

THE NITRATION OF TERPHENYLS

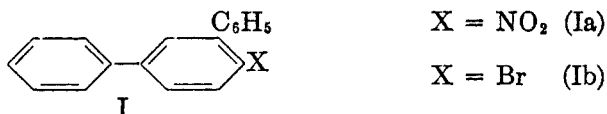
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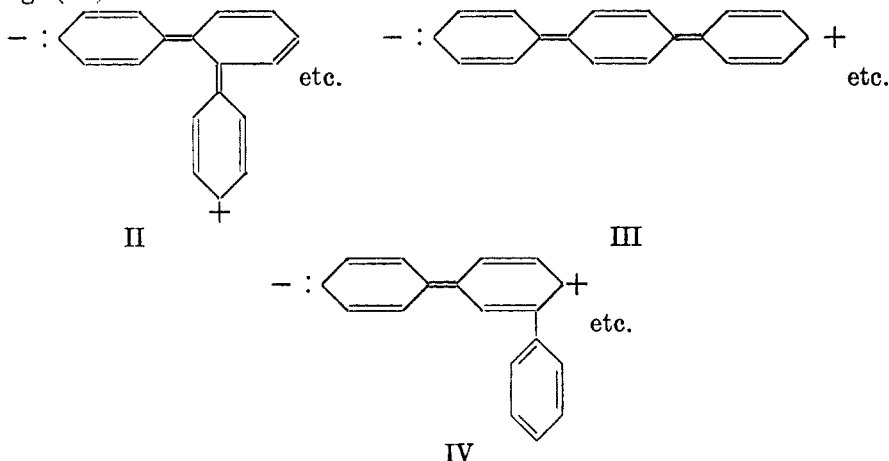
In connection with our investigation of the chemistry of *o*-terphenyl (1, 2, 3, 4, 5), the need arose for preparing monoamino derivatives of all the terphenyls. The most convenient procedure for their preparation appeared to be by reduction of the corresponding nitro compounds.

The usual method for securing nitro compounds, that is, employing a mixture of nitric and sulfuric acids, gives rise to polynitrated hydrocarbons. With *o*-terphenyl, for example, a mixture of unchanged hydrocarbon and polynitroterphenyls was obtained. The procedure in which ordinary fuming nitric acid (*d.* 1.49) in acetic acid is used, and which had been found satisfactory for the preparation of 4'-nitro-*m*-terphenyl (Ia) (6) failed to effect mononitration with *p*-terphenyl (7) and *o*-terphenyl. With *o*-terphenyl, when this procedure was used (with a 50% excess of nitric acid and the reaction heated for seventeen hours on a steam-bath), a large amount of *o*-terphenyl was recovered. The use of the stronger acid (*d.* 1.59) favored formation of dinitro derivatives.

This is not the only respect in which *m*-terphenyl differs from the other isomers. For example, *m*-terphenyl has been shown to undergo substitution invariably in the central ring (I) (6, 8, 9), whereas *o*- and *p*-terphenyl are attacked at the end carbon atom of an end ring.



It is possible that these differences in the chemical behavior of *m*-terphenyl are due to its inability to form resonance structures which involve interaction of all three rings, as can *o*-terphenyl (II) and *p*-terphenyl (III). With *m*-terphenyl, no resonance structures can be written which simultaneously involve more than two rings (IV).



However, this is probably only a partial explanation, for Pauling and Sherman (10) and Pullman (11) have indicated that the resonance structures which involve all three rings in the *ortho*- and *para*-terphenyls contribute to the complete structure of the molecules to a very small degree.

Eventually it was found that the desired mononitro-*o*-terphenyl could be obtained in the highest yield by carrying out the reaction in acetic acid and using a special mixture (2:1) of red, fuming (*d.* 1.59) and ordinary fuming (*d.* 1.49) nitric acids. The yields are still low, for there are always other products of nitration present, mostly isomeric mononitro compounds, which complicate the separation.

The procedure (2) previously described for preparing 4-nitro-*o*-terphenyl gave a mixture from which the desired isomer crystallized only after a year's standing, and the amine formed on reduction failed to remain crystalline. By the operations herein described a crystalline 4-nitro-*o*-terphenyl was obtained at once, and the amine is stable indefinitely.

Although 4-nitro-*p*-terphenyl had not hitherto been obtained by direct nitration (7), there was no difficulty in adapting the present procedure to *p*-terphenyl, and to 2,3,6-triphenyltoluene. Mononitro-4-butyl-*o*-terphenyl, similarly prepared, has been described in a previous paper (5).

In each instance, the nitro compounds were reduced to the corresponding amines. 4-*n*-Amylamino-*o*-terphenyl was obtained by direct alkylation of the amino compound.

EXPERIMENTAL

4-Nitro-o-terphenyl. A solution of 230 g. (1.0 mole) of Santowax O¹ in 500 ml. of glacial acetic acid was heated to 55–60°, and a solution of 50 ml. of fuming nitric acid (*d.* 1.49) and 100 ml. of red, fuming nitric acid (*d.* 1.59) was added dropwise during one hour. The temperature was kept at 55–60° by regulating the rate of addition and by cooling when necessary. The reaction mixture was then heated at the same temperature for five hours, cooled, and poured into 3000 ml. of water. It was allowed to stand overnight, whereupon the yellow tar became partially crystalline. The water was poured off, and the solid washed twice with water. Finally, the product was stirred with about 500 ml. of alcohol until it was completely crystalline and no lumps remained. It was filtered, washed with alcohol, and dried; the crude mixture of isomers weighed approximately 225 g. It was recrystallized from 2600 ml. of alcohol, with addition of sufficient 10% sodium carbonate solution to make the hot solution neutral to litmus.² Recrystallization from 1200 ml. of alcohol gave 104–110 g. (38–40%) of 4-nitro-*o*-terphenyl, melting at 111–114°.³ This is satisfactory for most purposes. The pure substance, which melts at 115.5–116.5°, can be obtained by repeated recrystallization from acetic acid.

¹ The Santowaxes are available commercially from the Monsanto Chemical Company. Santowax O contains approximately 95% *o*-terphenyl. Recrystallization of this material from ethanol before use, although raising its melting point 2 to 3°, did not improve the yield of the nitro compound.

² The solution was allowed to cool gradually to room temperature. Further cooling resulted in the separation of a mixture, containing a large amount of other isomers.

³ Concentration of the filtrates gave only oils or low-melting solids which resisted purification. When the oil resulting from complete removal of the solvent was distilled *in vacuo*, a 30 to 40% yield of a mixture of mononitroterphenyls was obtained (b.p. 186–191°/2 mm.). Separation of this mixture is difficult and impractical.

*Anal.*⁴ Calc'd for $C_{18}H_{13}NO_2$: C, 78.6; H, 4.7.

Found: C, 78.4; H, 4.5.

x-Nitro-o-terphenyl. Repeated recrystallization from ethanol and glacial acetic acid of the distillate obtained from the mother liquors in the preparation of 4-nitro-*o*-terphenyl (see footnote 3) yielded a small amount of an isomeric nitro-*o*-terphenyl. The compound crystallized from acetic acid as large, transparent, diamond-shaped crystals, m.p. 119.5°. The melting point of a mixture with 4-nitro-*o*-terphenyl was 88–102°.

Anal. Calc'd for $C_{18}H_{13}NO_2$: N, 5.1. Found: N, 5.1.

4-Amino-o-terphenyl. A hot solution of 140 g. of 4-nitro-*o*-terphenyl (m.p. 111–114°) in 1600 ml. of alcohol was placed in a low-pressure, copper bomb of 4500-ml. capacity. About 10 g. of Raney nickel and 5 g. of sodium carbonate were added, and hydrogen was introduced to a pressure of 50 lbs. The bomb was shaken and heated by steam until the absorption of hydrogen had ceased. It was necessary to introduce more hydrogen when the pressure dropped to 10–20 lbs. The hot reduction mixture was filtered by suction through a pad of Filter-Cel, the filtrate cooled to 0°, and the product removed by filtration. The first crop weighed 75.4 g., m.p. 117–118°. Concentration of the filtrate to 300 ml. gave an additional 41.8 g. (m.p. 116–117°), for a total yield of 117.2 g. (94%).

4-n-Amylamino-o-terphenyl. A mixture of 40 g. (0.163 mole) of 4-amino-*o*-terphenyl and 21.6 g. (0.204 mole) of *n*-amyl chloride was placed in a test tube (40 x 200 mm.) inside a 250-ml. bomb. Nitrogen was introduced to a pressure of 40 p.s.i. (2.7 atm.), and the bomb heated gradually, without shaking, to 180°. After one hour at 180–190°, the bomb was allowed to cool to room temperature. The product was removed, suspended in hot water, made alkaline with sodium carbonate, and extracted with ether. The ether solution was dried over potassium carbonate, and the ether evaporated. The residual oil was distilled *in vacuo*, yielding 22 g. (43%) of a nearly colorless, viscous oil with a strong blue fluorescence, b.p. 223–227° (4 mm.). Attempts to crystallize this oil were unsuccessful.

Anal. Calc'd for $C_{23}H_{25}N$: N, 4.4. Found: N, 4.6.

A *p*-nitrobenzanilide derivative was prepared by treatment of a dioxane solution of the amine and *p*-nitrobenzoyl chloride with 10% aqueous sodium hydroxide. The derivative separated as an oil which crystallized from alcohol after several days' standing. Two recrystallizations from alcohol yielded yellow prisms, m.p. 95.5–97°.

Anal. Calc'd for $C_{30}H_{23}N_2O_3$: N, 6.0. Found: N, 6.1.

4-Nitro-p-terphenyl. To a suspension of 23 g. (0.1 mole) of Santowax P¹ in 70 ml. of glacial acetic acid, heated to 98°, was added, dropwise, a solution of 10 ml. of nitric acid (*d.* 1.59) and 5 ml. of nitric acid (*d.* 1.49). The temperature was held at 95–98° during the addition, and for one-half hour thereafter. The mixture was allowed to cool, and the acid liquors were decanted from the solid product. The latter was suspended in water, filtered, and washed with water, soda solution, and a little ether. The crude yield was 19.7 g. (72%), m.p. 205–210°. Recrystallization from nitroethane raised the melting point to 210–214°. The value given in the literature (7) for 4-nitro-*p*-terphenyl is 212–213°.

4-Amino-p-terphenyl. A suspension of 10 g. of crude 4-nitro-*p*-terphenyl in 220 ml. of absolute alcohol was reduced in a manner similar to that used for 4-amino-*o*-terphenyl. When the reduction was complete, an additional 200 ml. of alcohol was added to dissolve the product completely in the hot solvent. This solution was filtered and cooled to give 5.0 g. (56%) of 4-amino-*p*-terphenyl; m.p. 200–201°. The value given in the literature (7) for 4-amino-*p*-terphenyl is 197–198°.

4'-Nitro-m-terphenyl. When the conditions used for the nitration of *o*-terphenyl were applied to Santowax M¹ (*m*-terphenyl), the yield of 4'-nitro-*m*-terphenyl (b.p. 189–194°/1 mm.) was low (23%), and a large amount (55%) of *m*-terphenyl was recovered. Since satisfactory methods for the preparation of 4'-nitro-*m*-terphenyl have been published (6, 13), no further attempt was made to adapt the present procedure to the nitration of *m*-terphenyl.

⁴ This sample was prepared by Miss E. R. Webster, formerly of these Laboratories.

4'-Amino-m-terphenyl. This compound was prepared by hydrogenation of the nitro compound over Raney nickel, and purified through the hydrochloride (9). The yield of amine in the form of pure white needles, m.p. 67–68°, was 34%.

x-Nitro-2,3,6-triphenyltoluene. A suspension of 5.0 g. (0.0156 mole) of 2,3,6-triphenyltoluene (12)⁵ in 25 ml. of glacial acetic acid was heated to 50°, and a solution of 1.5 ml. of nitric acid (*d.* 1.59), 0.75 ml. of nitric acid (*d.* 1.49), and 2 ml. of acetic acid was added in part. No reaction took place until the mixture was heated to 95–98°, at which temperature the remainder of the acid solution was added gradually. Complete solution soon took place, followed by the appearance of a white crystalline precipitate. Stirring was continued for one hour at 95–98°, and the mixture was then cooled, filtered, and washed with acetic acid. The yield was 3.8 g., m.p. 145–215°. After four recrystallizations from acetic acid, 1.1 g. (19%) of a pure nitro compound was obtained; m.p. 219.5–221.5°.

Anal. Calc'd for C₂₅H₁₉NO₂: N, 3.8. Found: N, 3.7.

x-Amino-2,3,6-triphenyltoluene. A suspension of 1.0 g. of this nitro compound in 100 ml. of absolute alcohol was reduced over Raney nickel. The yield of the amine in the form of pure white needles, m.p. 193–194°, was 0.75 g. (82%).

Anal. Calc'd for C₂₅H₂₁N: N, 4.2. Found: N, 4.1.

SUMMARY

Suitable conditions have been found for preparing mononitration products of several terphenyls. The corresponding amines and related compounds are also described.

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⁵ We are indebted to Mr. J. A. VanAllan of these Laboratories for a supply of this compound.