of dodecahydrotriphenylene in reactions involving cyclohexyne.[7] We have shown that this is not an important mechanism of formation of triphenylene in reactions involving organometallic compounds by generating benzyne in the presence of biphenylene. No increase in the normal yield of triphenylene was observed and the biphenylene was completely recovered.

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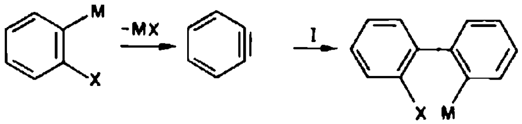
Apart from these negative inferences, the detection on many occasions of postulated intermediates provides strong direct evidence in favour of a sequential mechanism for triphenylene formation.[8] Further, the successful incorporation of a postulated intermediate into substituted triphenylenes has been briefly recorded.[1] The normal mechanism of triphenylene formation in reactions involving organometallic compounds undoubtedly involves a stepwise, rather than a concerted, reaction of an aryne with the organometallic compound (I), which acts as the aryne precursor, and with the resulting biphenyl (II).



I

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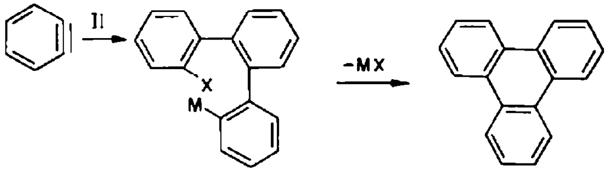
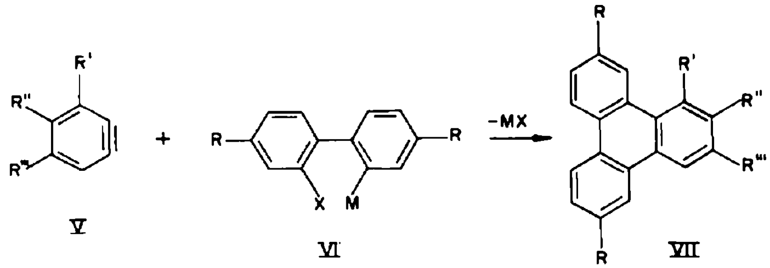


III

IV

Scale models of the terphenyl derivative (III) show that the metal and halogen atoms can be in an ideal orientation for an intramolecular Fitting reaction to occur, to give triphenylene (IV). It is noteworthy that, if the halogen in intermediates (I, II and III) is highly reactive towards metals or organometallic reagents, then the yield of triphenylene may be significantly reduced and *o*-quaterphenyl derivatives may be isolated.[8d,9]

The incorporation of a suitably substituted biphenyl intermediate (VI) establishes a new synthesis of some otherwise inaccessible substituted triphenylenes, whose structures are such that they cannot have been formed by a concerted trimerization. By use of this intermediate, we have prepared two known triphenylenes and four new triphenylenes (Table 1).



V

VI

VII

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[c] R. C. Hinton, F. G. Mann and I. T. Millar, *Ibid.* 4704 (1958);
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The structures of the new compounds have been confirmed by a combination of elemental analysis and spectroscopic methods.[10]

TABLE 1

VI (R = Me, X = F)	V	VII	Yield
M = MgI	R′ = R″ = R‴ = H	2,7-Dimethyltriphenylene	27%
M = Li	R′ = R″ = R‴ = H	2,7-Dimethyltriphenylene	50%
M = MgI	R′ = R‴ = H, R″ = Me	2,6,11-Trimethyltriphenylene	10%
M = Li	R′ = R‴ = H, R″ = Me	2,6,11-Trimethyltriphenylene	26%
M = MgI	R′ = Me, R″ = R‴ = H	1,6,11-Trimethyltriphenylene	13%
M = MgI	R′ = R‴ = H, R″ = OMe	6,11-Dimethyl-2-methoxytriphenylene	15%
M = MgI	R′ = R‴ = Me, R″ = H	1,3,6,11-Tetramethyltriphenylene	60%
M = Li	R′ = H, R″ = R‴ = Me	2,3,6,11-Tetramethyltriphenylene	20%

The preparation of the intermediate (VI; R = Me, X = F, M = Li or MgI) required the availability of such large quantities of 4,4′-dimethylbiphenyl as to render the use of the Ullmann and Krizewski-Turner condensation reactions uneconomic. We have obtained 4,4′-dimethylbiphenyl in 58% overall yield by the reaction of *p*-tolyl-lithium with 4-methylcyclohexanone,[11] dehydration of the resulting 4-methyl-1-(*p*-tolyl)cyclohexanol with formic acid,[12] followed by dehydrogenation of 4-methyl-1-(*p*-tolyl)-cyclohexene with chloranil.[13]

In the synthesis of 4,4′-dimethyl-2-fluoro-2′-iodo-biphenyl, a discrepancy was observed between the properties of 2-amino-4,4′-dimethyl-2′-fluorobiphenyl and those recorded in the literature.[14] The identity of the latter compound, obtained by reduction of 4,4′-dimethyl-2-fluoro-2′-nitrobiphenyl by two different methods, was established by elemental analysis, and conversion to and comparison with authentic 2,2′-difluoro-4,4′-dimethylbiphenyl.

It is well known[15,16] that aryl chlorides, bromides and iodides are rapidly and completely dehalogenated by hydrazine and PdC in ethanolic solution. The IR spectrum of the product obtained by the reduction of 4,4′-dimethyl-2-fluoro-2′-nitrobiphenyl by this method indicated that the resulting amine was partially dehalogenated.

We have improved the yields at various stages, particularly by using recent procedures for the introduction of fluorine,[17,18] and for the reduction of nitro groups.[19,20]

The unreliability of carboxylation as a method of assessing the usefulness of Grignard reagents and organolithium compounds derived from 2,2′-dihalobiphenyls

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has been commented on previously.[21] We find that 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl forms a mono Grignard reagent with magnesium in tetrahydrofuran, and a monolithio compound with n-butyllithium in ether in good yield. However, carboxylation gives 2-carboxy-4,4′-dimethyl-2′-fluorobiphenyl in only 10% yield together with 4,4′-dimethyl-2-fluorobiphenyl in 90% yield.

The use of UV absorption spectra in order to confirm the presence of the triphenylene nucleus and the effect of substituents on the maxima has been reported previously.[22,23] These workers showed that 2-methyltriphenylene shows a bathochromic shift of 20 Å without a change in intensity when compared with triphenylene, whereas 1-methyltriphenylene shows a bathochromic shift of 40 Å and a reduction in intensity. It has been suggested[22] that the spectra indicate that the 1-methyl substituent is forced out of the plane of the remainder of the molecule. X-ray crystallography[24] indicates that even triphenylene is not completely planar in the solid state; this is thought to be at least partly an intramolecular effect. The UV absorption maxima of the di-, tri- and tetra-methyl substituted triphenylenes show further bathochromic shifts. When a substituent is in a bay[10] (or angular[25]) position (e.g. position 1-), all maxima occur at longer wavelengths than in isomers without a

Table 2. Ultraviolet absorption maxima (mμ) in EtOH ($\log_{10} \varepsilon$ in parentheses)

Triphenylene derivative										
Unsubstituted	λ	248·5	257	273	284	302	312	321	327	334
		(4·97)	(5·18)	(4·40)	(4·26)	(3·50)	(3·00)	(2·90)	(2·88)	(2·88)
1-Methyl-(22)	λ	253·5	261	279	288					
		(4·74)	(5·05)	(4·16)	(4·14)					
2-Methyl-(22)	λ	250·5	259	275	285·5					
		(4·84)	(5·51)	(4·18)	(4·16)					
2,7-Dimethyl-	λ	252	261	276	288	317	325	332	340	348
		(4·96)	(5·21)	(4·28)	(4·22)	(2·92)	(2·74)	(2·94)	(2·68)	(2·89)
1,6,11-Trimethyl-	λ	256	264	280	291	309		335	344	351
		(4·89)	(5·06)	(4·39)	(4·46)	(3·63)		(2·97)	(2·64)	(2·91)
2,6,11-Trimethyl-	λ	253	262	278	289	318	325	334	341	349
		(4·99)	(5·21)	(4·31)	(4·25)	(2·98)	(2·98)	(2·76)	(2·64)	(2·82)
2,6,10-Trimethyl-(22)	λ	253·5	262·5	277·5	288·5					
		(4·87)	(5·50)	(4·20)	(4·17)					
1,3,6,11-Tetramethyl-	λ	258	266	279·5	292·5		330·5	338		354
		(4·82)	(5·01)	(5·25)	(4·15)		(2·64)	(2·84)		(2·77)
2,3,6,11-Tetramethyl-	λ	255	263·5	279	290		325·5	333·5	341	349
		(4·81)	(5·06)	(4·17)	(4·12)		(2·66)	(2·60)	(2·45)	(2·30)
2-Methoxy-6,11-dimethyl-	λ	256	264	282				337		353
		(4·91)	(5·09)	(4·26)				(3·21)		(3·21)

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bay methyl group. However, the spectra of the tri- and tetra-methyl triphenylenes show no reduction in intensity when a methyl group is in a bay position. It is of interest that, although the UV spectrum of 2-methoxy-6,11-dimethyltriphenylene shows a general similarity to the spectra of triphenylene and other substituted triphenylenes, some of the maxima are absent. PMR evidence on the planarity of these rings is discussed in a following paper.[10]

EXPERIMENTAL

Experiments with Mg and n-butyl-lithium were performed in a N_2 atm. Compounds are colourless unless otherwise described. M.ps are uncorrected. Pet. ether refers to that fraction b.p. 60–80° unless otherwise stated. UV spectra were recorded on a Unicam S.P.500 for ethanolic solutions. IR spectra were recorded on a Perkin–Elmer 237 for KBr discs (unless otherwise stated). Chromatographic separations were carried out on neutral alumina (Woelm, Activity I).

3-*Chloro-2-iodotoluene*. 2-Amino-3-chlorotoluene was diazotized and treated with KI aq to yield 3-*chloro-2-iodotoluene* b.p. 107–108°/2 mm (70%). (Found: C, 33·25; H, 2·45. $C_7H_6Cl\,I$ requires: C, 33·30; H, 2·40%.)

4-*Chloro-3-iodoanisole*. 3-Amino-4-chloroanisole was diazotized and treated with KI aq and gave 4-*chloro-3-iodoanisole*, b.p. 123°/1·5 mm; n_D^{22} 1·6260, (50%). (Found: C, 30·95; H, 2·25 $C_7H_6OCl\,I$ requires: C, 31·30; H, 2·25%.)

4,5-*Dimethyl-2-fluoro-bromobenzene*. 4-Amino-5-bromo-*o*-xylene (20 g, 0·1 M) in tetrahydrofuran (25 ml) was added to fluoroboric acid (60 ml, 40% solution) and water (15 ml). A solution of $NaNO_2$ (6·9 g) in water (15 ml) was added dropwise to the cold stirred solution. The precipitate of the diazonium fluoroborate was removed and washed with aqueous fluoroboric acid (200 ml, 5%), methanolic ether (1:9; 100 ml), ether (100 ml) and dried *in vacuo* (29·9 g, 100%). The diazonium salt was heated in absence of solvent and gave 4,5-*dimethyl-2-fluoro-bromobenzene* b.p. 106–107°/20 mm, m.p. 42° (12 g, 59%). (Found: C, 47·30; H, 4·00. $C_8H_8Br\,F$ requires: C, 47·35; H, 4·00%).

3,5-*Dimethyl-2-fluorobromobenzene* was prepared from 2-amino-3,5-dimethyl bromobenzene as for 4,5-dimethyl-2-fluorobromobenzene; b.p. 62–64°/1·5 mm, n_D^{22} 1·5320, (15 g, 74%). (Found: C, 47·30; H, 4·70. $C_8H_8Br\,F$ requires: C, 47·35; H, 4·00%).

1-(p-*Tolyl*)-4-*methylcyclohexanol*. 4-Methylcyclohexanone (224 g, 2M) in ether (200 ml) was added to *p*-tolyl-lithium {from *p*-bromotoluene (342 g, 2M), Li (28 g, 4 At. equiv.) in ether (1·5 L)} at a rate such that reflux was just maintained. The mixture was finally refluxed for 2 hr. prior to hydrolysis with cold in H_2SO_4 (500 ml). The ether layer was washed with water, extracted with sat $NaHSO_3$ aq, washed with water and dried (Na_2SO_4). After removal of solvent, the residue was distilled under reduced pressure to give the alcohol b.p. 136°/1 mm (lit[16] b.p. 115°/3 mm) (310 g, 77%).

1-(p-*Tolyl*)-4-*methylcyclohexene*. 1-(p-Tolyl)-4-methylcyclohexanol (204 g, 1 M) was briefly warmed with formic acid (1 l.) and set aside for 18 hr. The upper layer was separated, washed with water (4 × 250 ml), taken into ether (500 ml) and dried (Na_2SO_4). After removal of the solvent, the residue was distilled under reduced pressure to give the olefine b.p. 116–120°/1·5 mm (lit[16] b.p. 151·5°/18 mm) (185 g, 100%).

4,4′-*Dimethylbiphenyl*

A mixture 1-(*p*-tolyl)-4-methylcyclohexene (37·2 g, 0·2 M), chloranil (98·4 g, 0·4 M) and xylene (150 ml) was heated under reflux for 5 hr, cooled and pet. ether (150 ml) added. The precipitated tetrachlorohydroquinone (98 g, 98%) was removed and the filtrate washed with KOH aq (200 ml 4%) water (2 × 200 ml) and dried (Na_2SO_4). After removal of the solvents the product crystallized spontaneously (30·8 g, 82%). Recrystallization from benzene gave 4,4′-dimethylbiphenyl [m.p. and mixed m.p. 117–118° (lit[17] m.p. 125°) and identical IR spectra].

2-*Amino-4,4′-dimethylbiphenyl*

4,4′-Dimethyl-2-nitrobiphenyl[14] (22·7 g, 0·1 M), EtOH (300 ml) and PdC (300 mg, 5%) were warmed to 50° and hydrazine hydrate (30 ml) added slowly over 30 min, followed by a further

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addition of PdC (100 mg, 5%). The mixture was refluxed for 3 hr and after removal of the catalyst the filtrate was evaporated to dryness under red. press. The crystallized residue was recrystallized from aqueous EtOH m.p. 70° (lit[14] m.p. 62–63°) (17·7 g, 90%), acetyl derivative m.p. 116–117° (lit[14] m.p. 118–119°).

4,4'-Dimethyl-2-fluorobiphenyl

Fluoroboric acid (40 ml, 40%) and water (15 ml) were added to a solution of 2-amino-4,4'-dimethylbiphenyl (9·8 g, 0·05 M) in tetrahydrofuran (25 ml). The resulting solution was cooled to 5° and stirred while a solution of $NaNO_2$ (4 g) in water (10 ml) was added dropwise. After the suspension had been stirred for a further 30 min, the diazonium salt (12 g, 81%, dec 69–70°) was removed by filtration and washed with aqueous fluoroboric acid (200 ml, 5%), MeOH: ether (1:9; 50 ml), and ether (100 ml).

The diazonium salt (12 g) was suspended in dry benzene (150 ml) and warmed to 65° when smooth decomposition occurred. Filtration of the product through a short column of alumina (50 g) in ether: pet. ether (1:1) gave 4,4'-dimethyl-2-fluorobiphenyl m.p. 65–66° (6·0 g, 75%). Recrystallization from MeOH raised the m.p. to 69–70° (lit[14] m.p. 73–74°). The same overall yield was obtained via the diazonium hexafluorophosphate.[28]

2-Amino-4,4'-dimethyl-2'-fluorobiphenyl

Method 1. 4,4'-Dimethyl-2-fluoro-2'-nitrobiphenyl[14] (6 g) and $SnCl_2$ (30 g) were dissolved in HCl (150 ml) and the mixture refluxed for 2 hr. After basification the amine was taken into ether, dried (Na_2SO_4) and the solvent removed The residue crystallized to give the *amine* m.p. 50° (lit[14] m.p. 105–106°) (2·75 g, 51%).

Method 2. 4,4'-Dimethyl-2-fluoro-2'-nitrobiphenyl (24 g) in MeOH (100 ml) was added dropwise to a refluxing mixture of MeOH (150 ml), hydrazine hydrate (30 ml) and Raney Ni (~1 g). After completion of the addition, the mixture was refluxed for a further 30 min. The catalyst was removed by filtration and the filtrate evaporated to dryness under red. press. The crystalline residue (19·2 g, 77%) m.p. 52–53°, b.p. 145–148/0·5 mm. After recrystallization from aqueous EtOH (5X) the *amine* had m.p. 63–64° (lit[14] m.p. 105–106°). (Found: C, 77·80; H, 6·75; N, 6·35. $C_{14}H_{14}FN$ requires: C, 78·10; H, 6·60; N, 6·50%).

2,2'-Difluoro-4,4'-dimethylbiphenyl

2-Amino-4,4'-dimethyl (m.p. 63–64°, 1 g, 0·05 M) in HCl (4 ml) was cooled to 5° and diazotized with $NaNO_2$ (0·4 g) in water (2·5 ml). A solution of sodium fluoroborate (0·5 g) in water (1·5 ml) was slowly added to the diazonium solution while vigorous stirring was maintained. The gum, which initially formed, crystallized, was collected, washed with MeOH (10 ml) and ether (200 ml), and dried *in vacuo*. The diazonium salt decomposed smoothly in dry benzene at 70° and gave 2,2'-difluoro-4,4'-dimethylbiphenyl (0·80 g, 79%) m.p. and mixed m.p. 93° (lit[14] m.p. 93°) after recrystallization from EtOH. The IR spectrum was identical with a sample prepared from 2,2'-diamino-4,4'-dimethylbiphenyl.

4,4'-Dimethyl-2-fluoro-2'-iodobiphenyl

2-Amino-4,4'-dimethyl-2'-fluorobiphenyl (4·8 g, 0·02 M) in 2N H_2SO_4 (50 ml) was diazotized below 5° by the dropwise addition of a solution of $NaNO_2$ (1·4 g) in water (5·0 ml). The resulting solution was slowly added to an ice-cold solution of KI (20 g) in water (100 ml). The resulting oil was taken into ether, washed with $NaHSO_3$ aq, dried (Na_2SO_4) and the ether removed. The residue gave on distillation *4,4'-dimethyl-2-fluoro-2'-iodobiphenyl* (4·0 g, 70%) b.p. 114°/0·1 mm, n_D^{20} 1·6219, (Found: C, 51·45; H, 3·70. $C_{14}H_{12}FI$ requires: C, 51·55; H, 3·60%). Extensive decomposition occurred in some larger scale distillations. Purification by chromatography on alumina in pet. ether gave satisfactory results.

Interaction of o*-fluorobromobenzene and magnesium*

o-Fluorobromobenzene (17·5 g, 0·1 M) in tetrahydrofuran (150 ml) was added to Mg (2·67 g 1 at. equiv.) and tetrahydrofuran (25 ml) at a rate such that vigorous reflux was maintained. The mixture was refluxed for a further 1·5 hr before the clear yellow solution was hydrolysed with

[28] Thanks are due to the Ozark-Mahoning Company for a gift of ammonium hexafluorophosphate.

NH_4Cl aq. The aqueous layer was boiled to expel dissolved tetrahydrofuran, cooled and extracted with benzene. The organic solvents were removed and the residue distilled in steam to give 2-fluorobiphenyl (0·88 g) m.p. and mixed m.p. 72–73°[29] (lit[30] m.p. 73·5°), IR spectra identical. The residue crystallized and gave triphenylene (6·43 g, 84·5%) m.p. and mixed m.p. 189–191° (lit[31] m.p. 199°), IR spectra identical.

Interaction of o-*fluorobromobenzene and magnesium in the presence of biphenylene*

The above reaction was repeated (0·25 X) in the presence of biphenylene (3·8 g, 1 M). Biphenylene (3·79 g), m.p. and mixed m.p. 111° (lit[32] m.p. 111°) was recovered from the steam distillate (see above) and triphenylene (1·60 g) was isolated from the steam involatile fraction.

Interaction of 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl and magnesium

4,4′-Dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M) in tetrahydrofuran (25 ml) was added dropwise to a mixture of Mg (0·26 g, 1·1 at, equiv.) and tetrahydrofuran (10 ml). After the initial reaction had subsided the mixture was refluxed for a further 2 hr, cooled and carboxylated. After hydrolysis with 2N H_2SO_4 the organic layer was evaporated and taken into ether. The aqueous layer was boiled to expel any dissolved tetrahydrofuran and extracted with ether. The combined ether fractions were extracted with $KHCO_3$ aq which when acidified deposited *2-carboxy-4,4′-dimethyl-2′-fluorobiphenyl* (0·25 g, 10%) m.p. 156–158° after recrystallization from aqueous EtOH and pet. ether. (Found: C, 73·60; H, 5·40. $C_{15}H_{13}O_2F$ requires: C, 73·75; H, 5·35%). Evaporation of the ether gave 4,4′-dimethyl-2-fluorobiphenyl (2·0 g, 90%) m.p. and mixed m.p. 69–70°, IR spectra identical.

Interaction of 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl and n-*butyl-lithium in ether.*

4,4′-Dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M) in diethyl ether (30 ml) was added dropwise to a solution of n-butyl-lithium in diethyl ether (20 ml, 0·5 M solution, 1 equiv.). The mixture was stirred at ambient temp for 2 hr and then carboxylated. After hydrolysis with 2N H_2SO_4, the organic layer was extracted with $KHCO_3$ aq which when acidified, gave 2-carboxy-4,4′-dimethyl-2′-fluorobiphenyl (0·26 g, 10%) m.p. and mixed m.p. 156–158° after recrystallization from pet. ether, IR spectra identical.

Synthesis of Substituted Triphenylenes

2,7-Dimethyltriphenylene

Method 1. The Grignard reagent was prepared from 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M) and Mg (0·52 g, 2·2 at. equiv.) in tetrahydrofuran (25 ml) as above. The reaction mixture was cooled to ambient temp and *o*-fluorobromobenzene (1·75 g, 0·01 M) in tetrahydrofuran (25 ml) added dropwise over 30 min. The mixture was refluxed for 2 hr before hydrolysis with ice–2N H_2SO_4. The organic layer was evaporated and taken into pet. ether. The aqueous layer was boiled and extracted with pet. ether. The combined extracts were dried (Na_2SO_4), the volume reduced (to 25 ml) and placed on alumina (200 g). Elution with pet. ether gave two distinct fractions: (a) 4,4′-dimethyl-2-fluorobiphenyl (1·2 g, 60%), m.p. and mixed m.p. 69–70°, IR spectra identical: and (b) 2,7-dimethyltriphenylene (0·70 g, 27%), m.p. and mixed m.p. 134° (lit[33] m.p. 137°) IR and UV spectra identical. (Found: C, 93·50; H, 6·00. Calc. for $C_{20}H_{16}$: C, 93·75; H, 6·25%).

Method 2. The organolithium compound from 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M), n-butyl-lithium (40 ml, 0·5 M solution in ether, 2 equiv.) and ether (25 ml) was prepared as above and *o*-fluorobromobenzene (1·75 g, 0·01 M) in ether (25 ml) added dropwise over 30 min. Working up and purification as in method 1 gave (a) 4,4′-dimethyl-2-fluorobiphenyl (0·6 g, 30%) m.p. and mixed m.p. 69–70° and (b) 2,7-dimethyltriphenylene (1·35 g, 50%) m.p. and mixed m.p. 134°.

2,6,11-Trimethyltriphenylene

Method 1. From 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M) Mg (0·52 g, 2·2 at. equiv.) and 4-chloro-3-iodotoluene (2·40 g, 0·01 M) gave 2,6,11-trimethyltriphenylene (0·25 g, 10 %)

[29] Sample kindly provided by Professor G. Wittig.

[30] G. Schiemann and W. Roselius, *Ber. Dtsch. Chem. Ges.* **62**, 1805 (1929).

[31] C. Mannich, *Ber. Dtsch. Chem. Ges.* **40**, 160 (1907).

[32] W. C. Lothrop, *J. Amer. Chem. Soc.* **63**, 1187 (1941).

m.p. and mixed m.p. 135–136° (lit[23] m.p. 137°) IR and UV spectra identical. (Found: C, 93·30; H, 6·65. Calc. for $C_{21}H_{18}$: C, 93·25; H, 6·75%).

Method 2. From 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M), n-butyl-lithium (40 ml, 0·5 M solution) and 4-chloro-3-iodotoluene (2·40 g, 0·01 M) gave 2,6,11-trimethyltriphenylene (0·65 g, 26%) m.p. and mixed m.p. 135–136°.

6,11-*Dimethyl-2-methoxytriphenylene*

Method 3. From 4,4′-dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M), Mg (0·52 g, 2·2 at. equiv.) and 4-chloro-3-iodoanisole (2·72 g, 0·01 M) as in Method 1. Chromatography on alumina gave (a) 4,4′-dimethyl-2-fluorobiphenyl (0·70 g, 36%) m.p. and mixed m.p. 69–70° and (b) an oil which failed to crystallize but which when taken into benzene (2 ml) and treated with a saturated ethanolic solution of picric acid gave orange crystals of a picrate (0·70 g, 15%). The picrate when placed in benzene on a short column of alumina and eluted with benzene gave 6,11-*dimethyl-2-methoxy-triphenylene* (0·4 g) m.p. 133°. (Found: C, 87·70; H, 6·50. $C_{21}H_{18}O$ requires: C, 88·0; H, 6·35%).

1,6,11-*Trimethyltriphenylene*

Method 3. 4,4′-Dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M) Mg (0·52 g, 2·2 at. equiv.) and 3-chloro-2-iodotoluene (2·39 g, 0·01 M), gave a picrate (0·64 g, 13%) from which 1,6,11-*trimethyltriphenylene* (0·30 g) m.p. 108° was obtained. (Found: C, 93·05; H, 6·75. $C_{21}H_{18}$ requires: C, 93·25; H, 6·75%).

1,3,6,11-*Tetramethyltriphenylene*

Method 3. 4,4′-Dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M), Mg (0·52 g, 2·2 at. equiv.) and 2-fluoro-3,5-dimethylbromobenzene (2·03 g, 0·01 M), gave a picrate (3·1 g, 60%) from which 1,3,6,11-*tetramethyltriphenylene* (2·0 g) m.p. 124–125° was obtained. (Found: C, 93·10; H, 6·80. $C_{22}H_{20}$ requires: C, 93·0; H, 7·0%).

2,3,6,11-*Tetramethyltriphenylene*

Method 2. 4,4′-Dimethyl-2-fluoro-2′-iodobiphenyl (3·26 g, 0·01 M) in ether (25 ml), n-butyl-lithium (40 ml, 0·5 M solution in ether, 2 equiv.) and 2-fluoro-4,5-dimethylbromobenzene (2·03 g, 0·01 M) gave 2,3,6,11-*tetramethyltriphenylene* (0·574 g, 20%) m.p. 192–193°. (Found: C, 93·0; H, 7·0. $C_{22}H_{20}$ requires: C, 93·0; H, 7·0%).

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