

Regiospecific Synthesis of 2,3,6,7,10,11-Hexasubstituted Triphenylenes by Oxidative Photocyclisation of 3,3'',4,4'',5'-Hexasubstituted 1,1':2',1''-Terphenyls

Richard J. Bushby* and Christopher Hardy
Department of Organic Chemistry, The University, Leeds LS2 9JT

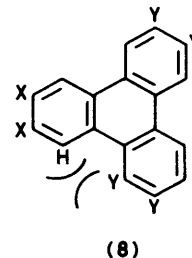
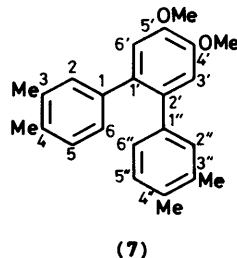
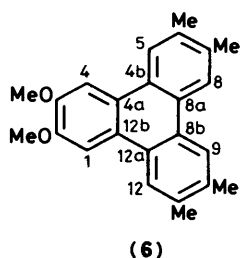
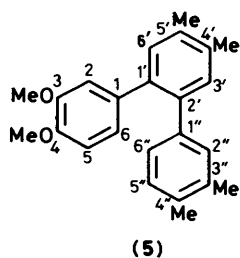
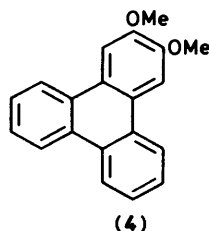
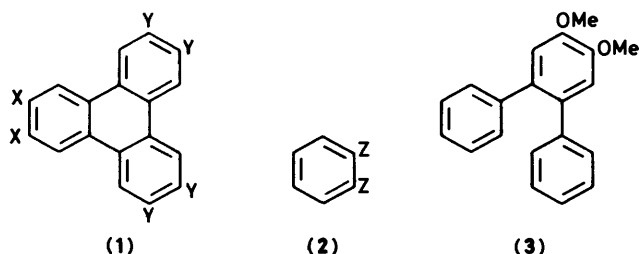
Photolysis of 4',5'-dimethoxy-1,1':2',1''-terphenyl (**3**) in the presence of iodine gives 2,3-dimethoxytriphenylene (**4**) (72%). A similar photolysis of either 3,4-dimethoxy-3'',4',4'',5'-tetramethyl-1,1':2',1''-terphenyl (**5**) or 4',5'-dimethoxy-3,3'',4,4''-tetramethyl-1,1':2',1''-terphenyl (**7**) gives 2,3-dimethoxy-6,7,10,11-tetramethyltriphenylene (**6**). The regiospecificity of these photocyclisation reactions makes this the best route to asymmetrical 2,3,6,7,10,11-hexasubstituted derivatives of triphenylene.

The recognition of disc-shaped molecules as potential mesogens¹ has opened up a whole new field of liquid crystal research. Many thermotropic 'discoidal' mesogens² and the recently described lyotropic 'discoidal' mesogens³ are 2,3,6,7,10,11-hexasubstituted derivatives of triphenylene (**1**). The relevant symmetrical hexa-alkoxytriphenylenes (**1**; X = Y = RO) can be easily obtained by oxidative trimerisation of a 1,2-dialkoxybenzene (**2**; Z=RO). For example,⁴ treatment of veratrole (**2**; Z=MeO) with chloranil in 70 vol. % aqueous sulphuric acid gives a good yield of 2,3,6,7,10,11-hexamethoxytriphenylene (**1**; X = Y = MeO). However, neither this route nor others used⁵ are easy to adapt for the synthesis of unsymmetrical hexasubstituted triphenylenes (**1**; X ≠ Y). A crossed oxidative trimerisation of two different dialkoxybenzenes [(**2**; Z = OR) with (**2**; Z = OR')] has been employed,⁶ but the separation of the resultant mixture of two symmetrical triphenylenes [(**1**; X = Y = OR) and (**1**; X = Y = OR')] and

two unsymmetrical triphenylenes [(**1**; X = OR, Y = OR') and (**1**; X = OR', Y = OR)] can be difficult. Similar problems attend the method based on partial hydrolysis and alkylation of triphenylenehexaol hexa-acetate (**1**; X = Y = OAc).⁷ In this paper we report a more rational solution to the problem, based on oxidative photocyclisation of a suitably substituted *ortho*-terphenyl. Most of these *ortho*-terphenyls are readily available through a standard sequence of Ullman reactions (see Experimental section).

Photolysis of *ortho*-terphenyl itself in the presence of an excess of iodine is known to give a near-quantitative yield of triphenylene.^{8,9} This reaction is readily adapted for those systems where there is a substituent on the central ring¹⁰ or in the *para* or one of the *ortho* positions of the outer rings.⁹ In these cases only one triphenylene cyclisation product can result. For example, we have found that photolysis of the *ortho*-terphenyl (**3**) in the presence of iodine gives a good yield (72% after recrystallisation) of the triphenylene (**4**). In cases where there are substituents in the *meta* positions of the outer rings of the *ortho*-terphenyl, however, there can, in principle, be a problem of regioselectivity. The hexasubstituted systems which we have investigated fall into this category but we find that in practice regioselectivity is not a problem. For example, photolysis of the *ortho*-terphenyl (**5**) in the presence of an excess of iodine, could, in principle, give four triphenylene products. In practice only one can be detected, *i.e.* the desired 2,3,6,7,10,11-hexasubstituted product (**6**). The identity of this product was established through the presence of only eight aromatic resonances in the ¹³C-n.m.r. spectrum (there should, in principle, be nine for compound (**6**) but twice as many for two of the alternative products), the fit of this spectrum to that calculated (see Experimental section), and the observation that it is also the only triphenylene produced by oxidative photocyclisation of the isomeric *ortho*-terphenyl (**7**).

The reason for the regioselectivity of these reactions is probably mainly steric. Formation of regioisomers of the type shown in formula (**8**) (or their dihydro precursors) involves the



introduction of strain. Frontier orbital factors do not appear to be important. Hückel M.O. calculations on compounds (5) and (7), using standard parameters to allow for the effect of substituents,¹¹ show larger coefficients at C-6 and -6' than at C-2 and -2' for ψ_{11} (SOMO₁ in the $\pi \rightarrow \pi^*$ excited state), but for ψ_{12} (SOMO₂ in the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excited states) those at C-2 and -2' are marginally greater than those at C-6 and -6'.

Experimental

Light petroleum refers to the fraction b.p. 60–80 °C. N.m.r. spectra were recorded in CDCl₃ solution. Photolyses were performed under a nitrogen atmosphere in an annular water-cooled silica reaction vessel containing a 100 W Hanovia medium-pressure mercury lamp. Chromatography on Kieselgel refers to short column chromatography using Merck Kieselgel G Silica gel.¹² Compounds for which only accurate mass data are given were homogeneous by t.l.c. and ¹H n.m.r.

4,5'-Dimethoxy-1,1':2',1''-terphenyl (3)¹³.—A solution of 4,5-dichloro-1,2-dimethoxybenzene (4.2 g) in ether (80 cm³) was added dropwise to a stirred solution of phenyl-lithium¹⁴ (from 0.9 g lithium) in ether (50 cm³) at 0 °C. The cooling bath was removed and the mixture stirred for 2 h. Solid CO₂ was added to decompose the excess of organolithium and the solution was washed with water, dried (MgSO₄), and evaporated under reduced pressure to give an oil which was chromatographed on Kieselgel. Initial elution with 45% benzene–light petroleum gave a semi-solid which was triturated with hexane to afford 1,2-dichloro-4,5-dimethoxybenzene (1.0 g). Further elution with benzene gave the terphenyl as a white crystalline solid (0.6 g, 14% based on starting material consumed), m.p. 140–142 °C (lit.¹³ 147 °C); δ_{H} 3.94 (6 H, s, 2 × ArOMe), 6.93 (2 H, s, 3'- and 6'-ArH), and 7.09–7.23 (10 H, m, remaining ArH); m/z 290 (M^+ , 100%), 247 (24), 229 (13), 215 (15), 203 ($M^+ - \text{C}_6\text{H}_5$, 19), 202 (24), and 102 (17).

2,3-Dimethoxytriphenylene (4).—A solution of 4,5'-dimethoxy-1,1':2',1''-terphenyl (0.29 g) and iodine (0.25 g) in dry benzene (150 cm³) was photolysed for 5 h. The dark solution was washed with aqueous sodium sulphite and water and dried (MgSO₄). The solvent was removed under reduced pressure to give the triphenylene which was recrystallised from methanol (0.21 g, 72%), m.p. 166–169 °C (lit.¹⁵ 164–165 °C); δ_{H} 4.10 (6 H, s, 2 × ArOMe), 7.55–7.66 (4 H, m, 6-, 7-, 10-, 11-ArH), 7.96 (2 H, s, 1- and 4-ArH), and 8.40–8.67 (4 H, m, 5-, 8-, 9-, 12-ArH); m/z 288 (M^+ , 100%), 273 ($M^+ - \text{CH}_3$, 6), 245 (16), 227 (16), 202 (29), and 144 (M^{2+} , 12%).

3,3',4,4'-Tetramethylbiphenyl and 3,4-Dimethoxy-3',4'-dimethylbiphenyl.—An intimate mixture of 1,2-dimethyl-4-iodobenzene (7 g, b.p. 138–140 °C at 45 mmHg),¹⁶ 1-iodo-3,4-dimethoxybenzene (6 g),¹⁷ and copper powder (15 g) was heated in a round bottomed flask equipped with an air condenser. At 235 °C an exothermic reaction occurred and the temperature rose to 280 °C. The temperature was held at 280 °C for 5 min and the mixture was then cooled and extracted repeatedly with boiling chloroform. The extract was evaporated under reduced pressure and the residual oil subjected to chromatography on Kieselgel. Elution with light petroleum gave first a small fraction of 1-iodo-3,4-dimethylbenzene followed by 3,3',4,4'-tetramethylbiphenyl as a white crystalline solid (1.4 g, 22%), m.p. 72–75 °C (lit.¹⁸ 76 °C); δ_{H} 2.31 (12 H, br s, Me) and 7.0–7.5 (6 H, m, ArH). Further elution with benzene gave 1,2-dimethoxybenzene and 1-iodo-3,4-dimethoxybenzene followed by 3,4-dimethoxy-3',4'-dimethylbiphenyl which was recrystallised from light petroleum (1.9 g, 35%), m.p. 61–62 °C (Found: C, 79.3; H, 7.5. C₁₆H₁₈O₂ requires C, 79.3; H, 7.5%); δ_{H} 2.30, 2.34

(each 3 H, s, ArMe), 3.90, 3.93 (each 3 H, s, ArOMe), and 6.8–7.5 (6 H, m, ArH). Further elution with chloroform gave 3,3',4,4'-tetramethoxybiphenyl (0.5 g, 8%), m.p. 128–130 °C (lit.¹⁹ 133–134 °C); δ_{H} 3.87, 3.91 (each 6 H, s, ArOMe), and 6.8–7.2 (6 H, m, ArH).

2-Iodo-3',4,4',5-tetramethylbiphenyl.—Iodic acid (0.16 g) was added over 20 min to a refluxing solution of 3,3',4,4'-tetramethylbiphenyl (0.42 g) and iodine (0.41 g) in glacial acetic acid. After refluxing for a further 7 h, water was added and the milky solution extracted with chloroform. The combined extracts were washed with aqueous sodium sulphite, aqueous sodium hydroxide and water, dried (MgSO₄), and evaporated under reduced pressure. Chromatography of the residue on Kieselgel with hexane as eluant gave 2-iodo-3',4,4',5-tetramethylbiphenyl (0.23 g, 35%) (Found: M^+ , 336.0380. C₁₆H₁₇I requires M^+ , 336.0517), as a viscous oil which slowly crystallised, m.p. 56–60 °C; δ_{H} 2.23 (9 H, s, 3 × ArMe), 2.31 (3 H, s, ArMe), 6.93–7.11 (4 H, m, 2', 5', 6', and 6-ArH), and 7.67 (1 H, s, 3-ArH); m/z 336 (M^+ , 100), 209 ($M^+ - \text{I}$, 8), 194 (36), and 179 (25%). Further elution afforded 2,2'-di-iodo-4,5,4',5'-tetramethylbiphenyl (0.12 g, 13%), m.p. 176–186 °C (lit.²⁰ 183 °C); δ_{H} 2.24, 2.28 (each 6 H, s, ArMe), 7.68 (2 H, s, 6-, and 6'-ArH), and 7.94 (2 H, s, 3- and 3'-ArH).

2-(Iodo-4,5-dimethoxy-3',4'-dimethylbiphenyl).—This compound, prepared in a similar manner to that described above and purified by chromatography on Kieselgel with benzene–light petroleum (1:1) as eluant, was obtained as an oil (88%) (Found: M^+ , 368.0279. C₁₆H₁₇IO₂ requires M^+ , 368.0275); δ_{H} 2.35 (6 H, br s, ArMe), 3.85, 3.91 (each 3 H, s, ArOMe), and 6.8–7.4 (5 H, m, ArH); m/z 368 (M^+ , 100%).

3,4-Dimethoxy-3',4',4'',5'-tetramethyl-1,1':2',1''-terphenyl (5).—An intimate mixture of 1-iodo-3,4-dimethoxybenzene (0.3 g), 2-iodo-3',4,4',5-tetramethylbiphenyl (0.21 g), and copper powder (0.85 g) was heated at 270 °C for 5 min. The mixture was cooled and extracted with refluxing chloroform. Removal of the solvent under reduced pressure gave an oil which was subjected to chromatography on Kieselgel with light petroleum as eluant to give first what was probably 3,3',4,4',4'',5',5''-octamethyl-1,1':2',1''-2',1''-quaterphenyl (60 mg crude, 23%) (Found: M^+ , 418.2655. C₃₂H₃₄ requires M^+ , 418.2660); δ_{H} 2.3 (12 H, br s, ArMe) and 7.1–7.5 (8 H, m, ArH); m/z 418 (M^+ , 3), 244 (15), 210 (100), 209 (25), and 208 (50%).

Continued elution with benzene gave the terphenyl (5) as an oil (70 mg, 32%) (Found: M^+ , 346.1941. C₂₄H₂₆O₂ requires M^+ , 346.1933); δ_{H} 2.17, 2.21, 2.36 (3 H, 3 H, and 6 H, 3 × s, ArMe), 3.87 (6 H, s, ArOMe), and 6.5–7.3 (7 H, m, ArH); m/z 346 (M^+ , 100) and 264 (53%). Further elution with chloroform afforded 3,3',4,4'-tetramethylbiphenyl (70 mg, 32%), with properties identical with those of the previously prepared sample.

Photolysis of 3,4-Dimethoxy-3',4',4'',5'-tetramethyl-1,1':2',1''-terphenyl (5).—A solution of the terphenyl (5) (70 mg) and iodine (0.5 g) in dry benzene (150 cm³) was photolysed for 6 h. The dark solution was washed with aqueous sodium sulphite and water and, dried (MgSO₄), and evaporated under reduced pressure to afford a solid which was purified by chromatography on Kieselgel with chloroform as eluant to give 2,3-dimethoxy-6,7,10,11-tetramethyltriphenylene (6); this was further purified by recrystallisation from benzene (30 mg, 43%), m.p. 185–188 °C (Found: C, 83.6; H, 7.0. C₂₄H₂₄O₂ requires C, 83.7; H, 7.0%); δ_{H} 2.51 (12 H, br s, ArMe), 4.10 (6 H, s, ArOMe), and 7.90, 8.14, and 8.30 (each 2 H, s, ArH); δ_{C} [5:1 CDCl₃–(CD₃)₂SO] 20.0 (ArMe), 56.0 (ArOMe), 104.9, 123.3, 123.5, 126.9, 127.1, 134.9, 135.4, and 149.1 (ArC). A rough prediction of the chemical shifts of the aromatic carbons can be obtained by

taking those of triphenylene itself²¹ and adding the parameters for the effect of substituents derived from benzene.²² This involves the first order approximation that substituent effects only operate over one ring. This gives δ_c 111.0 (C-1,C-4), 123.5 (C-4a, C-12b), 125.2 (C-5, C-8, C-9, C-12), 127.3 (C-4b, C-8a, C-8b, C-12a), 137.9 (C-6, C-7, C-10, C-11), and 144.8 (C-2, C-3). Consideration of the symmetry of the system suggests that the signals at 125.2, 127.3, and 137.9 should be split giving a maximum of nine signals: m/z 344 (M^+ , 100), 286 (14), 242 (32), 227 (11), 172 (M^{2+} , 10), and 78 (54%).

4',5'-Dimethoxy-3,3'',4,4''-tetramethyl-1,1':2',1''-terphenyl (7).—An intimate mixture of 1-iodo-4,5-dimethylbenzene (0.6 g), 2-iodo-4,5-dimethoxy-3',4'-dimethylbiphenyl (0.58 g), and copper powder (1.5 g) was heated at 270 °C for 5 min after which it was cooled and extracted with refluxing chloroform. The extract was evaporated under reduced pressure to give an oil which was chromatographed on Kieselgel with benzene as eluant to give first a mixture of 1-iodo-3,4-dimethylbenzene and 3,3',4,4'-tetramethylbiphenyl (0.25 g), as shown by ¹H-n.m.r. spectroscopy. Further elution with 1:1 benzene-chloroform gave the *terphenyl* (7) as an oil (0.21 g, 39%) (Found: M^+ , 346.1935. $C_{24}H_{26}O_2$ requires M^+ , 346.1932); δ_H 2.18, 2.22 (each 6 H, s, ArMe), 3.91 (6 H, s, ArOMe), and 6.7—7.1 (8 H, m, ArH); m/z 346 (M^+ , 100%). Further elution with chloroform gave an oil which was 4',4'',5',5''-tetramethoxy-3,3'',4,4''-tetramethyl-1,1':1'',2'',1'''-quaterphenyl (Found: M^+ , 482.2465. $C_{32}H_{34}O_4$ requires M^+ , 482.2457); δ_H 2.1, 2.21 (each 6 H, s, ArMe), 3.75, 3.87 (each 6 H, s, ArOMe), and 6.4—7.0 (10 H, m, ArH); m/z 482 (M^+ , 100%). The *terphenyl* (7) could also be prepared in low yield by the reaction of a 3,4-dimethylphenyl-lithium and 1,2-dichloro-4,5-dimethoxybenzene in a similar manner to that employed for the preparation of the *terphenyl* (3).

Photolysis of 4',5'-Dimethoxy-3,3'',4,4''-tetramethyl-1,1':2',1''-terphenyl (7).—A solution of the *terphenyl* (7) (70 mg) and iodine (50 mg) in dry benzene (75 cm³) was photolysed for 8 h. Work-up as before gave the triphenylene (6) as a white powdery solid (50 mg, 71%), with physical properties identical with those obtained when it was prepared from the *terphenyl* (5).

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