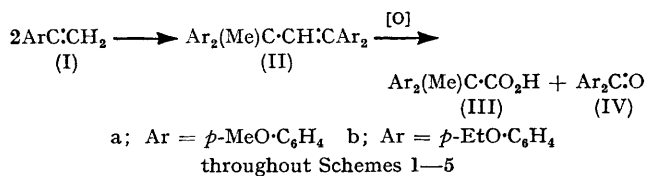


Reactions with Asymmetric Diarylethylenes. Part XV.¹ Dimerisation of 1,1-Bis-*p*-alkoxyphenylethylenes

By **Wadie Tadros,* Alfy Badie Sakla, and Sadek Elsayed Abdou**, Department of Chemistry, Faculty of Science, University of Cairo, Giza, A.R. Egypt

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 acid² but not glacial acetic acid-sulphuric acid.³ 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

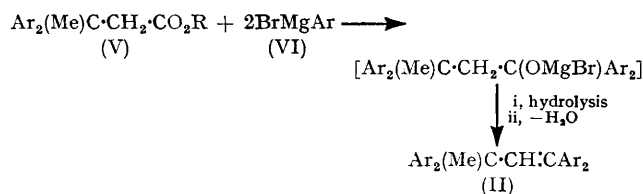


SCHEME 1

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

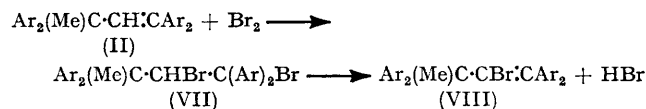
Compounds (IIa and b) did not revert to compounds (I) in the presence of acids although similar compounds are reported to do so.^{3,4} However, iodine did bring

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

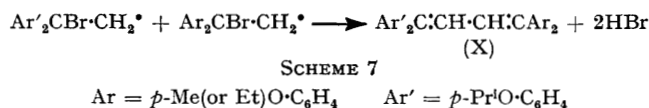
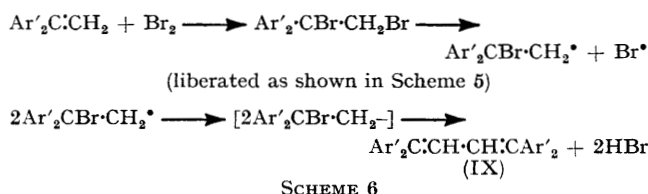
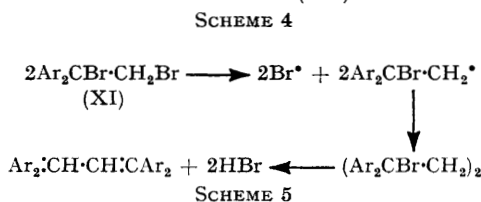
Compounds (VIIa and b) when heated with the isopropyl ether (I; Ar = *p*-Pr¹O·C₆H₄) evolved hydrogen bromide to give compounds (Ia and b) (see Scheme 4),

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

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

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

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

$$\begin{array}{c} \text{(VII)} + \text{HBr} \longrightarrow \text{Ar}_2\text{CBr}\cdot\text{CH}_2\text{Br} + \\ \text{(XI)} \\ \text{(XII)} \xrightarrow{-\text{HBr}} \text{Ar}_2\text{C}\cdot\text{CH}_2 \\ \text{(I)} \end{array}$$


EXPERIMENTAL

(ii) Similarly, 1,1-bis-*p*-ethoxyphenylethylene (2.68 g) gave unchanged 1,1-bis-*p*-ethoxyphenylethylene (1.69 g), m.p. and mixed δ 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. $C_{36}H_{40}O_4$ requires C, 80.6; H, 7.45%).

α -Bis-*p*-ethoxyphenylpropionic acid (2 g, ca. 62%) was also prepared from α -bis-*p*-hydroxyphenylpropionic acid (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°.

⁸ B. Jones, *J. Chem. Soc.*, 1936, 1854.

Synthesis of the Dimers.—(i) A solution of methyl $\beta\beta$ -bis-*p*-methoxyphenylbutyrate⁷ (10 g, 0.0318 mol) in dry ether (25 ml), was gradually added to *p*-methoxyphenyl-magnesium 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 (MgSO₄), 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*-ethoxyphenylbutyrate⁹ (10 g, 0.028 mol) in ether (25 ml); *p*-ethoxyphenyl-magnesium 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) λ_{\max} 266 (log ϵ 4.07) and 198 nm (4.82); (IIb) λ_{\max} 266 (log ϵ 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 mixed⁵ 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 mixed⁶ 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. C₃₂H₃₂Br₂O₄ 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. C₃₆H₄₀Br₂O₄ 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. C₃₂H₃₁BrO₄ requires C, 68.7; H, 5.55; Br, 14.3%),

λ_{\max} 272–264 (log ϵ 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. C₃₆H₃₉BrO₄ requires C, 70.25; H, 6.35; Br, 13.0%), λ_{\max} 260–269 (log ϵ 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 mixed⁸ m.p. 142°. Acidification of the alkaline filtrate (HCl) gave $\alpha\alpha$ -bis-*p*-methoxyphenylpropionic acid (0.24 g), m.p. and mixed⁷ m.p. 105–106° (water).

(ii) Similarly, the ethoxyphenyl analogue (0.6 g) gave *pp'*-diethoxybenzophenone (0.22 g), m.p. and mixed⁸ m.p. 132–133° (95% ethanol) and $\alpha\alpha$ -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 mixed¹⁰ 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 mixed⁶ 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 mixed¹⁰ 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 mixed⁶ 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

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

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

mixed ¹⁰ 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 ¹¹ 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 ¹¹ 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 ⁵ 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 ⁶ 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 ¹² m.p. 162° (glacial acetic acid), 1,1,4,4-tetrakis-*p*-isopropoxyphenylbuta-1,3-diene (0.11 g), m.p. and mixed ¹¹ m.p. 187—188° (95% ethanol), and 1,1-bis-*p*-ethoxyphenylethylene (0.019 g) with m.p. and mixed ⁶ 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 ⁵ m.p. 142°, and 2-chloro-1,1-bis-*p*-methoxyphenylethylene (0.24 g), m.p. and mixed ¹³ 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 ⁶ m.p. 142°, and 2-chloro-1,1-bis-*p*-ethoxyphenylethylene (0.29 g), m.p. and mixed ¹³ m.p. 76°.

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

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. C₃₂H₃₄O₄ 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. C₃₆H₄₂O₄ 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 ¹⁴ 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°.

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

¹⁴ A. I. Vogel, 'A Text Book of Practical Organic Chemistry,' Longmans Green, London, 3rd edn., 1967, p. 870.

¹¹ W. Tadros, *J. Chem. Soc.*, 1954, 2966.

¹² W. Tadros and A. B. Sakla, *J. Chem. Soc.*, 1957, 3210.