

Synthesis of meta-Terphenyl-2,4,6,2',5',2'',4'',6''-D₈

P. Ph. H. L. OTTO*, F. STEIN* and G. JUPPE**

* Central Laboratory TNO, Delft, Netherlands.

** Euratom, CCR, Ispra, Italy (1).

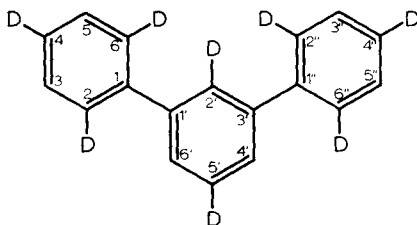
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SUMMARY

A synthesis of meta-terphenyl-2,4,6,2',5',2'',4'',6''-D₈ has been carried out. From iodobenzene-2,4,6-D₃ and 2,6-dibromo-1,4-dinitrobenzene, the compound 2',5'-dinitro-meta-terphenyl-2,4,6,2'',4'',6''-D₆ is formed (Ullmann reaction). By reduction of the nitrogroups and subsequent reductive diazotization, two deuterium atoms are introduced into the centre ring at positions 2' and 5'. The labelled meta-terphenyl has been obtained in 15 % yield, based on labelled iodobenzene. Deuterium substitution is $\geq 98\%$ at positions 2,4,6,2',5',2'',4'' and 6'', and $\leq 1\%$ at the other positions.

1. — INTRODUCTION

For the study of properties of organic reactor coolants, a series of specific deuterated terphenyls were desired. This report describes the synthesis of one of these, meta-terphenyl-2, 4, 6, 2', 5', 2'', 4'', 6''-D₈.



Direct deuteration of the meta-terphenyl molecule specifically at these positions, or direct introduction of groups which can be replaced by deuterium, does not seem feasible. The synthetic route followed, therefore, includes, as one of the reaction steps, the connection of properly substituted aromatic rings : in a double Ullman reaction 2', 5'-dinitro-meta-terphenyl is formed

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from labelled iodobenzene and 2,6-dibromo-1,4-dinitrobenzene (see Fig. 1). The nitrogroups have a favourable influence on the course of this reaction[1]; in two following steps : catalytic reduction to aminogroups and subsequent diazotization and reduction in deuterated hypophosphorous acid, the nitrogroups are replaced by deuterium.

The possibility of randomization of the deuterium distribution in the outer benzene rings during the Ullman reaction, or during the catalytic reduction of the nitrogroups, has been a point of concern. In order to obtain evidence on the deuterium distribution in the final product, the deuterium contents of the meta-terphenyl- D_8 and degradation compounds according to the scheme shown in Figure 2, were determined. Similar reaction steps had been used previously for degradation of tritiated polyphenyls ^(5, 6, 7). It was then shown that neither isotope effects nor aromatic tritium/hydrogen exchange play a part. Randomization in the outer rings would result in decreased deuterium content in methyl 3,5-dinitrobenzoate- D_3 .

The deuterium content in 4'-nitro-meta-terphenyl- D_8 could prove that no deuterium is found at position 4'. The preparation of 4'-nitro-meta-terphenyl by nitration of meta-terphenyl is described in the literature ^(8, 9, 10). However, our results showed that the nitro-meta-terphenyl obtained is a mixture of isomers and therefore no conclusions could be drawn about the positions of the deuterium atoms in the centre ring. Further nitration led to pure 4,4',4''-trinitro-meta-terphenyl- D_8 . As to the method for introducing deuterium into the centre ring, reductive diazotization has sometimes been used in connection with specific labelling, for example : Best and Wilson ⁽³⁾ prepared benzene-1,3,5- D_3 from aniline-2,4,6- D_3 and found that the deamination process did not affect the nuclear hydrogen atoms; for the case of 2-amino-para-terphenyl we could prove that in the deamination reaction with tritiated hypophosphorous acid, the hydrogen isotope is introduced exclusively on the 2-position ⁽⁷⁾. So, fortunately, there is not much doubt about the position of the deuterium atoms, introduced in the last step into the centre ring of the meta-terphenyl molecule.

Deuterium analyses have been carried out by means of mass spectroscopy and N. M. R. From the average numbers of deuterium atoms per molecule, found for meta-terphenyl- D_8 and degradation products, the degree of deuterium substitution at several positions of the meta-terphenyl molecule has been calculated.

2. — MATERIALS AND METHODS

Iodobenzene-2,4,6- D_3 can be obtained from labelled aniline ^(2,3,4). Aniline-2, 4, 6, N, N- D_5 deuteriochloride was prepared by exchange between aniline hydrochloride and heavy water; equilibrium was attained in 24 hours at 100° C ^(3, 11).

Deuteration of the aromatic nucleus is exclusive at the ortho and

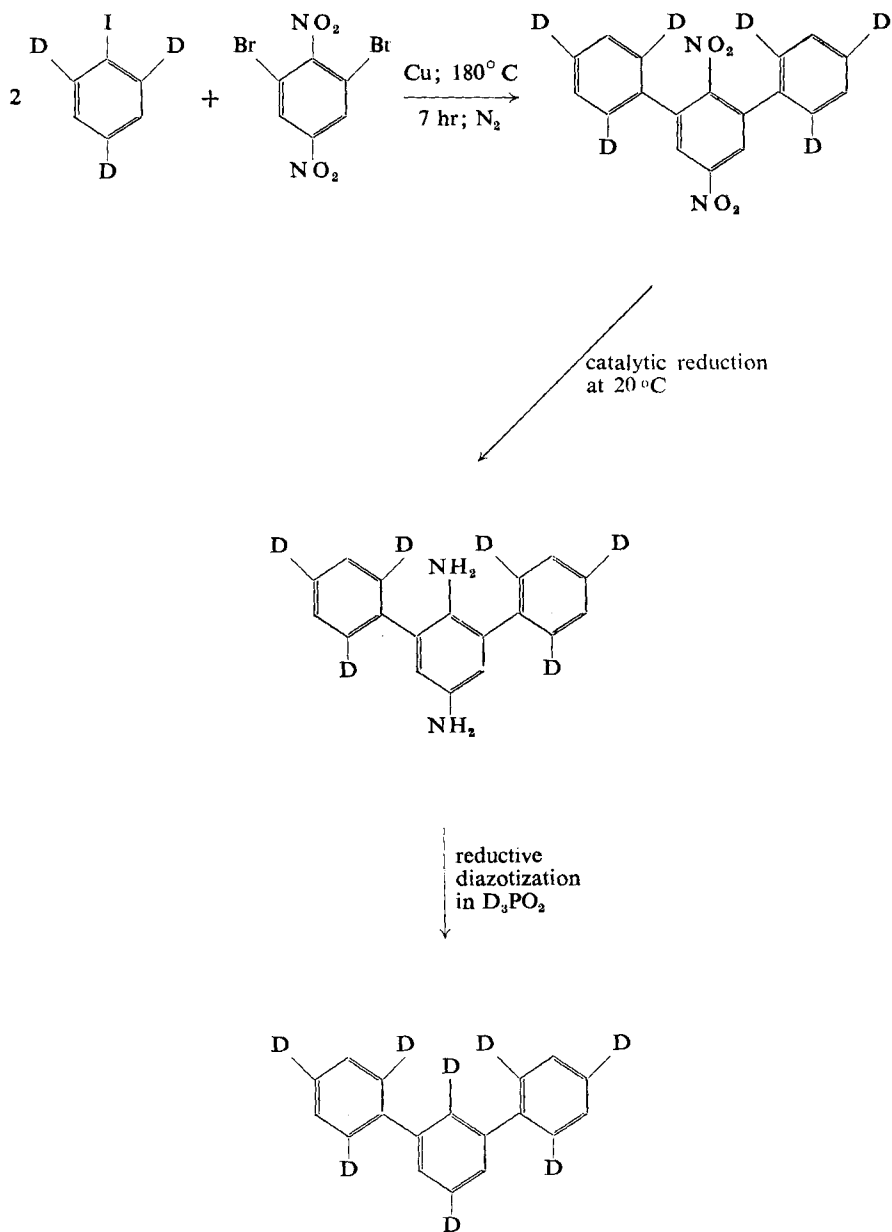


FIG. 1. Synthesis of meta-terphenyl-D₈

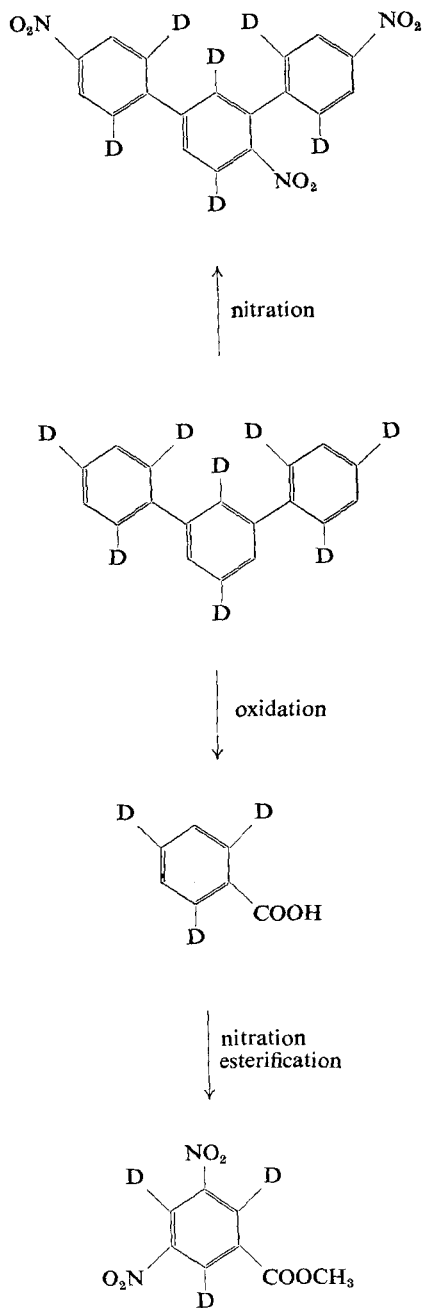


FIG. 2. Degradation of meta-terphenyl

para positions ⁽²⁾. We checked this by heating aniline hydrochloride with tritiated water for 6 days at 100° C; the specific activity of the aniline-2,4,6-T hydrochloride was 13 $\mu\text{C}/\text{mM}$, and that of 2,4,6-tribromoaniline prepared from it was $\leq 3.10^{-3} \mu\text{C}/\text{mM}$.

Iodobenzene-2,4,6-D₃ was obtained from aniline-2,4,6,N,N-D₅ deuterochloride by diazotization in the presence of potassium iodide ^(12 p. 598). The result shows that there is no loss of deuterium from the aromatic nucleus in this reaction.

2,5-Dibromo-1,4-dinitrobenzene is described in the literature ⁽¹³⁾. The compound was more conveniently prepared from 2,6-dibromo-4-nitroaniline by oxidation with hydrogen peroxide in acetic acid (compare with ⁽¹⁴⁾).

The Ullmann reaction. In first experiments, the reaction was carried out with 2 moles of iodobenzene per one mole of 2,5-dibromo-1,4-dinitrobenzene. It was found that addition of excess iodobenzene near the end of the reaction has the advantage of reducing considerably the amount of monosubstitution product, 3-bromo-2,5-dinitrobiphenyl, which is difficult to separate from 2',5'-dinitro-meta-terphenyl. The yield of the latter compound, based on iodobenzene, is also slightly increased.

Reduction of 2',5'-dinitro-meta-terphenyl. In exploratory experiments we searched for mild reaction conditions (low temperature, short reaction times) in order to minimize the possibility of randomization of deuterium in the outer rings. A series of reductions were carried out in ethanol at 20° C with hydrogen in the presence of these catalysts : Raney-nickel, palladium on barium sulphate, palladium on carbon or platinum black. In all cases, the first nitro group was quickly reduced, but then the reaction slowed down. Reaction times varied from one and a half hours for platinum black to 5 hours or more for the other catalysts. This behaviour may be attributed to stabilization by resonance between the nitro and amino group in para positions. Best results were obtained when the reduction was carried out in ethanol containing hydrochloric acid, with hydrogen in the presence of platinum black, at 20° C. The reaction was completed in 30-40 minutes. We also tried some reductions with hydrazine. A reduction carried out in ethanol in the presence of a catalyst, required a temperature of 80° C for several hours. Reduction with hydrazine alone, carried out in glycol, required 150° C for three hours and led to a mixture of products, which were not further investigated.

Reductive diazotization ⁽¹⁵⁾. In the reduction of diazonium salts with hypophosphorous acid, a hydrogen atom directly bound to phosphorous substitutes the diazonium group ⁽¹⁶⁾. Deuterated hypophosphorous acid can be obtained by deuterium exchange between the free acid and deuterium oxide ^(17, 18). The isotope effects on the exchange equilibrium and on the reaction rate are known. Franke and Mönch ⁽¹⁹⁾ found a value of 1.8 for the partition coefficient $K = \frac{([\text{H}])}{([\text{D}])}_{\text{hypophosphite}} : \frac{([\text{H}])}{([\text{D}])}_{\text{water}}$. Alexander

and Burge⁽²⁰⁾ estimated that the rate at which deuterium is introduced into the aromatic ring is $\frac{1}{2}$ to $\frac{1}{6}$ as fast as the rate at which hydrogen is introduced.

Therefore care was taken to deuterate the hypophosphorous acid as highly as feasible. We have carried out both diazotation and reduction in the same solvent : a mixture of highly deuterated hypophosphorous acid and heavy water.

Mass spectrometry. Mass spectra of the labelled compounds were run at an ionizing voltage at which the corresponding unlabelled compounds did not show fragmentation peaks P-1, P-2 etc. From the relative peak heights in the parent peak region, mole fractions of molecules with different numbers of deuterium atoms, were calculated. Corrections were made for presence of isotopes ¹³C, ¹⁷O, ¹⁸O and ¹⁵N. The results are summarized in Table 1.

N. M. R.-spectra. These spectra were run with a Varian-A60 spectrometer. The results are shown in Table 2 and Figures 3 and 4.

3. — EXPERIMENTAL

SYNTHESIS

2,6-Dibromo-1,4-dinitrobenzene.

A suspension of 2,6-dibromo-4-nitro-aniline (74 g, 0.25 mole) in acetic acid (1,750 ml), concentrated sulphuric acid (20 ml) and hydrogen peroxide 30 % (300 ml) was stirred well, heated to 90° C and kept at this temperature for 14 hours. A mixture of acetic acid (160 ml) and hydrogen peroxide 30 % (160 ml) was added, and the temperature maintained at 90° C for 6 hours. Hydrogen peroxide 30 % (100 ml) was added, and the mixture kept at 90° C for another 14 hours. From the cooled solution, a small amount of brown precipitate was filtered off, and the filtrate poured into ice-water (4 l). 2,6-Dibromo-1,4-dinitrobenzene crystallized out. After three recrystallizations from ethanol/water 2 : 1 (v/v), the yield was 60 g (0.184 mole, 73 %), m.p. 130.9-131.4° C.

2',5'-Dinitro-meta-terphenyl-2, 4, 6, 2'', 4'', 6''-D₆.

Iodobenzene-2, 4, 6-D₃ (50 mM, 10.4 g), 2,6-dibromo-1,4-dinitrobenzene (25 mM, 8.2 g) and copper powder («B. D. H. precipitated») were heated at 190-200° C for six hours in an atmosphere of nitrogen. The reaction mixture was stirred well. The copper powder (250 mA, 15.9 g) was added in twelve equal portions at intervals of half an hour. An excess of iodobenzene-2, 4, 6-D₃ (20 mM, 4.1 g) was added, in the course of the last two hours, in four portions of one gram each. The reaction mixture was extracted several times with hot benzene (500 ml in all). The benzene solution was filtered and concentrated to half of the volume. By means of thin-layer chromatographic

TABLE 1. Isotope content by mass spectrometric analysis

Compound	Relative Peak Heights	Ionizing voltage	Composition		Average number of deuterium atoms per molecule
			D-atoms in molecule	mole %	
^a Iodobenzene-D ₃ C ₆ H ₅ D ₃ I m.w. 207	P + 1 66 P 1 000 P - 1 14.6 P - 2 0	20	3 2	98.6 1.4	2.98 ₃
^a Meta-terphenyl-D ₈ C ₁₈ H ₆ D ₈ m.w. 238	P + 2 20 P + 1 200 P 1 000 P - 1 95 P - 2 11.6	18	10 9 8 7 6	(0.08) 0.6 89.8 8.5 1.1	7.90 ₂
^a Benzoic acid-D ₃ C ₇ H ₅ D ₃ O ₂ m.w. 125	^a P + 1 145 P 1 000 P - 1 31.5 P - 2 2.5	18	^e 3 2 1	96.8 3.0 0.2	2.96 ₆
^c Methyl 3,5-dinitrobenzoate-D ₃ C ₈ H ₃ D ₃ N ₂ O ₆ m.w. 229	P + 2 16.2 P + 1 96.1 P 1 000 P - 1 30.6 P - 2 4.4 P - 3 6.0	12	3 2 1 0	96.1 2.9 0.4 0.6	2.94 ₆
^a Nitro-meta-terphenyl D ₈ C ₁₈ H ₅ D ₈ NO ₂ m.w. 283	P + 2 24 P + 1 195 P 1 000 P - 1 625 P - 2 55 P - 3 10	16	8 7 6 5	56 40 3.4 0.6	7.51
^b Trinitro-meta-terphenyl-D ₆ C ₁₈ H ₅ D ₆ N ₃ O ₆ m.w. 371	P + 3 5.0 P + 2 36.3 P + 1 212.3 P 1 000 P - 1 52.0 P - 2 4.2	12	6 5 4	94.7 4.9 0.4	5.94 ₃

^a run on mass spectrometer model AEI MS9, at Polak's Frutal Works, Amersfoort.

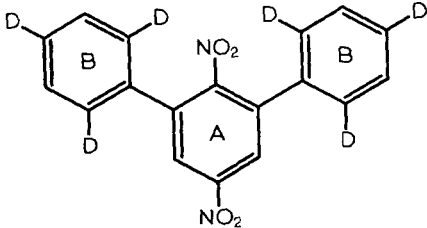
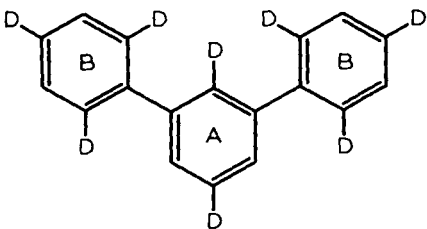
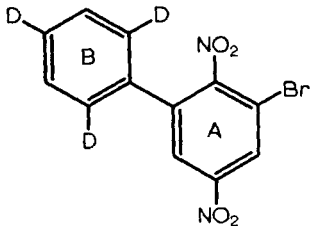
^b run on mass spectrometer model AEI MS9, provided with a direct introduction system, Unilever Research Laboratory, Vlaardingen.

^c run on mass spectrometer Hitachi-Perkin Elmer, model RMU-6E, by Dr. E. Talman.

^d deuterium oxide contamination of the mass spectrometer has resulted in partial deuteration of carboxyl hydrogen.

^e figures refer to deuterium atoms in aromatic nucleus.

TABLE 2. N. M. R.-spectra

compound	chemical shift ^a δ(ppm)	ratio peak areas H _{ring A} / H _{ring B}	
		found ^a	calculated ^b
 <p>in butanon</p>	ring A 8.38 ring B 7.53	0.496 ± 6 %	0.500
 <p>in CCl₄</p>	ring A 7.50 ring B 7.40	0.54 ^c	0.500
 <p>in butanon</p>	ring A 8.43; 8.70 (AB spectr. J = 2.5 cps) ring B 7.58	1.03 ± 5 %	1.00

^a reference tetramethyl-silane.

^b calculated value for 100 % deuterium substitution at desired positions.

^c inaccurate figure, due to overlap of peaks.

^d ratio of the average of six determinations of the integrated intensities of the peaks

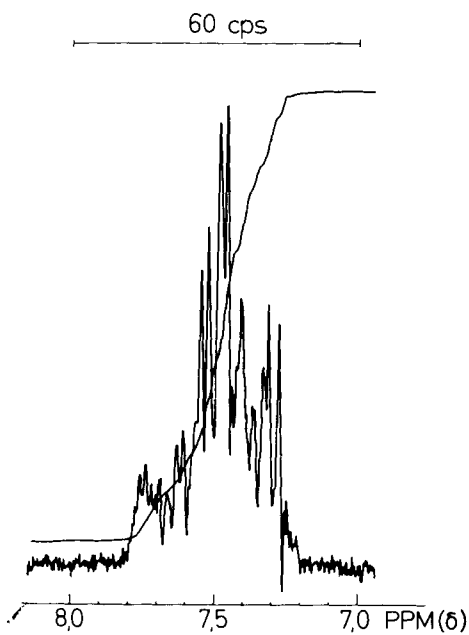


FIG. 3. N. M. R. spectrum of meta-terphenyl

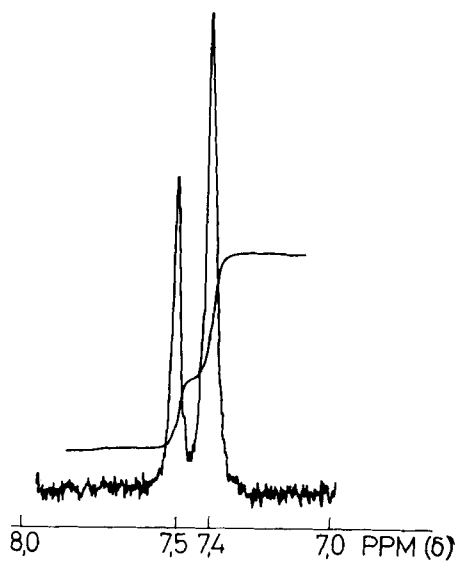


FIG. 4. N. M. R. spectrum of meta-terphenyl-D₈.

analysis (see below) it was shown that the reaction mixture contained, mentioned in the order of decreasing r_F values : a small amount of biphenyl, no 2,6-dibromo-1,4-dinitrobenzene, a trace of 3-bromo-2,5-dinitrobiphenyl, the main product 2,5-dinitro-meta-terphenyl, and a series of products with smaller r_F values. For pre-purification, the benzene solution was passed over a silicagel column (100 g silicagel, Merck, 0.05-0.20 mm; length of column 60 cm, diameter ca 2 cm). The column was washed with benzene until no more 2,5-dinitro-meta-terphenyl was found in the eluent. The combined fractions were taken to dryness. The residue was dissolved in 30 ml benzene/heptane 2 : 3, and chromatographed over silicagel (divided over two columns each containing 200 g silicagel, Merck, 0.05-0.20 mm; length of column 140 cm, diameter ca 2 cm). Samples of the fractions were analyzed thin-layer chromatographically. Fractions of comparable purity were combined and chromatographed over aluminium oxide (Merck, aluminium oxide according to Brockmann, activity grade 11-111) in nitroethane/heptane 1 : 10. After recrystallization from ethanol the total yield was 3.98 g (12.2 mM, 35 % based on iodobenzene- D_3). The melting points of the several crops were : 105-106° C (30 mg); 106-107° C (0.29 g); 107-108° C (1.50 g); 108-109° C (1.83 g) and 109-109.5° C (0.33 g).

Meta-terphenyl- 2, 4, 6, 2', 5', 2'', 4'', 6''-D₈.

2',5'-Dinitro-meta-terphenyl-2,4,6,2'',4'',6''- D_6 (12 mM, 3.91 g) was dissolved in ethanol (375 ml) and 1 N hydrochloric acid (30 ml), and reduced at room temperature with hydrogen gas at one atm. in the presence of platinum black catalyst (from 700 mg platinum oxide). It was found that efficient stirring of the mixture is required. The calculated amount of hydrogen was taken up in 40 minutes.

A few ml of concentrated hydrochloric acid were added, the catalyst was filtered off and the solution taken to dryness in vacuo. White crystals of 2', 5'-diamino-meta-terphenyl-2, 4, 6, 2'', 4'', 6''- D_6 dihydrochloride were obtained in almost quantitative yield, m.p. 262-264° C. Labile hydrogen was replaced by deuterium by dissolving the product in deuterium oxide (50 ml) and distilling off the solvent in vacuo. This procedure was repeated twice. The 2', 5'-diamino-meta-terphenyl-2, 4, 6, 2'', 4'', 6'', N, N, N', N'- D_{10} dideuteriochloride was dissolved in hypophosphorous acid- D_3 (25 g, 360 mM of D_3PO_2 in 25 g D_2O 99.9 %) and diazotized at -5° C with sodium nitrite (24 mM, ca 1.8 g) dissolved in D_2O 99.9 % (10 ml) After standing overnight at room temperature, the reaction mixture was extracted with benzene (250 ml in total). The benzene solution was diluted with an equal volume of *n*-hexane and, for pre-purification, passed over an aluminium oxide column (aluminium oxide according to Brockmann, Merck, activity grade 11-111; length of column 40 cm, diameter 1.7 cm). The column was washed with about 300 ml benzene/hexane 1 : 10, and the combined fractions were taken to dryness in vacuo. The crude product (2.4 g) contained, as was shown

by means of thin-layer chromatography, some biphenyl, the meta-terphenyl and a series of products with lower r_F values. It was next purified by chromatography over an aluminum oxide column (length 90 cm, diameter 2.0 cm) in *n*-hexane. Fractions of comparable purity were combined, taken to dryness in vacuo and sublimed. The yield of meta-terphenyl-D₈ was 1.3 g (5.4 mM = 45 %). The melting points of several crops were 73-80° C (200 mg), 84.9-86.3° C (360 mg), 86.8-87.4° C (620 mg) and 85.3-86.3° C (120 mg).

Hypophosphorous acid-D₃

Hypophosphorous acid (30 g) was dissolved in deuterium oxide. After standing at room temperature for 20 hours, the solvent was distilled off in vacuo. This procedure was carried out five times with 60 ml of D₂O 99.7 % and eventually with 40 g, 20 g and 20 g of D₂O 99.9 %. The yield was about 25 g, deuterium content 99.65 % (by N. M. R.).

DEGRADATION

Benzoic acid-2, 4, 6-D₃

Meta-terphenyl-2, 4, 6, 2', 5', 2'', 4'', 6''-D₈ (1 mM, 238 mg) was oxidized in boiling acetic acid (20 ml) with chromium trioxide (15 mM, 1.5 g), which was added in small amounts in the course of 30 min. After addition of the chromium trioxide, the mixture was boiled for 15 minutes more, then poured into cold water (100 ml) and extracted with ether (6 × 25 ml). The ethereal solution was washed with water (2 × 10 ml) and evaporated to dryness in vacuo. The residue was sublimed in vacuo. Benzoic acid-2,4,6-D₃ was obtained in 70 % yield (175 mg, 1.4 mM), m.p. 118.5-120.5° C.

Methyl 3, 5-dinitrobenzoate-2, 4, 6-D₃

Benzoic acid was converted into methyl 3, 5-dinitrobenzoate-2, 4, 6-D₃ by the method described previously ⁽⁶⁾.

Nitro-meta-terphenyl.

A mixture of meta-terphenyl-D₈ (50 mg, 0.22 mM), acetic acid (0.65 ml) and nitric acid (0.20 ml, *d* 1.42) was heated at 90° C for 2-3 hours. Water was added and the mixture extracted with ether. The ether solution was washed with dilute alkali and water, dried over MgSO₄ and the ether removed in vacuo. The product, an oil which contained only traces of meta-terphenyl, was chromatographed over a silicagel column (length 40 cm, diameter 1.7 cm) in benzene/heptane 2 : 3. The yield was 37 mg of a pale yellow oil, the components of which could not be separated by thin-layer chromatography on silicagel in benzene/heptane 2 : 3; on bentone/celite 1 : 1 in heptane; or by means of gas chromatography on bentone 34/silicon gum SE-30 1 : 1 on chromosorb-W.

4, 4', 4''-Trinito-meta-terphenyl-2, 6, 2', 5', 2'', 6''-D₆.

A mixture of meta-terphenyl-D₈ (50 mg, 0.22 mM), acetic acid (0.25 ml) and nitric acid (0.20 ml, *d* 1.50) was heated at 100° C for one hour, another quantity of acetic acid (0.25 ml) and nitric acid (0.20 ml) added, and heating continued for one hour. After a drop of water was added, a product crystallized out. It was recrystallized several times from nitroethane/heptane 2 : 1 (0.3 ml) and from acetic acid (0.3 ml). Finally a product was obtained with a m.p. of 203.2-204.8° C. The yield was 11 mg (0.03 mM, 13 %).

THIN-LAYER CHROMATOGRAPHY.

Analyses were carried out on silicagel (a layer of 0.25 mm silicagel HF₂₅₄, Merck; activation of layer by heating for one hour at 110° C) in benzene/heptane 2 : 3. Detection : under U. V. light. The following r_F values were found : biphenyl 0.50; meta-terphenyl 0.47; 2,6-dibromo-1,4-dinitrobenzene 0.23; 3-bromo-2,5-dinitrobiphenyl 0.20; 2',5'-dinitro-meta-terphenyl 0.17; nitro-meta-terphenyl 0.17; 4,4',4''-trinitro-meta-terphenyl 0.01.

4. — DISCUSSION

The shortage of deuterium atoms found for 4'-nitro-meta-terphenyl-D₈ cannot be the result of the presence of deuterium at the 4'-position in the meta-terphenyl-D₈ molecules; in that case 4,4',4''-trinitro-meta-terphenyl-D₈ should show an equal deficiency. For that reason, the mono-nitro derivative, which has only been obtained as an oil^(8, 9), must be a mixture of isomers, most probably of 4-nitro- and 4'-nitro-meta-terphenyl.

The average number of deuterium atoms per meta-terphenyl molecule is 7.90. The average number of deuterium atoms in each of the outer rings equals the number found for benzoic acid, viz. 2.97. Consequently, on the average 1.97 deuterium atoms are found in the centre ring. If one accepts that the deuterium atoms are equally distributed over both positions 2' and 5', the degree of substitution is 98.5 %. The average number of deuterium atoms on positions 2, 4 and 6 together equals the number found for methyl 3,5-dinitro-benzoate-2,4,6-D₃, viz. 2.95. If one assumes an equal distribution, the degree of substitution is 98.3 % on positions 2, 4, 6, 2'', 4'' and 6''. As to positions 4 and 4'', this is in agreement with the difference in number of deuterium atoms found between meta-terphenyl-D₈ and 4,4',4''-trinitro-meta-terphenyl-D₆.

From the small difference between benzoic acid-D₃ and methyl 3,5-dinitro-benzoate-D₃ follows a degree of substitution of about 1 % on positions 3, 5, 3'' and 5''.

Summarizing, we conclude that deuterium substitution is ≥ 98 % at positions 2, 4, 6, 2', 5', 2'', 4'', and 6'' and ≤ 1 % at the other positions. The N. M. R.-spectra are in agreement with this picture.

CONCLUSION

Coupling of aromatic nuclei by an Ullmann reaction, catalytic reduction of aromatic nitrogroups and reductive diazotization can be carried out without appreciably affecting the positions of labelling atoms in the aromatic rings. They are appropriate reaction steps in synthesis of specifically deuterated polyphenyls.

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REFERENCES

1. FANTA, P. E. — The Ullmann Synthesis of Biaryls. *Chem. Reviews*, **64** : 613 (1964).
2. BEST, A. P. and WILSON, C. L. — Direct Introduction of Deuterium into the Aromatic Nucleus. Part II. Orientation by Certain Substituents. *J. Chem. Soc.*, **1938** : 28.
3. BEST, A. P. and WILSON, C. L. — Structure of Benzene. Part XIII. Hydrogen Exchange Reactions with Benzene Derivatives. *J. Chem. Soc.*, **1946** : 239.
4. AKAWIE, R. I., SCARBOROUGH, J. M. and BURR, J. G. — Synthesis of Deuterated Biphenyls. *J. Org. Chem.*, **24** : 946 (1959).
5. OTTO, P. Ph. H. L. and JUPPE, G. — Synthesis of Tritiated p-Terphenyls, Labelled at Specific Positions. *Journal of Labelled Compounds*, **1** : 115 (1965); Euratom Report, EUR 2529.e (1965).
6. OTTO, P. Ph. H. L. and JUPPE, G. — Synthesis of Tritiated Biphenyls, Labelled at Specific Positions. *J. Labelled Compounds*, **2** : 349 (1966).
7. OTTO, P. Ph. H. L. — Unpublished result.
8. WARDNER, C. A. and LOWY, A. — Nitration of meta-Diphenylbenzene and Derivatives of nitro-meta-Diphenylbenzene. *J. Am. Chem. Soc.*, **54** : 2510 (1932).
9. FRANCE, H., HEILBRON, I. M. and HEY, D. H. — Studies in the Terphenyl Series. Part III. The preparation and Nitration of m-Terphenyl. *J. Chem. Soc.*, **1939** : 1288.
10. ALLEN, C. F. H. and BURNES, D. M. — The Nitration of Terphenyls. *J. Org. Chem.*, **14** : 175 (1949).
11. BUSER, E., BÜRER, T. und GÜNTARD, Hs. H. — Komplexe Gleichgewichte bei Deuterierungen durch wiederholten Austausch. *Helv. Chim. Acta*, **43** : 161 (1960).
12. VOGEL, A. I. — Practical Organic Chemistry. Longman, Green and Co., London 1956.
13. KÖRNER, G. and CONTARDI. — Dinitroderivati delle benzine metadiologenate. *Atti della Reale Accademia dei Lincei* (5), **22** II, 625 (1913).
14. HOLMES, R. R. and BAYER, R. P. — A Simple Method for the Direct Oxidation of Aromatic Amines to Nitroso Compounds. *J. Am. Chem. Soc.*, **82** : 3454 (1960).
15. KORNBLUM, N. — Replacement of the Aromatic Primary Amino Group by Hydrogen. Organic Reactions, Vol. II, p. 262. J. Wiley and Sons, Inc., New York, 1946.

16. MIKLUKHIN, G. P. and REKASHEVA, A. F. — Mechanism of the Reduction of Diazonium Salts. Reduction with Hypophosphorous Acid. *Doklady Akad. Nauk S. S. S. R.*, **85** : 827 (1952); *Chem. Abstr.*, **47** : 4855f (1953).
17. ERLIENMEYER, H., SCHOENAUER, W. und SCHWARZENBACH, G. — Über Austauschversuche in Wasser und Deuteriumoxyd. *Helv. Chim. Acta*, **20** : 726 (1937).
18. HAMMOND, G. S. and GRUNDMEIER, W. — The Mechanism of the Benzidine Rearrangement III. The Rearrangement of p, p'-Dideuterohydrazobenzene. *J. Am. Chem. Soc.*, **77** : 2444 (1955).
19. FRANKE, W. und MÖNCH, J. — Der Mechanismus der Hypophosphitspaltung nach Versuchen mit Deuterium als Indicator. *Liebigs Ann. Chem.*, **550** : 1 (1941).
20. ALEXANDER, E. R. and BURGE, R. E. — The Hypophosphorous Acid Deamination of Diazonium Salts in Deuterium Oxide. *J. Am. Chem. Soc.*, **72**, 3100 (1950).