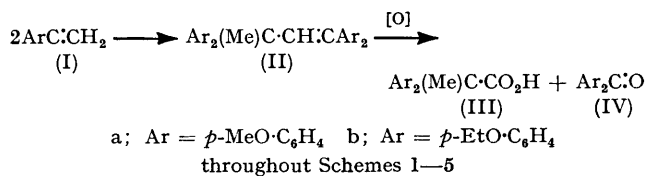


## Reactions with Asymmetric Diarylethylenes. Part XV.<sup>1</sup> Dimerisation of 1,1-Bis-*p*-alkoxyphenylethylenes

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Dimerisation of 1,1-bis-*p*-methoxy(or -ethoxy)phenylethylene with hydrogen chloride or bromide, trichloroacetic acid, or glacial acetic acid-sulphuric acid gave 1,1,3,3-tetrakis-*p*-methoxy(or -ethoxy)phenylbut-1-ene, identified on the basis of synthetic, degradative, and reduction studies and n.m.r. spectral evidence. Chlorination of the dimer gave the corresponding monomer and its chloro-derivative, whereas bromination gave the dibromo-dimer, which could be converted into the corresponding buta-1,3-diene. Iodination gave only the monomer. The mechanism of the reactions with bromine and chlorine is discussed.

DIMERISATION of the olefin (Ia) is reported to give the dimer (IIa) (as a component of an oil) in the presence of trichloroacetic acid<sup>2</sup> but not glacial acetic acid-sulphuric acid.<sup>3</sup> Here we report the isolation of the crystalline dimers (IIa) and (IIb) by reactions catalysed by hydrogen chloride, hydrogen bromide, trichloroacetic acid, and acetic acid-sulphuric acid. Molecular weight determinations and degradative oxidation to give compounds (III) and (IV) (see Scheme 1 and Experimental

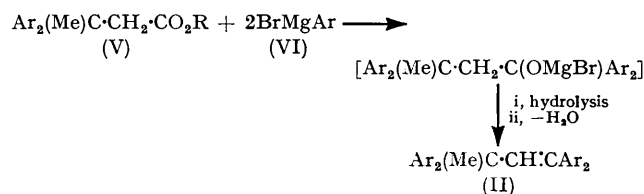


SCHEME 1

section) support the structures assigned to the products. Compound (II) was also unambiguously synthesised from compounds (V) and (VI) (see Scheme 2).

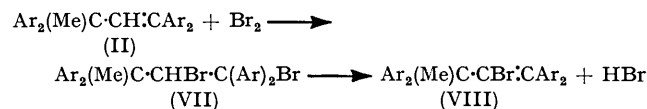
Compounds (IIa and b) did not revert to compounds (I) in the presence of acids although similar compounds are reported to do so.<sup>3,4</sup> However, iodine did bring

about this reversion, although bromine and chlorine reacted differently. Thus, treatment of (IIa and b) with bromine gave the compounds (VIIa and b) which,



SCHEME 2

with ethanolic potassium hydroxide, gave compounds (VIIIa and b).



SCHEME 3

Compounds (VIIa and b) when heated with the isopropyl ether (I; Ar = *p*-Pr<sup>t</sup>O·C<sub>6</sub>H<sub>4</sub>) evolved hydrogen bromide to give compounds (Ia and b) (see Scheme 4),

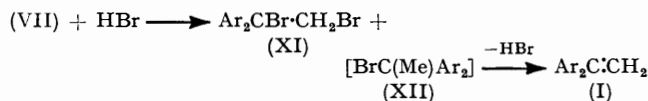
<sup>1</sup> Part XIV, W. Tadros, A. B. Sakla, M. Gindy, and N. Fouad, *J. Chem. Soc. (C)*, 1970, 1923.

<sup>2</sup> A. G. Evans, N. Jones, P. M. S. Jones, and J. H. Thomas, *J. Chem. Soc.*, 1956, 2757.

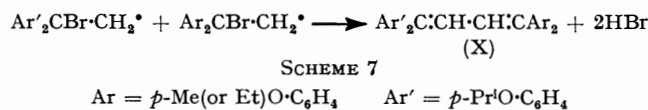
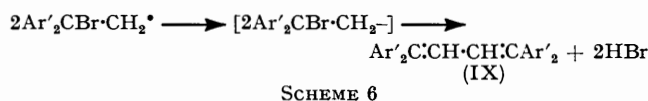
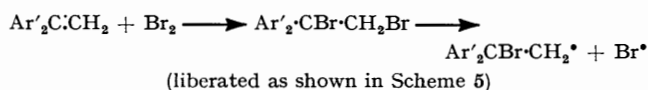
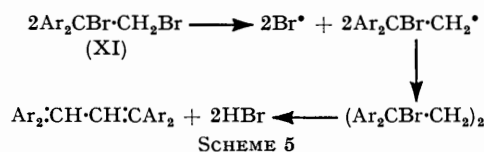
<sup>3</sup> O. Schmitz-Dumont, K. Thömke, and H. Diebold, *Ber.*, 1937, **70**, 175.

<sup>4</sup> A. G. Evans, P. M. S. Jones, and J. H. Thomas, *J. Chem. Soc.*, 1958, 4563.

(IXa and b) (see Scheme 5), (IX; Ar = *p*-Pr<sup>i</sup>O·C<sub>6</sub>H<sub>4</sub>) (see Scheme 6), and (Xa and b) (see Scheme 7). Formation of these products indicates that compounds (VIIa and b) are cleaved to give (XIa and b) and (XIIa and b), which form compounds (Ia and b). That formation of the butadiene (IX) and (Xa and b) takes place by a free-radical mechanism is indicated by the presence of compound (IX; Ar = *p*-Pr<sup>i</sup>O·C<sub>6</sub>H<sub>4</sub>).



SCHEME 4



Since compound (VII) was recovered unchanged when heated alone in chloroform, whereas passage of hydrogen bromide or hydrogen chloride through the solution induced formation of compounds (IXa and b), cleavage of compound (VII) is effected by acidic catalysts. The reaction with chlorine gave compounds (Ia and b) and 2-chloro-1,1-bis-*p*-methoxy(or -ethoxy)phenylethylene.

#### EXPERIMENTAL

**Dimerisation of 1,1-Bis-*p*-methoxy(or -ethoxy)phenylethylene.**—(a) *By hydrogen halides.* (i) Hydrogen bromide or chloride was bubbled through a boiling solution of 1,1-bis-*p*-methoxyphenylethylene (2.4 g, 0.01 mol) in carbon disulphide or ether (25 ml) for 5 h. The solvent was removed and the residue was fractionally crystallised from 95% ethanol to give unchanged 1,1-bis-*p*-methoxyphenylethylene (1.51 g), m.p. and mixed<sup>5</sup> m.p. 142°, together with 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.79 g) as yellow crystals, m.p. 77° (Found: C, 79.8; H, 6.7. C<sub>32</sub>H<sub>32</sub>O<sub>4</sub> requires C, 80.0; H, 6.65%).

(ii) Similarly, 1,1-bis-*p*-ethoxyphenylethylene (2.68 g) gave unchanged 1,1-bis-*p*-ethoxyphenylethylene (1.69 g), m.p. and mixed<sup>6</sup> m.p. 142°, and 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (0.9 g), m.p. 108° (Found: C, 80.45; H, 7.35. C<sub>36</sub>H<sub>40</sub>O<sub>4</sub> requires C, 80.6; H, 7.45%).

<sup>5</sup> P. Pfeiffer and R. Wizinger, *Annalen*, 1928, **461**, 132.

<sup>6</sup> W. Tadros and G. Aziz, *J. Chem. Soc.*, 1951, 2553.

(b) *By trichloroacetic acid.*<sup>2</sup> (i) To a solution of 1,1-bis-*p*-methoxyphenylethylene (2 g) in benzene (25 ml), trichloroacetic acid (8 g) was added. The benzene layer was washed with water, dried (CaCl<sub>2</sub>), then distilled. The yellow oil thus obtained crystallised from acetic acid to give unchanged 1,1-bis-*p*-methoxyphenylethylene (0.84 g). The acetic acid mother liquor was diluted with water (100 ml) and the yellow precipitate was filtered off, washed with water, then crystallised (95% ethanol) to give 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (1.1 g), m.p. and mixed m.p. 77°.

(ii) Similarly 1,1-bis-*p*-ethoxyphenylethylene (2 g) gave 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (1.36 g), m.p. and mixed m.p. 108° (from 95% ethanol).

(c) *By acetic acid-sulphuric acid.* (i) A mixture of 1,1-bis-*p*-methoxyphenylethylene (2.4 g) and glacial acetic acid (48 ml) was treated with acetic acid-concentrated sulphuric acid (4.8 ml; 4:1 v/v). The mixture was left at 25° C for 14 days, then poured on ice-water (150 ml) and extracted with ether. The extract was washed with sodium hydroxide solution (10%) and water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The residue was fractionally crystallised (95% ethanol) to give 1,1-bis-*p*-methoxyphenylethylene (1.87 g), m.p. and mixed<sup>5</sup> m.p. 142°, together with 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.48 g), m.p. and mixed m.p. 77°.

(ii) Similarly 1,1-bis-*p*-ethoxyphenylethylene (2.68 g) gave 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (0.59 g), m.p. and mixed m.p. 108°, together with unchanged 1,1-bis-*p*-ethoxyphenylethylene (2.07 g), m.p. and mixed<sup>6</sup> m.p. 142°.

**Irreversibility of the Dimerisation Reactions.**—Hydrogen chloride (or bromide) was bubbled through a boiling solution of 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.48 g) in carbon disulphide (25 ml) for 3 h. The solution was evaporated to give mainly unchanged 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (ca. 0.45 g), m.p. and mixed m.p. 77°. Under the same conditions 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene was completely unchanged.

**Oxidation of the Dimers.**—(i) A mixture of 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.5 g) and potassium permanganate (0.5 g) in acetone (15 ml) was heated to boiling on a steam-bath for 30 min. The solvent was recovered, the residue was treated with boiling aqueous sodium carbonate, and the solution was filtered. The filtrate was acidified (HCl) to give  $\alpha$ -bis-*p*-methoxyphenylpropionic acid (0.2 g), m.p. and mixed m.p.<sup>7</sup> 106° (from water). The organic residue which remained (along with manganese dioxide) was digested with 95% ethanol to give *pp'*-dimethoxybenzophenone (0.21 g), m.p. and mixed<sup>8</sup> m.p. 142°.

(ii) Oxidation of 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (0.5 g) gave  $\alpha$ -bis-*p*-ethoxyphenylpropionic acid (0.24 g), m.p. 171° (from water) (Found: C, 72.7; H, 7.05. C<sub>19</sub>H<sub>22</sub>O<sub>4</sub> requires C, 72.6; H, 7.0%), and *pp'*-diethoxybenzophenone (0.2 g), m.p. and mixed<sup>8</sup> m.p. 132–133° (from 95% ethanol).

$\alpha$ -Bis-*p*-ethoxyphenylpropionic acid (2 g, ca. 62%) was also prepared from  $\alpha$ -bis-*p*-hydroxyphenylpropionic acid<sup>7</sup> (2.58 g), ethyl iodide (5.37 g), and ethanolic sodium ethoxide [sodium (0.8 g) and ethanol (15 ml)]; m.p. and mixed m.p. 171°.

<sup>7</sup> C. L. Parris, R. Dowbenko, R. V. Smith, N. A. Jacobson, J. W. Pearce, and R. M. Christenson, *J. Org. Chem.*, 1962, **27**, 455.

<sup>8</sup> B. Jones, *J. Chem. Soc.*, 1936, 1854.

*Synthesis of the Dimers.*—(i) A solution of methyl  $\beta\beta$ -bis-*p*-methoxyphenylbutyrate<sup>7</sup> (10 g, 0.0318 mol) in dry ether (25 ml), was gradually added to *p*-methoxyphenylmagnesium bromide [*p*-bromoanisole (17.8 g, 0.0954 mol) and magnesium (2.318 g, 0.0954 g atom) in dry ether (35 ml)] at room temperature during 3 h with stirring. Next day the mixture was decomposed with aqueous ammonium chloride. The ethereal layer was washed with water, dried (MgSO<sub>4</sub>), and evaporated. The residue gave 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (8.48 g), m.p. and mixed m.p. 77° (from 95% ethanol).

(ii) 1,1,3,3-Tetrakis-*p*-ethoxyphenylbut-1-ene (9.2 g), similarly synthesised [ethyl  $\beta\beta$ -bis-*p*-ethoxyphenylbutyrate<sup>9</sup> (10 g, 0.028 mol) in ether (25 ml); *p*-ethoxyphenylmagnesium bromide from *p*-bromophenetole (7.88 g, 0.084 mol), magnesium (2.04 g, 0.084 g atom), and ether (34 ml)], separated from 95% ethanol with m.p. and mixed m.p. 108°.

The u.v. spectra (Beckman DK-1 spectrophotometer) of the dimers obtained by either method were identical: (IIa)  $\lambda_{\max}$  266 (log  $\epsilon$  4.07) and 198 nm (4.82); (IIb)  $\lambda_{\max}$  266 (log  $\epsilon$  4.10) and 199 nm (4.88).

*Reactions of the Dimers with Halogens.*—(A) *Iodine.*

(i) Iodine (0.254 g, 0.001 mol) in chloroform (10 ml) was added at room temperature to a solution of 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.48 g, 0.001 mol) in the same solvent (5 ml). The mixture was left overnight at room temperature, and the chloroform was distilled off. Crystallisation of the residue from 95% ethanol gave 1,1-bis-*p*-methoxyphenylethylene (0.46 g), m.p. and mixed<sup>5</sup> m.p. 142°.

(ii) Similarly 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (0.536 g, 0.001 mol) gave 1,1-bis-*p*-ethoxyphenylethylene (0.51 g), m.p. and mixed<sup>6</sup> m.p. 142°.

(B) *Bromine.*—(a) (i) 1,2-Dibromo-1,1,3,3-tetrakis-*p*-methoxyphenylbutane. A solution of bromine (0.233 g, 0.00145 mol) in chloroform (10 ml) was added at room temperature to a solution of 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.7 g, 0.00145 mol) in the same solvent (10 ml). The solvent was recovered at room temperature under reduced pressure and the product crystallised from 95% ethanol to give the *dibromide* (0.9 g) as pale yellow crystals, m.p. 75–76° (Found: C, 60.4; H, 4.9; Br, 25.2. C<sub>32</sub>H<sub>32</sub>Br<sub>2</sub>O<sub>4</sub> requires C, 60.0; H, 5.0; Br, 25.0%).

(ii) 1,2-Dibromo-1,1,3,3-tetrakis-*p*-ethoxyphenylbutane. Similarly prepared from 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (0.536 g, 0.001 mol), this *dibromide* (0.65 g) was obtained as pale yellow crystals, m.p. 54° (95% ethanol) (Found: C, 62.05; H, 5.6; Br, 23.1. C<sub>36</sub>H<sub>40</sub>Br<sub>2</sub>O<sub>4</sub> requires C, 62.05; H, 5.75; Br, 23.0%). Either dibromide was recovered unchanged when heated to boiling in chloroform solution for 1 h.

(b) (i) 2-Bromo-1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene. A mixture of 1,2-dibromo-1,1,3,3-tetrakis-*p*-methoxyphenylbutane (0.64 g) and potassium hydroxide (0.5 g) in 95% ethanol (20 ml) was heated to boiling on a steam-bath for 3 h. The mixture was diluted with ice-water (50 ml) and extracted with ether. The ethereal layer was washed with water until free from alkali and evaporated. The residue crystallised from 95% ethanol to give 2-bromo-1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.54 g) as pale yellow crystals, m.p. 60–61° (Found: C, 68.55; H, 5.5; Br, 14.0. C<sub>32</sub>H<sub>31</sub>BrO<sub>4</sub> requires C, 68.7; H, 5.55; Br, 14.3%),

$\lambda_{\max}$  272–264 (log  $\epsilon$  4.55), 255 (4.56), 249 (4.58), and 218 nm (4.60).

(ii) 2-Bromo-1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene. Similarly prepared from 1,2-dibromo-1,1,3,3-tetrakis-*p*-ethoxyphenylbutane (0.72 g), this *bromo-olefin* (0.61 g) was obtained as yellow crystals, m.p. 50° (95% ethanol) (Found: C, 70.2; H, 6.25; Br, 13.25. C<sub>36</sub>H<sub>39</sub>BrO<sub>4</sub> requires C, 70.25; H, 6.35; Br, 13.0%),  $\lambda_{\max}$  260–269 (log  $\epsilon$  4.70), 255 (4.72), 249 (4.75), and 218 nm (4.76).

When hydrogen bromide was bubbled through a boiling solution of either bromo-olefin in chloroform for 1 h, the compound was recovered unchanged.

(c) (i) *Ozonolysis of 2-bromo-1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene.* A stream of ozonised oxygen (ca. 3%) was passed through a cold solution of the bromo-olefin (0.5 g) in carbon tetrachloride (100 ml) for 5 h. The ozonide was decomposed with distilled water, and the carbon tetrachloride was evaporated. The residue was filtered off and treated with aqueous 10% sodium hydroxide. The undissolved fraction was taken up in ether; the solution was washed with water and evaporated. The residue crystallised from 95% ethanol to give *pp'*-dimethoxybenzophenone (0.2 g), m.p. and mixed<sup>8</sup> m.p. 142°. Acidification of the alkaline filtrate (HCl) gave  $\alpha$ -bis-*p*-methoxyphenylpropionic acid (0.24 g), m.p. and mixed<sup>7</sup> m.p. 105–106° (water).

(ii) Similarly, the ethoxyphenyl analogue (0.6 g) gave *pp'*-diethoxybenzophenone (0.22 g), m.p. and mixed<sup>8</sup> m.p. 132–133° (95% ethanol) and  $\alpha$ -bis-*p*-ethoxyphenylpropionic acid (0.26 g), m.p. and mixed m.p. 171° (see before).

(d) *Conversion of the dibromides (VII) into 1,1,4,4-tetrakis-*p*-methoxy(or -ethoxy)phenylbuta-1,3-diene.* (1) (i) The dibromide (VIIa) (8 g) was heated to its m.p. (75–76°) for 2 min. Extraction with 95% ethanol gave 1,1,4,4-tetrakis-*p*-methoxyphenylbuta-1,3-diene (5.8 g), m.p. and mixed<sup>10</sup> m.p. 204–205°. The ethanolic mother liquor gave (on concentration and cooling) 2-bromo-1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (15 mg) [m.p. and mixed m.p. (60–61°) and u.v. spectrum].

(ii) Similarly, the dibromide (VIIb) (8 g) (at 54° for 2 min) gave 1,1,4,4-tetrakis-*p*-ethoxyphenylbuta-1,3-diene (5.9 g), m.p. and mixed<sup>6</sup> m.p. 206–207°, together with 2-bromo-1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (12 mg) [m.p. and mixed m.p. (50°) and u.v. spectrum].

(2) (i) Dry hydrogen bromide was bubbled through a solution of the dibromide (VIIa) (0.5 g) in chloroform (15 ml) at room temperature for 1 min (or hydrogen chloride for 1 h). The solution was evaporated and the residue crystallised from glacial acetic acid to give 1,1,4,4-tetrakis-*p*-methoxyphenylbuta-1,3-diene (0.35 g), m.p. and mixed<sup>10</sup> m.p. 204–205°.

(ii) Similarly, the dibromide (VIIb) (0.5 g) gave 1,1,4,4-tetrakis-*p*-ethoxyphenylbuta-1,3-diene (0.36 g), m.p. and mixed<sup>6</sup> m.p. 206–207° (from glacial acetic acid).

(3) *Reactions of the dibromides (VII) with 1,1-bis-*p*-isopropoxyphenylethylene.* (i) A mixture of equimolecular quantities (0.001 mol) of the dibromide (VIIa) (0.64 g) and 1,1-bis-*p*-isopropoxyphenylethylene (0.296 g) was heated on a steam-bath for 10 min. The product was digested with 95% ethanol (20 ml) and the insoluble fraction crystallised from glacial acetic acid to give 1,1,4,4-tetrakis-*p*-methoxyphenylbuta-1,3-diene (0.11 g) as yellow crystals, m.p. and

<sup>9</sup> B. D. Patel and K. V. Bokil, *J. Univ. Bombay*, 1942, **10**, 5 (*Chem. Abs.*, 1943, **37**, 623<sup>a</sup>).

<sup>10</sup> F. Bergmann, J. Szmuszkowicz, and E. Dimant, *J. Amer. Chem. Soc.*, 1949, **71**, 2968.

mixed<sup>10</sup> m.p. 204—205°. The ethanolic mother liquor while still warm deposited yellow crystals, which gave (from glacial acetic acid) 1,1-bis-*p*-isopropoxyphenyl-4,4-bis-*p*-methoxyphenylbuta-1,3-diene (0.32 g), m.p. and mixed<sup>11</sup> m.p. 155°. On cooling the ethanolic mother liquor a precipitate was obtained which crystallised from 95% ethanol to give 1,1,4,4-tetrakis-*p*-isopropoxyphenylbuta-1,3-diene (0.1 g) as yellow crystals, m.p. and mixed<sup>11</sup> m.p. 187—188°. Concentration and cooling of the ethanolic mother liquor gave 1,1-bis-*p*-methoxyphenylethylene (0.021 g), m.p. and mixed<sup>5</sup> m.p. 142°.

(ii) The dibromide (VIIb) (0.696 g) gave 1,1,4,4-tetrakis-*p*-ethoxyphenylbuta-1,3-diene (0.095 g), m.p. and mixed<sup>6</sup> m.p. 206—207° (glacial acetic acid), 1,1-bis-*p*-ethoxyphenyl-4,4-bis-*p*-isopropoxyphenylbuta-1,3-diene (0.36 g) as yellow crystals, m.p. and mixed<sup>12</sup> m.p. 162° (glacial acetic acid), 1,1,4,4-tetrakis-*p*-isopropoxyphenylbuta-1,3-diene (0.11 g), m.p. and mixed<sup>11</sup> m.p. 187—188° (95% ethanol), and 1,1-bis-*p*-ethoxyphenylethylene (0.019 g) with m.p. and mixed<sup>6</sup> m.p. 142°.

1,1-Bis-*p*-methoxy-, -ethoxy-, and -isopropoxy-phenylethylenes are not affected by hydrogen bromide under the same experimental conditions.

(C) *Chlorine*. (i) An equimolecular quantity (0.001 mol) of chlorine (0.071 g) in carbon tetrachloride (3.1 ml) was added at room temperature to a solution of 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.48 g) in the same solvent (10 ml). The solvent was recovered under reduced pressure and the residue was fractionally crystallised from 95% ethanol to give 1,1-bis-*p*-methoxyphenylethylene (0.2 g), m.p. and mixed<sup>5</sup> m.p. 142°, and 2-chloro-1,1-bis-*p*-methoxyphenylethylene (0.24 g), m.p. and mixed<sup>13</sup> m.p. 78°.

(ii) Similarly, 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (0.536 g) gave 1,1-bis-*p*-ethoxyphenylethylene (0.23 g), m.p. and mixed<sup>6</sup> m.p. 142°, and 2-chloro-1,1-bis-*p*-ethoxyphenylethylene (0.29 g), m.p. and mixed<sup>13</sup> m.p. 76°.

*Reduction of the Dimers*.—(i) Sodium (10.5 g) was added

<sup>11</sup> W. Tadros, *J. Chem. Soc.*, 1954, 2966.

<sup>12</sup> W. Tadros and A. B. Sakla, *J. Chem. Soc.*, 1957, 3210.

gradually in small portions to a solution of 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (1 g) in isopentyl alcohol (125 ml) at 25° with shaking. The mixture was then heated on a steam-bath with shaking. Isopentyl alcohol was steam-distilled off and the residue was extracted with ether. The extract was evaporated and the oil thus obtained crystallised from 95% ethanol to give 1,1,3,3-tetrakis-*p*-methoxyphenylbutane (0.52 g), m.p. 87° (Found: C, 79.95; H, 7.0. C<sub>32</sub>H<sub>34</sub>O<sub>4</sub> requires C, 79.65; H, 7.05%). The ethanolic mother liquor gave, on cooling, unchanged 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.35 g), m.p. and mixed m.p. 77°.

Similarly, 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (1 g) was reduced [sodium (11.72 g), isopentyl alcohol (140 ml)] to give 1,1,3,3-tetrakis-*p*-ethoxyphenylbutane (0.6 g), m.p. 101—102° (from 95% ethanol) (Found: C, 80.1; H, 7.7. C<sub>36</sub>H<sub>42</sub>O<sub>4</sub> requires C, 80.3; H, 7.8%).

(ii) *Catalytic hydrogenation*. (a) A solution of 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.2 g) in ethyl acetate (35 ml) was shaken with hydrogen over Raney nickel<sup>14</sup> sludge (0.5 g) at room temperature and atmospheric pressure for 1.5 h. The solution was filtered and the solvent was recovered. The residue crystallised from 95% ethanol to give 1,1,3,3-tetrakis-*p*-methoxyphenylbutane (0.17 g), m.p. and mixed m.p. 87°. Similarly, 1,1,3,3-tetrakis-*p*-ethoxyphenylbut-1-ene (0.3 g) gave 1,1,3,3-tetrakis-*p*-ethoxyphenylbutane (0.23 g), m.p. and mixed m.p. 101—102°.

(b) Repetition of experiment (a) with Adams platinum oxide (0.1 g) reduced 1,1,3,3-tetrakis-*p*-methoxyphenylbut-1-ene (0.2 g) to 1,1,3,3-tetrakis-*p*-methoxyphenylbutane (0.18 g), m.p. and mixed m.p. 87°, and the ethoxy-analogue (0.2 g) gave 1,1,3,3-tetrakis-*p*-ethoxyphenylbutane (0.17 g), m.p. and mixed m.p. 101—102°.

[2/512 Received, 6th March, 1972]

<sup>13</sup> W. Tadros, A. B. Sakla, and Y. Akhnookh, *J. Chem. Soc.*, 1956, 2701.

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