

273. Studies in the Terphenyl Series. Part III. The Preparation and Nitration of *m*-Terphenyl.

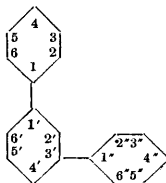
By H. FRANCE, I. M. HEILBRON, and D. H. HEY.

Known methods for the preparation of *m*-terphenyl (1 : 3-diphenylbenzene) are reviewed and two new methods are described, which may be represented briefly as follows : (a) phenyldihydroresorcinol \rightarrow 5-chloro-1-phenyl- Δ^4 -cyclohexen-3-one \rightarrow 3-phenylcyclohexanone \rightarrow 1 : 3-diphenylcyclohexanol \rightarrow 1 : 3-diphenyl- Δ^3 -cyclohexene \rightarrow *m*-terphenyl; (b) nitroso-*m*-nitroacetanilide \rightarrow 3-nitrodiphenyl \rightarrow 3-aminodiphenyl \rightarrow 3-nitrosoacetamidodiphenyl \rightarrow *m*-terphenyl. The nitration of the hydrocarbon gives 4'-nitro-*m*-terphenyl, the constitution of which is proved by its oxidation to 2-nitrodiphenyl-5-carboxylic acid, which is synthesised by an unambiguous method. Further nitration of the hydrocarbon yields a dinitro- and finally a trinitro-derivative. Constitutions for the latter are suggested.

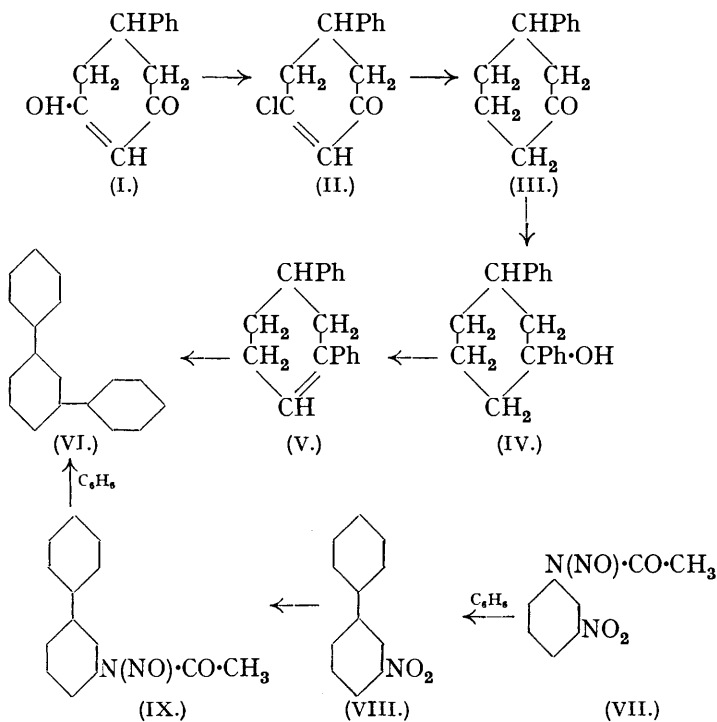
There has been no systematic investigation of the chemistry of *m*-terphenyl* (1 : 3-diphenylbenzene) although the hydrocarbon has been obtained, usually in small quantity, by several previous investigators. The pyrogenic synthesis of the hydrocarbon, in which it is produced in small yield together with diphenyl and *p*-terphenyl, has been recorded by several workers, who obtained it either by passing benzene vapour through a red-hot tube (Schultz, *Annalen*, 1874, **174**, 230; Schmidt and Schultz, *ibid.*, 1880, **203**, 118; Carnelley, J., 1880, **37**, 712; Olgiati, *Ber.*, 1894, **27**, 3385; Mannich, *ibid.*, 1907, **40**, 159) or by heating benzene under pressure at 525° for 48 hours (Herndon and Reid, *J. Amer. Chem. Soc.*, 1928, **50**, 3069). It thus forms a normal by-product in the preparation of diphenyl from benzene. It is also formed, together with *p*-terphenyl and chlorobenzene, when solid benzenediazonium chloride is allowed to react with molten diphenyl in the presence of aluminium chloride (Möhlau and Berger, *Ber.*, 1893, **26**, 1998). The hydrocarbon was synthesised by Chattaway and Evans (J., 1896, **69**, 980) by the action of sodium on a solution of *m*-dichlorobenzene and chlorobenzene in boiling xylene. *m*-Terphenyl has also been isolated in small amount from diverse reactions including the dry distillation of 3 : 5-diphenylbenzoic acid (Gastaldi and Cherchi, *Gazzetta*, 1915, **45**, ii, 251), and the dehydrogenation of either 1 : 3-diphenylcyclohexane (Nenitzescu and Curcăneanu, *Ber.*, 1937, **70**, 346) or the mixture of isomeric dodecahydroterphenyls obtained by the Friedel-Crafts condensation of *p*-cyclohexylcyclohexyl bromide with benzene (von Braun, Irmisch, and Nelles, *Ber.*, 1933, **66**, 1471).

In the present investigation two new methods of preparation of *m*-terphenyl have been developed. In the first, phenyldihydroresorcinol (I), readily prepared from benzylideneacetone and malonic ester (Vörländer, *Ber.*, 1894, **27**, 205; Michael, *ibid.*, p. 2126; Crossley and Renouf, J., 1915, **107**, 608), was converted by means of phosphorus trichloride in chloroform solution into 5-chloro-1-phenyl- Δ^4 -cyclohexen-3-one (II) as described by Boyd, Clifford, and Probert (J., 1920, **117**, 1383). These authors converted the latter into 3-phenylcyclohexanone (III) by reduction with sodium in moist ether to yield 3-phenylcyclohexanol, which in turn was oxidised to the required ketone by means of chromic acid. It is now shown that the chloro-ketone (II) can be converted directly into 3-phenylcyclohexanone (III) by hydrogenation in the presence of a palladium catalyst. The ketone (III) was then treated with phenylmagnesium bromide in the usual way to yield the tertiary alcohol (IV), which without further purification was dehydrated with formic acid to give

* The method of numbering the carbon atoms in *m*-terphenyl used in this series of papers is as follows :



1 : 3-diphenyl- Δ^3 -cyclohexene (V) (and/or the isomeric 1 : 3-diphenyl- Δ^2 -cyclohexene), which finally yielded *m*-terphenyl (VI) on dehydrogenation with sulphur in boiling quinoline.

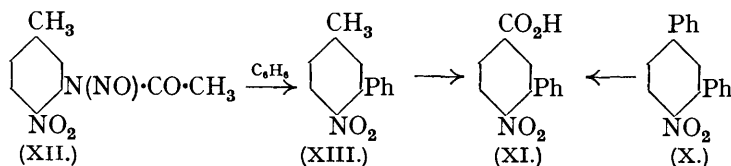


In the second method of synthesis, 3-nitrodiphenyl (VIII), prepared in 63% yield from the interaction of nitroso-*m*-nitroacetanilide (VII) with benzene, was reduced to 3-amino-diphenyl and subsequently acetylated and nitrosated in the usual manner. The resulting 3-nitrosoacetamidodiphenyl (IX) reacted with benzene to give *m*-terphenyl (VI).

The direct nitration of *m*-terphenyl with fuming nitric acid was found by Schmidt and Schultz (*loc. cit.*) to yield a trinitro-derivative of unknown constitution. Attention was redirected to the subject by Wardner and Lowy (*J. Amer. Chem. Soc.*, 1932, **54**, 2510). By treatment of *m*-terphenyl in suspension in acetic anhydride at 0° with fuming nitric acid and subsequent warming, they obtained a mononitro-derivative as an uncrystallisable oil, which on oxidation yielded a hitherto unreported nitrodiphenylcarboxylic acid, which could not be further oxidised. They regarded this nitro-*m*-terphenyl as either 2- or 4'-nitro-*m*-terphenyl. These authors also described the corresponding base obtained by catalytic reduction of the nitro-compound. They further showed that on treatment of the hydrocarbon with a mixture of sulphuric and nitric acids at 40° a dinitro-derivative resulted from which a small amount of *p*-nitrobenzoic acid could be isolated on oxidation. Finally, a trinitro-derivative, apparently identical with that previously prepared by Schmidt and Schultz (*loc. cit.*), was formed on treatment of *m*-terphenyl, or its mononitro-derivative, with fuming nitric acid in glacial acetic acid at 30°. The trinitro-derivative, as previously observed by Schmidt and Schultz (*loc. cit.*), was resistant to oxidation by chromic acid.

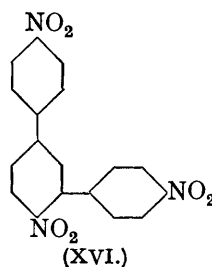
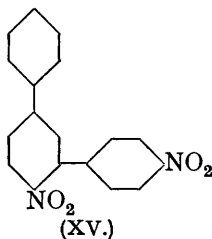
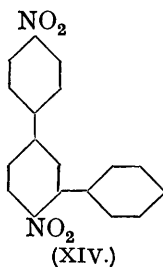
The nitration of *m*-terphenyl has now been reinvestigated. A mononitro-derivative, corresponding in properties with that described by Wardner and Lowy (*loc. cit.*), was prepared on treatment of *m*-terphenyl with concentrated nitric acid in glacial acetic acid at 85–90°. On oxidation it gave in good yield an acid, probably identical with that described by these authors, which is now shown by unambiguous synthesis to be 2-nitrodiphenyl-5-carboxylic acid (XI), thus proving the mononitro-derivative of the hydrocarbon to be 4'-nitro-*m*-terphenyl (X). The synthesis of the acid was effected by allowing the nitroso-derivative (XII) of 4-nitro-*m*-acetotoluidide to react with benzene, followed by

oxidation of the resulting 2-nitro-5-methylphenyl (XIII) to the required 2-nitrodiphenyl-5-carboxylic acid (XI). It is noteworthy that in the direct chlorination and bromination



of *m*-terphenyl it has been shown (Cook and Cook, *J. Amer. Chem. Soc.*, 1933, **55**, 1212) that the halogen atom enters the 4'-position. 4'-Acetamido-*m*-terphenyl was prepared from 4'-nitro-*m*-terphenyl in the usual way and found to correspond in melting point with that of the product previously described but not characterised by Wardner and Lowy (*loc. cit.*). A dinitro-derivative of *m*-terphenyl, apparently identical with that reported by Wardner and Lowy (*loc. cit.*), was prepared on treatment of the hydrocarbon with concentrated nitric acid at about 90° for 20 minutes and, as previously observed, oxidation yielded *p*-nitrobenzoic acid. Nitration of either *m*-terphenyl or 4'-nitro-*m*-terphenyl with fuming nitric acid in glacial acetic acid solution gave a trinitro-*m*-terphenyl, apparently identical with that obtained by the earlier workers, which was unaffected by boiling with chromic anhydride in glacial acetic acid solution.

With regard to the constitution of the dinitro-*m*-terphenyl, the presence of a nitro-group in position 4', as established by the proof of the constitution of the mononitro-*m*-terphenyl, together with the fact that *p*-nitrobenzoic acid is obtained on oxidation, suggests two possible structures, *viz.*, (XIV) and (XV), but the available experimental evidence is not sufficient to enable an unequivocal decision to be made between them. In the case of the trinitro-*m*-terphenyl the resistance to oxidation suggests the presence of one nitro-group in each of the three nuclei (cf. 4 : 2' : 4''-trinitro-*p*-terphenyl; France, Heilbron, and Hey, *J.*, 1938, 1364). One nitro-group is at position 4', since further nitration of 4'-nitro-*m*-terphenyl yields the trinitro-*m*-terphenyl. The remaining two nitro-groups are most probably at positions 4 and 4'' as in (XVI).



EXPERIMENTAL.

3-Phenylcyclohexanone.—5-Chloro-1-phenyl- Δ^4 -cyclohexen-3-one (18.5 g.), prepared as described by Boyd, Clifford, and Probert (*loc. cit.*), in alcohol (140 c.c.) was hydrogenated at room temperature in the presence of gum arabic (0.5 g.), dissolved in the minimum amount of water, and palladium chloride (0.5 g.) (cf. Skita and Franck, *Ber.*, 1911, **44**, 2862). The absorption of hydrogen was extremely rapid, the reaction being complete in 5–7 mins. After filtration, the reaction mixture was evaporated to half bulk, diluted with water, and thoroughly extracted with ether. Distillation of the extract at 155–157°/15 mm. gave 3-phenylcyclohexanone (11 g.), identified as its semicarbazone, which separated from alcohol in needles, m. p. 166–167° (Found : C, 67.9; H, 7.3. Calc. for $C_{13}H_{17}ON_3$: C, 68.0; H, 7.4%). Boyd, Clifford, and Probert (*loc. cit.*) record m. p. 166–167° for 3-phenylcyclohexanonesemicarbazone.

***m*-Terphenyl (Method I).**—A solution of 3-phenylcyclohexanone (18 g.) in absolute ether (25 c.c.) was added gradually to an ice-cold solution of phenylmagnesium bromide in absolute ether (45 c.c.) (prepared from bromobenzene, 18 g.; magnesium, 2.7 g.), and after the initial reaction had subsided, the mixture was gently refluxed for 1 hour. After the addition of iced 5% sulphuric acid, the crude tertiary alcohol, extracted with ether, was obtained as a

colourless oil (26 g.), which, without further purification, was dehydrated by dissolving in 98% formic acid (100 c.c.) (cf. Sherwood, Short, and Stansfield, J., 1932, 1833). The solution rapidly became turbid, and in the course of 2 hours separated into two layers. After dilution with water, the product was extracted with ether, and the extract washed successively with dilute alkali and water. Evaporation of the ether gave 1 : 3-diphenyl- Δ^3 -cyclohexene (and/or 1 : 3-diphenyl- Δ^2 -cyclohexene) (13 g.) as a colourless oil, b. p. 198—200°/18 mm. (Found : C, 92.5; H, 7.4. $C_{18}H_{18}$ requires C, 92.3; H, 7.7%). The product was dehydrogenated by boiling in solution in quinoline (35 c.c.), containing sulphur (5 g.), for 36 hours. After removal of quinoline with hot dilute sulphuric acid, distillation of the residue at 90°/10⁻² mm. gave *m*-terphenyl (9 g.), which separated from hot alcohol in colourless needles, m. p. 89° (Found : C, 93.6; H, 6.2. Calc. for $C_{18}H_{14}$: C, 93.9; H, 6.1%).

3-Nitrodiphenyl.—Nitrous fumes were passed for 2—3 hours into a stirred solution of *m*-nitroacetanilide (10 g.) in a mixture of glacial acetic acid (150 c.c.) and acetic anhydride (50 c.c.) cooled to 8°. The nitroso-compound, which separated as a yellow oil on dilution of the resultant deep green solution with iced water, was immediately extracted with benzene (600 c.c.), and the extract, after being rapidly washed twice with iced water to remove acetic acid as far as possible, was kept at room temperature over anhydrous sodium sulphate, whereupon nitrogen was slowly evolved. After 24 hours the decanted solution was concentrated, and distillation of the residue at 200—205°/20 mm. gave 3-nitrodiphenyl (7 g., 63%), which crystallised from methyl alcohol in yellow plates, m. p. 58—59°. This method of preparation is an improvement on those of Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, 46, 2339) and of Blakey and Scarborough (J., 1927, 3003), which give 3-nitrodiphenyl in yields of 18 and ca. 15% respectively. The yield of 3-nitrodiphenyl depends on the quantity of nitrous fumes used and the speed at which they are introduced. Under-nitrosation results in contamination of the product with unchanged *m*-nitroacetanilide, and over-nitrosation leads to gross decomposition.

***m*-Terphenyl (Method II).**—Nitrous fumes were passed for 3 hours into a stirred solution of 3-acetamidodiphenyl (10 g.) (prepared from 3-nitrodiphenyl as described by Blakey and Scarborough, *loc. cit.*) in a mixture of glacial acetic acid (100 c.c.) and acetic anhydride (25 c.c.), containing phosphoric oxide (1 g.), cooled to 8°. The nitroso-compound, which separated as an oily solid when the resulting deep green solution was poured into excess iced water, was extracted with benzene (600 c.c.) and treated exactly as described above in the preparation of 3-nitrodiphenyl. After removal of excess benzene, the dark brown residue on distillation at 90°/10⁻² mm. gave *m*-terphenyl (2.6 g.), m. p. 89° from alcohol.

Nitration of *m*-Terphenyl.—(i) A solution of nitric acid (*d* 1.42, 20 c.c.) in glacial acetic acid (15 c.c.) was added to a solution of *m*-terphenyl (5 g.) in glacial acetic acid (50 c.c.) at 60°. No reaction was apparent at this temperature, but on heating at 85—90° for 2—3 hours nitrous fumes were evolved. The viscous yellow oil which separated on pouring the reaction mixture into water was extracted with ether, and the extract washed successively with dilute alkali and water. The residual oil obtained on removal of the ether gave, on distillation at 80°/10⁻² mm., 4'-nitro-*m*-terphenyl (4.5 g.) as a pale yellow oil, which could not be crystallised from the usual solvents and did not solidify on keeping for 15 months (Found : C, 78.5; H, 4.7. $C_{18}H_{13}O_2N$ requires C, 78.3; H, 4.9%). Reduction of 4'-nitro-*m*-terphenyl with stannous chloride in hydrochloric acid solution in the usual way yielded the amine which, however, could not be obtained in a crystalline state (cf. Wardner and Lowy, *loc. cit.*, who give m. p. 64°). On boiling with acetic anhydride, it gave 4'-acetamido-*m*-terphenyl, which crystallised from 60% alcohol in colourless needles, m. p. 116—117° (Found : C, 83.2; H, 6.1. $C_{20}H_{17}ON$ requires C, 83.6; H, 6.0%). Wardner and Lowy (*loc. cit.*) record m. p. 117° for their acetamido-*m*-terphenyl.

(ii) A mixture of *m*-terphenyl (2 g.) and nitric acid (*d* 1.42, 30 c.c.) was warmed to 80—90° with frequent shaking, the hydrocarbon gradually passing into solution. After a further 15 minutes the mixture was cooled, and the separated solid, crystallised several times from glacial acetic acid, gave a dinitro-*m*-terphenyl (0.4 g.) in small yellow prisms, m. p. 213—215°, apparently identical with the similar compound described by Wardner and Lowy (*loc. cit.*) who give m. p. 214° (Found : C, 67.1; H, 3.6. Calc. for $C_{18}H_{12}O_4N_2$: C, 67.3; H, 3.75%). From the original filtrate a yellow oil was obtained on dilution with water which corresponded in properties with the mononitro-compound described above.

(iii) Fuming nitric acid (*d* 1.5, 3.5 c.c.) was added dropwise during 15 minutes to a mixture of *m*-terphenyl (1 g.) and glacial acetic acid (5 c.c.) at 40°, and the solution finally heated at 100° for 1 hour. The addition of a few drops of water to the cold reaction mixture caused deposition of a yellow crystalline solid (1 g.), which separated from glacial acetic acid in pale yellow needles, m. p. 199—200°, apparently identical with the trinitro-*m*-terphenyl described by

Wardner and Lowy (*loc. cit.*), who record m. p. 204° (Found: C, 59.2; H, 3.3; N, 11.35. Calc. for $C_{18}H_{11}O_6N_3$: C, 59.2; H, 3.0; N, 11.5%).

Nitration of 4'-Nitro-m-terphenyl.—Fuming nitric acid (d 1.5, 3.5 c.c.) was added dropwise to a solution of 4'-nitro-*m*-terphenyl (0.5 g.) in glacial acetic acid (5 c.c.) at 30°, and the temperature was finally raised to 90° for 30 minutes. The yellow solid, which separated on dilution of the reaction mixture with water, crystallised from glacial acetic acid in yellow needles, m. p. 199—200° both alone and admixed with the trinitro-compound obtained by direct nitration of the hydrocarbon.

Oxidation of 4'-Nitro-m-terphenyl.—To a solution of the nitro-compound (2 g.) in hot glacial acetic acid (20 c.c.), a solution of chromic anhydride (10 g.) in a mixture of water (5 c.c.) and glacial acetic acid (20 c.c.) was added dropwise, and the mixture boiled for 5 hours under reflux; the product, which was precipitated by the addition of water, was filtered off, dissolved in ether, and extracted with alkali. Acidification of the alkaline extract precipitated 2-nitro-diphenyl-5-carboxylic acid (0.6 g.), which crystallised from alcohol in yellow plates, m. p. 220—221°, undepressed on admixture with an authentic specimen prepared as described below. Wardner and Lowy (*loc. cit.*) record m. p. 227° (after sublimation) for the acid obtained on oxidation of their nitro-*m*-terphenyl.

2-Nitro-5-methyldiphenyl.—4-Nitro-*m*-acetotoluidide (m. p. 86—87°) was prepared by nitration of *m*-acetotoluidide by the method of Cohen and Dakin (J., 1903, **83**, 333) in which it is formed in small yield together with the 6-isomeride, and was shown to be identical with a sample kindly supplied by Dr. A. McGookin of Liverpool University. Nitrosation of 4-nitro-*m*-acetotoluidide (5 g.) dissolved in a mixture of glacial acetic acid (100 c.c.), acetic anhydride (50 c.c.), and phosphoric oxide (1 g.) in the usual way gave an oily nitroso-compound, which was extracted with benzene (500 c.c.) and kept at 35°. After removal of benzene, the residue on distillation at 140—150°/1 mm., gave 2-nitro-5-methyldiphenyl (3.5 g.), which crystallised from alcohol in yellow needles, m. p. 86—87° (Found: C, 73.5; H, 5.1. $C_{13}H_{11}O_2N$ requires C, 73.2; H, 5.2%).

2-Nitrodiphenyl-5-carboxylic acid.—A solution of 2-nitro-5-methyldiphenyl (2.5 g.) in glacial acetic acid (40 c.c.) was refluxed with a solution of chromic anhydride (3 g.) in 80% aqueous acetic acid (12 c.c.) for 2 hours, and the product, precipitated with water, was filtered off, dissolved in ether, and extracted with alkali. Acidification of the alkaline extract gave 2-nitro-diphenyl-5-carboxylic acid (0.4 g.), which separated from alcohol in yellow plates, m. p. 220—221° (Found: C, 64.4; H, 3.8. $C_{13}H_9O_4N$ requires C, 64.2; H, 3.7%). Evaporation of the ethereal extract gave unchanged 2-nitro-5-methyldiphenyl.

Oxidation of Dinitro-m-terphenyl.—The dinitro-compound (0.4 g.), oxidised in boiling glacial acetic acid with excess chromic anhydride in the usual way, gave *p*-nitrobenzoic acid (0.1 g.), m. p. and mixed m. p. 238°. Apart from a small amount of starting material, no other product could be isolated.

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