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The Chemistry of *o*-Terphenyl. II. Derivatives Prepared from the Hydrocarbon

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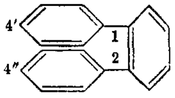
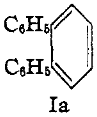
The chemical behavior of *o*-terphenyl has not hitherto been determined, mainly on account of its inaccessibility.[1] All derivatives reported in the literature have contained the substituent groups in the central ring. They have resulted from degradation of more complex molecules or from diene syntheses.[2] Indeed, this last reaction furnishes the most suitable procedure for synthesizing such derivatives. Having accumulated a supply of the hydrocarbon,[3] its reactions were investigated, using standard procedures. Predictions as to the position to be taken by entering groups would vary according to which mode of representation was used. Thus, formula Ia would lead one to expect substitution on the central ring, while I would suggest the more likely possibilities of groups entering the side rings. The system of numbering adopted regards the side rings as substituents, and the numbers are, therefore, primed.[3]



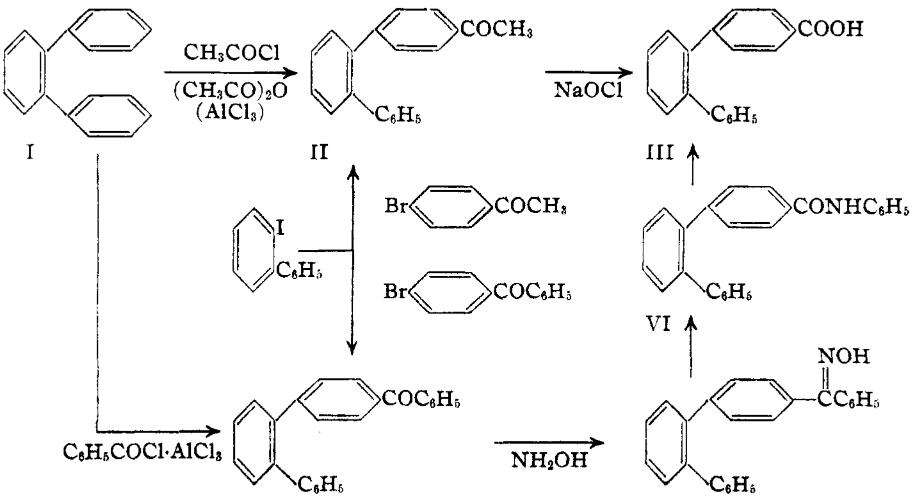
I



Ia

The Friedel–Crafts reaction was of particular interest because the first simple degradation product previously secured had been a benzoyl-*o*-terphenyl[2a]; this was not identical with the ketone found by the action of benzoyl chloride upon *o*-terphenyl in the presence of anhydrous aluminum chloride. Since the latter reagent, by itself or in a melt with sodium chloride gives rise to side reactions,[3] a mixture of products usually results.

CHART I



4'-Acetyl-*o*-terphenyl II is secured by the action of acetyl chloride or acetic anhydride upon the hydrocarbon in the presence of anhydrous aluminum chloride. It was also synthesized by a Wurtz reaction from *o*-iodobiphenyl and *p*-bromoacetophenone, to confirm its structure. By means of sodium hypochlorite, it was converted to the 4'-carboxylic acid III.

When benzoyl chloride was employed, a difficultly separable mixture resulted, but by using the Perrier double compound, $C_6H_5COCl\cdot AlCl_3$, a phenyl ketone IV was obtained in high yield and purity. The same ketone was also secured by a Wurtz synthesis. This ketone gave an oxime V, which formed an anilide VI by the Beckmann rearrangement; hydrolysis of the anilide furnished 4'-carboxy-*o*-terphenyl III and aniline. These reactions are summarized in Chart I.

Bromination, as would be anticipated, gave a mixture, but by variations in technique it was possible to isolate several homogeneous substitution products. The first homogeneous product is 4',4''-dibromo-*o*-terphenyl, VII. The structure was determined by oxidation, when *p*-bromobenzoic acid was secured; therefore, in the dibromo derivative the bromine atoms are in the para position.

The further action of bromine gave first a tribromo and then a tetrabromo substitution prod-

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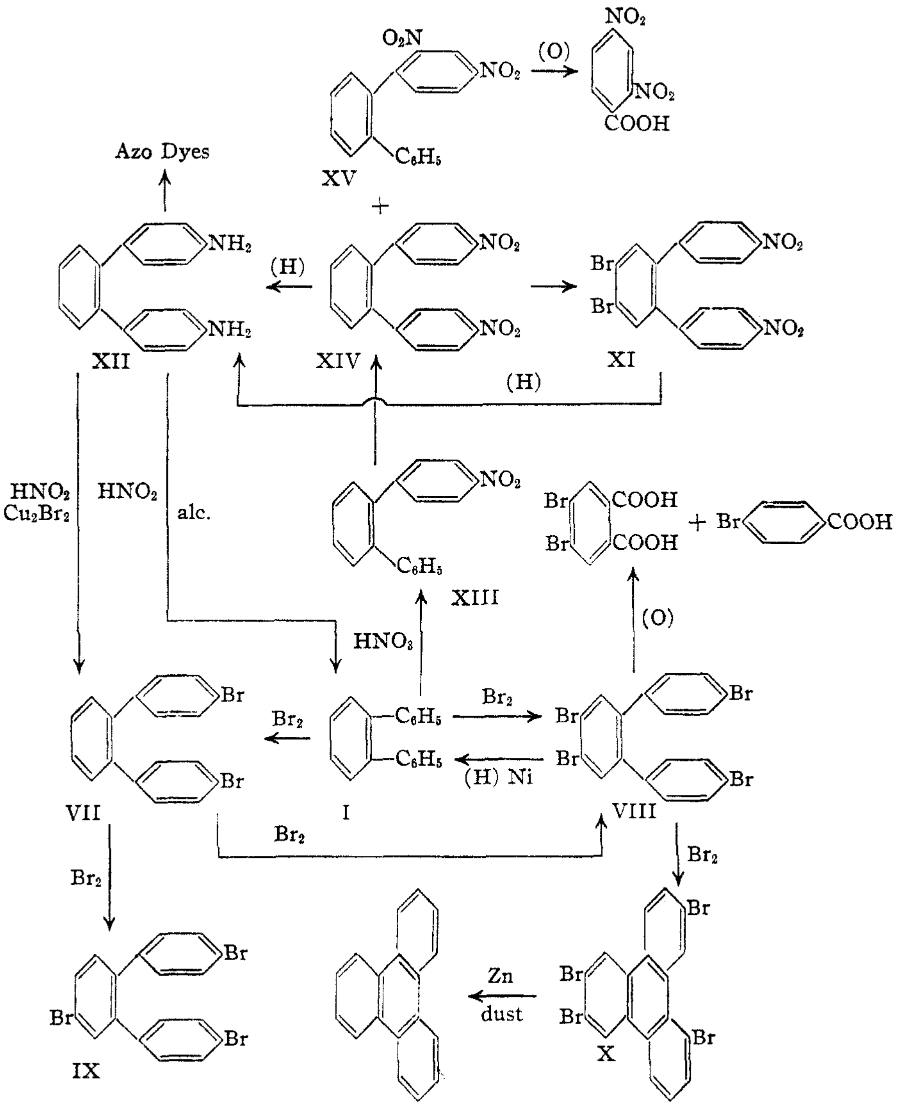
[1] It has recently been called to our attention by Dr. R. L. Jenkins, of the Monsanto Chemical Company that their product, "Santowax O," is about 85% *o*-terphenyl.

[2] (a) Allen and Spanagel, THIS JOURNAL, **55**, 3773 (1933); (b) Allen, Bell, Bell and VanAllan, *ibid.*, **62**, 656 (1940); (c) Allen and VanAllan, *ibid.*, **64**, 1260 (1942).

[3] Allen and Pingert, *ibid.*, **64**, 1365 (1942).

CHART II



uct. Upon oxidation of the latter a large amount of *p*-bromobenzoic acid and a small quantity of 4,5-dibromophthalic acid were produced; the substance is, therefore, 4,4′,4″,5-tetrabromo-*o*-terphenyl, VIII. The tribromo derivative, IX, has the bromine atoms in the 4,4′,4″-positions, for (a) further bromination gives the tetrabromo-*o*-terphenyl, and (b) oxidation gives a high yield of *p*-bromobenzoic acid. The end-product of the action of bromine is 3,5,10,11-tetrabromotriphenylene, X, the halogen acting as a dehydrogenating agent, upon the tetrabromo-*o*-terphenyl. That the four-ring system is present is shown by the formation of triphenylene on zinc dust distillation.

4′,4″-Dinitro-*o*-terphenyl gives a dibromo derivative, XI, upon bromination, which presumably has the bromine atoms in the same positions as the tetrabromo compound, for it has the same general appearance and physical properties. The melting points are identical and there is no depression on admixture—one of the uncommon instances in which two different substances have no effect on their respective melting points. On reduction by hydrogen in the presence of Raney nickel, the bromine is removed and the corresponding amine, XII, is found—thus triphenylene ring closure has not occurred. Attempts to synthesize 4′,4″-dicyano-*o*-terphenyl by the Rosenmund method were unsuccessful. The reactions are shown in Chart II.

Nitration gives first the 4′-nitro derivative, XIII, and then a mixture of two isomeric dinitro-*o*-terphenyls; the nature of the product is largely controllable according to the experimental conditions. One of the dinitro derivatives is the 4′,4″-isomer, XIV, and the other is the 2′,4′-isomer, XV, since upon oxidation the former gives only *p*-nitrobenzoic acid, and the latter, 2,4-dinitrobenzoic acid. Mixed acid gave a mixture of products that appeared to contain some of a trinitro derivative.

Reduction of the nitro compounds yields the corresponding amines; the 4′,4″-diamine, XII, was converted by means of the diazo reaction into (a) *o*-terphenyl, showing the ring system was still intact, and (b) 4′,4″-dibromo-*o*-terphenyl, VII, thus affording additional proof of structure in both series. The diamine was also diazotized and coupled with some of the common naphthalene dye intermediates to give azo dyes.

Experimental

The behavior of *o*-terphenyl in chemical reactions is very subject to slight changes in technique, and an understanding of certain of its peculiarities is essential for successful repetition of the procedures. Under comparable conditions, it is less active than the meta- and para-isomers, so that some degree of forcing may be necessary to initiate a reaction. However, complications due to isomerization and ring closure[3] render it important not to drive the reactions to completion in most instances. Mixtures are thus produced, the separation of which is not always readily accomplished; if the conditions are such as to favor the formation of products in molecular proportions, the mixed crystals may defy as many as twenty fractional crystallizations from several solvents.

One of the obscure factors that may influence the experimental results is the solvent from which the hydrocarbon was crystallized. This effect is not understood. As an example, traces of moisture or alcohol favor polybromination; this is in line with the view that aromatic halogenation proceeds through an ionic mechanism.[4] *o*-Terphenyl and some of its derivatives retain traces of solvent very tenaciously; one-quarter to one-half per cent. of ethanol is not removed over a long period of time *in vacuo;* this affects analytical results only slightly, but may determine the course of substitution to a large degree. Small amounts of acetic acid have a strong inhibiting effect upon bromination and nitration; it is also possible to boil glacial acetic acid solutions of the hydrocarbon with bromine or fuming nitric acid without appreciable substitution.

A. The Ketones, I; 4'-Benzoyl-*o*-terphenyl; 4-*o*-Xenylbenzophenone, II. (a). Friedel-Crafts Synthesis.—To the Perrier double compound from 1.4 g. each of benzoyl chloride and aluminum chloride in 8 cc. of carbon disulfide was added 2.3 g. of *o*-terphenyl, and the mixture was refluxed for a half hour, left at room temperature for several hours and again refluxed a half hour. It was then decomposed in the usual manner, extracting with ether; on evaporation, the residue, 3.3 g., was steam-distilled from a solution made alkaline by 1 g. of potassium carbonate—only a trace of unchanged hydrocarbon was removed. The ketone was taken up in ether, treated with decolorizing carbon, and the solvent removed. After recrystallization from absolute ethanol, the ketone formed compact prisms, m. p. 111°. It crystallizes readily from dry methanol and benzene.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.8; H, 5.4. Found: C, 89.3; H, 5.3.

(b) **Ullmann Synthesis.**—An intimate mixture of 5 g. each of *p*-bromobenzophenone and *o*-iodobiphenyl, and 10 g. of copper bronze[5] was heated in a sealed tube at 240° for four hours. The contents were then extracted with benzene in a Soxhlet apparatus, and the extract distilled *in vacuo*, collecting the portion boiling above 190° at 3 mm. After a redistillation, the substance was fractionally crystallized from absolute ethanol, when 0.35 g. of *o*-xenylbenzophenone was secured. There was no depression of melting point when mixed with the ketone described in (a).

(c) **The Oxime, V.**—This was obtained in two modifications, the lower-melting form first obtained changing into the higher-melting on standing, or inoculating, or in the presence of hydrochloric acid. Once the higher-melting point had been obtained, it was thereafter impossible to isolate the low-melting form again.

A solution of 200 mg. of the purest ketone in 7 cc. of ethanol was mixed with an equal weight of hydroxylamine hydrochloride, and 15 drops of 35% sodium hydroxide was added. After gently refluxing for four hours, it was diluted with 28 cc. of water and acidified to litmus with *sulfuric* acid (*hydrochloric* acid gave the higher-melting form at once). After a thorough washing it was recrystallized from absolute ethanol, and then from petroleum ether at −60°. The oxime (210 mg.) then had a melting point of 68°. As described above, it changed to another form, which melted at 138°, showing a barely perceptible shrinking at about 68°. Both oximes gave the same anilide.

Anal. Calcd. for $C_{25}H_{19}ON$: N, 4.0. Found: N, 4.2, 4.0.

(d) **Hydrolysis of the Anilide to 4'-Carboxy-*o*-terphenyl, III.**—The anilide was not easily hydrolyzed without resinification. The best procedure was to reflux a mixture of 0.15 g. of anilide, 50 cc. of ethanol, and 15 cc. of 40% sodium hydroxide for seventy-two hours. After acidification and three recrystallizations, the acid (yield, 0.1 g.) was pure; m. p. 203°.

II. 4'-Acetyl-*o*-terphenyl, II.—(a) **Direct acetylation of the hydrocarbon** in solution invariably leads to mixtures, the aluminum chloride causing rearrangements.[3] Until a pure specimen is available for inoculation, it is almost a hopeless task to try to separate the mixtures. When acetic anhydride in nitrobenzene was used, the decomposed reaction product was extracted with ether, and this extract shaken two hours with Norite (without this treatment crystallization did not take place). The yield of ketone was 2.1 g., m. p. 94°; from 9.2 g. of *o*-terphenyl. After two months, 2.6 g. more of the less pure ketone, m. p. 93°, had separated, making the total yield 43%. Acetyl chloride, or carbon disulfide as a solvent, resulted in low-melting ketone.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.2; H, 5.9. Found: C, 88.0; H, 5.8.

(b) **Ullmann Synthesis.**—A mixture of 22 g. of *o*-iodobiphenyl and 19.4 g. of *p*-iodoacetophenone was heated

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(4) Price, *Chem. Rev.*, **29**, 39 (1941).

(5) "Org. Syntheses," **20**, 46 (1940).

TABLE I

PROPERTIES OF BROMINATED HYDROCARBONS

No.	Substituents	M. p., °C.	Crystal form	Empirical formula	Analyses, % Calcd.	Analyses, % Found
VII	4′,4″-Dibromo-	170[a]	Rods or leaflets	$C_{18}H_{12}Br_2$	41.2	41.1
IX	4,4′,4″-Tribromo-	170[a,e]	Rods	$C_{18}H_{11}Br_3$	51.4	52.2
VIII	4,4′,4″,5-Tetrabromo-	228[b,d]	Prisms	$C_{18}H_{10}Br_4$	58.3	58.2
X	3,5,10,11-Tetrabromotriphenylene	+450[c]	Microcrystalline powder	$C_{18}H_8Br_4$	58.8	58.7

[a] Mixed melting point, about 155°. [b] In one instance, an isomer, m. p. 120°, with previous sintering, was isolated—it contained 58.4% bromine. [c] On a copper block; a specimen, synthesized from triphenylene, melted at the same point under the same conditions. [d] A 1:1 mixture of tri- and tetrabromo compounds, m. p. 212–214°, often crystallized—it could not be separated by crystallization. [e] Mol. wt. calcd., 467; found (in benzene) 469, 479.

with stirring in an oil-bath until the temperature had reached 220°. Then 40 g. of activated[5] copper bronze was added over a period of one hour. After cooling, the acetone extract was distilled in a Hickman vacuum (at about 3 micra). The fraction that passed over at 200–205° was fractionally crystallized from absolute ethanol; the yield was 6.7 g.

(c) **Oxidation with sodium hypochlorite** in aqueous methanol gave 4′-carboxy-*o*-terphenyl, m. p. 203°, identical with the product from the phenyl ketone, described above.

B. Bromination.—The three isomeric terphenyls in the crystalline state in aqueous suspension react readily with bromine; *o*-terphenyl exhibits this behavior more strongly than the isomers. Furthermore, it is practically impossible to brominate *o*-terphenyl dissolved in an organic solvent, though there is no difficulty with the isomers. The products of the bromination are mixtures, whatever the technique, but certain individuals predominate in each variation. In some instances, elution by a solvent removes a considerable quantity of undesirable by-products. In practically every case it is essential to submit the mixture of products to systematic fractional crystallization.[6] Glacial acetic acid seems to be the most generally useful solvent. In some instances, polybrominated products are very soluble and are largely removable in the first wash, along with unreacted hydrocarbon. Since space requirements prohibit the complete detailed procedures, only a brief description of the more essential features of each bromination will be given.

i.—Solid *o*-terphenyl and dry bromine vapor in a closed vessel at room temperature gave mainly di-, tri-, and tetrabromo-*o*-terphenyls. The hydrocarbon slowly liquefies and resolidifies; at this point the yield of 4′,4″-dibromo-*o*-terphenyl is at the maximum. The time (two to twenty hours) depends upon variable factors, such as size of the run.

ii.—Similar conditions but in the presence of water vapor; here the tribromo compound predominates. The same result is attained if the hydrocarbon is ground in a mortar with water, and triturated with bromine for short periods of time. A curious but unexplained observation is that in the presence of water the tribromo compound is the end-product.

iii.—Longer exposure (one to thirty days) to bromine by either of the foregoing procedures; in this case the tetrabromo-*o*-terphenyl predominates. If this is desired as a principal product, it can be obtained very quickly by adding solid hydrocarbon to excess liquid bromine, evaporating to dryness, and separating the polybromotriphenylenes.

iv.—Further exposure of the lower bromo compounds to bromine either as vapor or liquid first gives the tetrabromotriphenylene, X, *quantitatively* which is further very slowly polybrominated, but no other pure individual substance was isolated. The triphenylene derivatives have high melting points (450–600°) and are easily removed because of their relative insolubility.

The properties of the various brominated products are collected in Table I.

Ring closure of the tetrabromo-*o*-terphenyl to the tetrabromotriphenylene was brought about by heating with nitrating acid, and separating the resinous mixture by suitable manipulations. This reaction thus affords confirmatory proof that the tetrabromo-*o*-terphenyl is still open-chained; *i. e.*, the ring has not been closed in the brominations.

V. Proofs of Structure.—(a) **4′,4″-Dibromo-*o*-terphenyl** was oxidized in the usual manner, using chromium trioxide in acetic acid for forty-eight hours. The yield of *p*-bromobenzoic acid was 58%; it was identified by comparison with an available specimen.

(b) **4,4′,4″,5-Tetrabromo-*o*-terphenyl** was synthesized by further bromination of 4′,4″-dibromo-*o*-terphenyl, thus locating two of the bromine atoms. Upon oxidation with chromium trioxide in acetic acid for four days and appropriate manipulation, a 60% yield of *p*-bromobenzoic acid was isolated, showing that none of the additional bromine had entered the end rings already containing bromine. There was also isolated a small amount of 4,5-dibromophthalic acid, identified by conversion to the anhydride, m. p. 215°, and identical with a sample at hand.[7]

(c) **3,5,10,11-Tetrabromotriphenylene** was reduced by heating micro samples with zinc dust in a 10-in. capillary tube; the triphenylene sublimed into the upper end of the tube. This was cut off and the hydrocarbon identified as such by comparison with an authentic sample. The ordinary macro zinc dust distillation takes place too slowly and yields mixtures.

VI. 3,6-Dimethyl-4,4′,4″,5-tetrabromo-*o*-terphenyl, m. p. 205°, was prepared by a similar procedure from some available 3,6-dimethyl-*o*-terphenyl.[2c]

Anal. Calcd. for $C_{20}H_{14}Br_4$: Br, 55.8. Found: Br, 55.8.

Upon oxidation only *p*-bromobenzoic acid was isolated. In this substance, the bromine atoms can only be in the

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(6) The material losses are prohibitive unless the purification is carried out in accordance with some such procedure, recombining all mother liquors and recovering all residues.

(7) We are indebted to Dr. C. V. Wilson for this authentic specimen.

4,5-positions of the central ring, the 3 and 6 positions being occupied by methyl groups.

C. Nitration. I. 4′-Nitro-*o*-terphenyl, XIII, and Related Products.—(a) To a solution of 23 g. of *o*-terphenyl in 150 cc. of 99–100% acetic anhydride below 0° was added, dropwise, and with stirring, 8.5 cc. of nitric acid (sp. gr. 1.44). The temperature was kept below 5° for two hours, then allowed to rise to room temperature and stirred overnight. It was then poured upon ice and sodium carbonate, and, when all the acid had been neutralized, extracted with ether. The dried ether extract was concentrated and 2–3 g. of dinitro derivatives filtered; a small further amount was filtered on further concentration, rinsing the solid with dry ether. The combined filtrate and rinse was redried over anhydrous magnesium sulfate and the residual oil after removal of the solvent distilled *in vacuo.* After recovering about 1 g. of hydrocarbon, the fraction, b. p. 180–200° (3 mm.), was collected and redistilled (b. p. 191–193° (3 mm.)); the yield was 21.6 g. (78%) of a thick oil which solidified to a honey-colored glass. After one year, during which it was remelted and resolidified several times, it crystallized. It separates in flakes from acetic acid, m. p. 105–106°.

Anal. Calcd. for $C_{14}H_{13}O_2N$: N, 5.1. Found: N, 5.3.

(b) **4′-Amino-*o*-terphenyl.**—Reduction was carried out in alcoholic solution in the presence of a Raney nickel catalyst. It crystallizes in rosets of fine needles; the melting point, at first 108°, drops, on standing, to 103–104° and the amine becomes slightly pasty.

Anal. Calcd. for $C_{18}H_{15}N$: N, 5.8. Found: N, 6.1.

The benzoyl derivative, obtained through a Schotten–Baumann reaction, formed needles when crystallized from absolute ethanol; m. p. 175°.

Anal. Calcd. for $C_{25}H_{19}ON$: N, 4.0. Found: N, 3.9.

II. 4′,4″-Dinitro-*o*-terphenyl, XIV; (a) From *o*-Terphenyl.—A solution of 6.9 g. of the hydrocarbon in 50 cc. of 99–100% acetic anhydride was treated, dropwise, with 5 cc. of fuming nitric acid (sp. gr. 1.52) at 10°; after two hours, cooling was discontinued—a solid slowly separated. The mixture was decomposed as usual by iced sodium carbonate, ether extracted, and the solid filtered; the ether contains most of the mononitro compound and any unreacted hydrocarbon. The solid (6.4 g.) was fractionally crystallized from acetic acid, giving about equal amounts of the 4′,4″-dinitro-*o*-terphenyl, m. p. 218°, and its 2′,4′-isomer, m. p. 169°—this is more soluble.

Anal. Calcd. for $C_{18}H_{12}O_4N_2$: N, 8.8. Found: (4′,4″-) N, 8.7; (2′, 4′-) N, 8.7.

(b) **From Mononitro Derivative in Ia.**—A solution of 5 g. of XIII in 120 cc. of acetic anhydride was cooled to 10°, and five 2-cc. portions of fuming nitric acid were added. After allowing to stand overnight and working up in the usual way, 6 g. of material was obtained, from which 3.1 g. of 4′,4″-dinitro-*o*-terphenyl was isolated after several recrystallizations.

(c) **Oxidation.**—This was carried out by the customary procedure using chromium trioxide in acetic acid overnight. The yield of *p*-nitrobenzoic acid from the 4′,4″-dinitro-*o*-terphenyl was 56%; a mixed melting point was not depressed. The 2′,4′-isomer gave 2,4-dinitrobenzoic acid, m. p. 181°.[8]

(d) **4′,4″-Diamino-*o*-terphenyl, XII,** was secured by reduction of the corresponding nitro compound essentially as described under the monoamine. It crystallizes in hard, waxy rosets from absolute ethanol, m. p. 149°.

Anal. Calcd. for $C_{28}H_{20}O_2N_2$: N, 6.7. Found: N, 6.6.

It is stable in an inert atmosphere, but in the laboratory air soon turns waxy and the melting point falls.

The diamine was tetrazotized in the usual way, except for the replacement by hydrogen reaction, which will be described below. It is essential to work in dilute solutions (1.5 g. per liter) to avoid resin formation. For the Sandmyer reaction, the tetrazotized solution was run into a 48% hydrobromic acid solution containing freshly prepared cuprous bromide. The 4′,4″-dibromo-*o*-terphenyl was filtered and recrystallized from acetic acid. It was identical with the product of dibromination.

For the reduction reaction, 0.64 g. of diamine in 50 cc. of cold, absolute ethanol, containing 10 cc. of concentrated sulfuric acid, was tetrazotized at 0°. It was then warmed gently in warm tap water, and finally heated on the steam-bath. After dilution with water, the doughy precipitate was manipulated, and 0.14 g. (22%) of *o*-terphenyl isolated and identified. The remainder had a phenolic odor and failed to crystallize.

A separately prepared tetrazo solution was coupled with alkaline β-naphthol; an immediate scarlet precipitate was formed; it melted, with decomposition, at 209°. Analysis indicated that but one end had coupled, the other, apparently, having been hydrolyzed to a phenolic group.

Anal. Calcd. for $C_{28}H_{20}O_2N_2$: N, 6.7. Found: N, 6.6.

Other, water-soluble dyes will be described in a later paper.

(e) **4′,4″-Dinitro-4,5-dibromo-*o*-terphenyl, XI,** was prepared by exposing the dinitro-*o*-terphenyl to bromine vapor for twenty-four hours, as described under bromination. Purification was accomplished through the judicious use of alcohol and acetic acid; there is some insoluble material, presumably the corresponding triphenylene derivative. The dibromodinitro derivative crystallizes in fine rods, m. p. 228°.

Anal. Calcd. for $C_{18}H_{10}O_4N_2Br_2$: N, 5.9. Found: N, 6.2.

Summary

The chemical behavior of *o*-terphenyl has been determined in the Friedel–Crafts reaction, and with the reagents bromine and nitric acid. The structures of the resulting substances have been determined; their reactions and those of related products are described.

ROCHESTER, N. Y. RECEIVED JULY 21, 1942

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[8] Claus and Habberstadt, *Ber.*, **13**, 815 (1880).