532. *Butadienes and Related Compounds. Part III.* Further Study of the Factors bearing on the Formation of* 1 : 1 : 4 : 4-*Tetra-arylbuta*-1 : 3-*dienes.*

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The butadiene is formed from di-*p*-alkoxyphenylvinyl bromide (1) when its solution in acetic acid is exposed to direct sunlight in atmosphere of nitrogen or carbon dioxide, (2) when its solution in acetic saturated with hydrogen chloride, in this case di-*p*-alkoxyphenylvinyl chloride being also obtained, or (3) in presence of anthrone. The di-*p*-alkoxyphenylvinyl halide undergoes the reaction in the solid state in presence of gaseous hydrogen bromide. The influence of substituents, temperature, etc., previously reported is confirmed. *p*-Ethylthio-, *p*-methyl-, *p*-chloro-, and *p*-bromo-phenylbutadiene are obtained by thermal decomposition of the corresponding vinyl bromides. Structures are confirmed by ozonolysis.

When exposed to direct sunlight in solution in acetic acid or carbon tetrachloride, di-*p*-chloro- or di-*p*-bromo-phenylvinyl bromide is oxidised to the corresponding benzophenone.

This paper presents a further study of the factors bearing on the formation of 1 : 1 : 4 : 4-tetra-arylbuta-1 : 3-dienes in an attempt to throw light on the mechanism of their formation. It was reported * that when a solution of 2 : 2-di-*p*-methoxy- or 2 : 2-di-*p*-ethoxy-phenylvinyl bromide in acetic acid was left in the dark for 18 months the compound was recovered unchanged. 1 : 1 : 4 : 4-Tetra-*p*-methoxy- or -ethoxy-phenylbuta-1 : 3-diene was, however, readily formed together with brown dealkylation products when a solution of the vinyl bromide in acetic was exposed to direct sunlight in an atmosphere of nitrogen or carbon dioxide, apparently according to the scheme :

$$2\mathrm{Ar_2C{:}CHBr} \longrightarrow 2\mathrm{Br}\cdot + 2\mathrm{Ar_2C{:}CH}\cdot \longrightarrow [\mathrm{Ar_2C{:}CH}\cdot]_2$$

It was also shown [1] that refluxing a solution of the di-*p*-alkoxyarylvinyl bromide in acetic acid saturated with hydrogen bromide gave the butadiene. The reaction took place also (1) at room temperature but more slowly, (2) when hydrogen bromide was replaced by hydrogen chloride (di-*p*-alkoxyphenylvinyl chloride being also formed), and (3) when the solid vinyl chloride or bromide was left in a vessel filled with gaseous hydrogen bromide; the reaction did not, however, proceed when dry gaseous hydrogen bromide was used. It was noteworthy that the di-*p*-alkoxyarylvinyl chloride gave the butadiene readily when the acetic acid solvent was saturated with hydrogen bromide and not hydrogen chloride. The mechanism of addition and the rôle played by the halogen acids in this type of reaction will be discussed in a later communication.

The butadiene was also formed when the vinyl bromide was heated with anthrone alone or in solution in acetic acid, 9-bromoanthrone and 9 : 9-dianthronyl being also obtained; comment on this finding is postponed.

The effect of different *para*-substituents on the formation of the butadienes * was confirmed. Whereas bromination of 1 : 1-di-*p*-alkoxyphenylethylene in boiling acetic acid gave readily the butadiene, that of the *p*-chloro-, *p*-bromo-, and *p*-methyl analogues (see below the effect of the methyl group on reactions in acetic acid saturated with hydrogen bromide) was not accompanied by the formation of the butadiene in spite of the solution's being refluxed for 9 hr. On bromination of 1 : 1-di-*p*-ethylthiophenylethylene, the butadiene was obtained after prolonged boiling (6 hr.). When a mixture of 1 : 1-di-*p*-chloro- or -bromo-phenylethylene (1 mol.) and the vinyl bromide (1 mol.) in solution in acetic acid was refluxed for 9 hr., the butadiene was not formed even when the solution was saturated with hydrogen bromide. On the other hand, the tetra-*p*-ethylthio- and the

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* Part II, *J.*, 1954, 2966.

[1] Tadros and Aziz, *J.*, 1951, 2553.

-*p*-methyl-arylbutadiene were obtained when a solution of the ethylene and the vinyl bromide in acetic acid saturated with hydrogen bromide was refluxed for a relatively short time (15—30 min.).

The butadienes were also obtained by thermal decomposition of the vinyl bromides. It was noted that the temperature at which thermal decomposition readily took place was 165° for the *p*-methoxy-compound,[1] 210—230° for the *p*-ethylthio- and *p*-methyl-, and 280—300° for the *p*-chloro- and *p*-bromo-compound, showing parallelism with the influence of the *para*-substituent on the ease of formation of the butadiene. It is interesting that the presence of radicals such as the methyl with $+I$ effect or the halogens chlorine and bromine with $-I+T$ effect in place of the alkoxyl groups did not favour formation of the butadiene. Alkoxy-groups and halogen atoms show $-I+T$ effects, but the former groups possess a weak $-I$ displacement together with a strong $+T$ displacement whereas for halogen atoms both forms of displacement are important.[2]

1 : 1 : 4 : 4-Tetra-*p*-methylphenylbuta-1 : 3-diene was previously prepared[3] by reduction of 2 : 2 : 2-trichloro-1 : 1-di-*p*-methylphenylethane, and the *p*-bromo-butadiene was obtained[4] by rearrangement of 1 : 1 : 4 : 4-tetra-*p*-bromophenylbut-2-yne with alcoholic ethoxide or pentyloxide, the acetylene itself resulting from cathodic reduction of 2 : 2-di-*p*-bromophenyl-1 : 1 : 1-trichloroethane.

The structures of the *p*-ethylthio-, *p*-methyl-, and *p*-bromo-arylbutadienes were confirmed by ozonolysis.

Like the *p*-alkoxyarylvinyl bromides,[1] the *p*-chloro- and the *p*-bromo-analogues were oxidised to the corresponding ketones when exposed to direct sunlight in solution in acetic acid or carbon tetrachloride.

Di-*p*-methoxyphenylvinyl chloride, which was obtained by dehydrochlorination of 1 : 1-dichloro-2 : 2-di-*p*-methoxyphenylethane[5, 6] or by a Friedel–Crafts reaction,[7] and the corresponding ethoxy-chloro-compound were readily obtained by chlorination of the ethylenes in solution in carbon tetrachloride with sulphuryl chloride instead of chlorine.[1]

EXPERIMENTAL

*1 : 2-Dibromo-1 : 1-di-*p*-ethylthiophenylethane.*—A solution of bromine (0·53 g., 1 mol.) in acetic (10 c.c.) was added to a warm solution of 1 : 1-di-*p*-ethylthiophenylethylene[8] (1 g., 1 mol.) in the same solvent (10 c.c.). The precipitated *dibromide* obtained on cooling was filtered off and crystallised from alcohol as colourless or pale yellow crystals (0·6 g.), m. p. 104° (Found: C, 47·2; H, 3·9; Br, 34·4; S, 14·1. $C_{18}H_{20}Br_2S_2$ requires C, 47·0; H, 4·3; Br, 34·8; S, 13·9%).

*Di-*p*-substituted Diphenylvinyl Bromides.*—These were prepared by adding an equimolecular quantity of bromine in chloroform, carbon tetrachloride, or ether to the di-*p*-substituted phenylethylene in the same solvent (1 g. in 100 c.c.). The solutions were then shaken with aqueous sodium carbonate or hydroxide (*ca.* 5%), and with water, dried ($CaCl_2$), and filtered, and the solvent partly removed on the water-bath. The rest of the solvent was removed after addition of a little alcohol at 60° at the water-pump. The vinyl bromides separated from alcohol as colourless crystals. Thus were prepared *di-*p*-chloro-*, m. p. 72° (Found: C, 50·5; H, 2·7; Hal, 46·2. $C_{14}H_9Cl_2Br$ requires C, 51·2; H, 2·7; Hal, 46·0%), *di-*p*-bromo-*, m. p. 104° (Found: C, 40·0; H, 1·9; Br, 57·9. $C_{14}H_9Br_3$ requires C, 40·3; H, 2·2; Br, 57·6%), and *di-*p*-ethylthio-phenylvinyl bromide*, m. p. 42° (Found: C, 56·7; H, 5·3; Br, 20·8; S, 16·1. $C_{18}H_{19}BrS_2$ requires C, 57·0; H, 5·0; Br, 21·1; S, 16·9%).

*Di-*p*-alkoxyphenylvinyl Chlorides.*—These were prepared in almost quantitative yield by adding an equimolecular quantity of sulphuryl chloride in carbon tetrachloride to the di-*p*-alkoxyphenylethylene in the same solvent (1 g. in 30 c.c.). A vigorous reaction which took

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[2] Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons, Ltd., London, 1953, p. 249.

[3] Brand and Matsui, *Ber.*, 1913, **46**, 2942; Brand and Wendel, *J. prakt. Chem.*, 1927, **115**, 335.

[4] Brand and Krücke-Amelung, *Ber.*, 1939, **72**, 1029.

[5] Wiechell, *Annalen*, 1894, **279**, 337.

[6] Brand, *Ber.*, 1913, **46**, 2935.

[7] Mentzer and Xuong, *Compt. rend.*, 1946, **222**, 1004; *Bull. Soc. chim. France*, 1947, 885.

[8] Tadros and Saad, *J.*, 1954, 1155.

place at room temperature was complete within 15 min. Solvent was removed on the water-bath, and the residue crystallised from alcohol as colourless crystals. Thus were prepared di-*p*-methoxyphenylvinyl chloride, m. p. 78° (Wiechell[5] gave m. p. 76°, and Brand[6] m. p. 80—81°) (Found: C, 70·3; H, 5·8; Cl, 12·8. Calc. for $C_{16}H_{15}O_2Cl$: C, 69·9; H, 5·4; Cl, 12·9%), and di-*p*-ethoxyphenylvinyl chloride, m. p. 76° (Found: C, 71·3; H, 6·3; Cl, 11·4. Calc. for $C_{18}H_{19}O_2Cl$: C, 71·4; H, 6·3; Cl, 11·7%).

Effect of Halogen Acids.—(A) *In acetic acid.* (*a*) Effect of hydrogen chloride on the vinyl bromides. When a solution of di-*p*-methoxyphenylvinyl bromide (1 g.) in acetic acid saturated with hydrogen chloride was left at room temperature for one day, or heated on the water-bath for 40 min. or refluxed for 5 min., an olive-green or dark brown colour developed, and 1 : 1 : 4 : 4-tetra-*p*-methoxyphenylbuta-1 : 3-diene, m. p. and mixed m. p. 206°, was formed (yield: 0·1, 0·03, and 0·5 g. respectively). The acetic acid mother-liquor was neutralised with sodium carbonate, and the viscid material which separated was extracted with ether. The ethereal layer was dried ($CaCl_2$) and filtered, then the solvent was removed at room temperature. The residue was digested for 1 hr. on the water-bath with alcoholic potassium hydroxide (2 g. in 30 c.c.). On dilution a precipitate was obtained which separated from alcohol (charcoal) as colourless crystals, m. p. 78° alone or mixed with di-*p*-methoxyphenylvinyl chloride (Found: Cl, 13·2. Calc. for $C_{16}H_{15}O_2Cl$: Cl, 12·9%). Di-*p*-ethoxyphenylvinyl bromide behaved similarly, giving 1 : 1 : 4 : 4-tetra-*p*-ethoxyphenylbuta-1 : 3-diene (m. p. and mixed m. p. 207°) and di-*p*-ethoxyphenylvinyl chloride, m. p. and mixed m. p. 76° (Found: Cl, 11·2. Calc. for $C_{18}H_{19}O_2Cl$: Cl, 11·7%). The same chlorides were obtained when the intermediate viscid substances were left in alcohol for 2—3 days.

(*b*) Effect of hydrogen chloride on the vinyl chlorides. When a solution of di-*p*-methoxy- or -ethoxy-phenylvinyl chloride in acetic acid saturated with hydrogen chloride was refluxed for 5 hr., no butadiene was formed and the chloride was recovered unchanged.

(*c*) Effect of hydrogen bromide on the vinyl chlorides. When a solution of di-*p*-methoxy- or -ethoxy-phenylvinyl chloride (1 g.) in acetic acid (10 c.c.) saturated with hydrogen bromide was left at room temperature for one day or refluxed for 5 min., 1 : 1 : 4 : 4-tetra-*p*-alkoxy-phenylbuta-1 : 3-diene (*ca.* 0·5 g.) was obtained showing no m. p. depressions when admixed with authentic samples. The acetic acid mother-liquors were diluted with water and neutralised with sodium carbonate, viscid materials separating, which were extracted with alcoholic potassium hydroxide as above. Di-*p*-alkoxyphenylvinyl chlorides were obtained showing no depression when admixed with authentic samples.

(B) *In the solid state.* (*a*) When di-*p*-methoxy- or -ethoxy-phenylvinyl bromide (1 g.) was left in an atmosphere of hydrogen bromide, which was not completely dry, in a desiccator for 3 days, the compound gradually changed to rose, red, and finally dark violet. The product was treated with alcohol (25 c.c.) and the 1 : 1 : 4 : 4-tetra-*p*-alkoxyphenylbuta-1 : 3-diene (*ca.* 0·5 g.) thus obtained was filtered off. The alcoholic mother-liquor was digested for 1 hr. with potassium hydroxide (2 g.). On dilution, unchanged vinyl bromide was obtained.

(*b*) When di-*p*-methoxy- or -ethoxy-phenylvinyl chloride (1 g.) was left in an atmosphere of hydrogen bromide (not dry) for 11 days, it became rose, red, and finally dark violet in colour. When the product was treated with alcohol, the corresponding butadiene (*ca.* 0·3 g.) did not dissolve and was filtered off. When the alcoholic mother-liquor was digested with potassium hydroxide as above, the vinyl chloride was obtained.

Preparation of Butadienes.—(a) 1 : 1 : 4 : 4-*Tetra*-p-*ethylthiophenylbuta*-1 : 3-*diene*. (i) A solution of bromine (0·27 g., 1 atom-equiv.) in glacial acetic acid (5 c.c.) was added to 1 : 1-di-*p*-ethylthiophenylethylene (1 g., 1 mol.) in the same solvent (10 c.c.), and the solution was refluxed for 6 hr. On cooling, 1 : 1 : 4 : 4-tetra-*p*-ethylthiophenylbuta-1 : 3-diene separated and from acetic acid formed brownish-yellow crystals, m. p. 156° (0·4 g.) (Found: C, 71·8; H, 6·1; S, 21·4. $C_{36}H_{38}S_4$ requires C, 72·2; H, 6·3; S, 21·3%). (ii) The butadiene (0·24 g.) was obtained when a solution of 1 : 1-di-*p*-ethylthiophenylethylene (0·30 g., 1 mol.) and di-*p*-ethylthiophenylvinyl bromide (0·379 g., 1 mol.) in glacial acetic acid saturated with hydrogen bromide (10 c.c.) was refluxed for 20—30 min.

(b) 1 : 1 : 4 : 4-*Tetra*-p-*methylphenylbuta*-1 : 3-*diene*. This compound could not be prepared by method (i) above, but it was obtained by method (ii) (ethylene, 0·208 g., 1 mol.; vinyl bromide, 0·287 g., 1 mol.; acetic acid saturated with hydrogen bromide, 10 c.c.; yield, 0·15 g. of butadiene). When heated, the solution became olive-green. The butadiene separated from ethyl acetate as pale yellow crystals, m. p. 248—250° (Brand *et al.*[3] gave m. p. 255°) (Found: C, 92·4; H, 7·2. Calc. for $C_{32}H_{30}$: C, 92·8; H, 7·2%).

(c) *Preparation of butadienes by thermal decomposition.* The *p*-ethylthio-, *p*-methyl-, *p*-chloro-, and *p*-bromo-compounds were obtained (*ca.* 10%) when the vinyl bromide (1 g.) was heated under an air condenser. Decomposition took place at temperatures given on p. 2702. The dark brown materials obtained were triturated with warm acetone, and the insoluble fractions were filtered off. The solvent was removed and the residue crystallised from ethyl acetate. The *p*-ethylthio-, *p*-methyl-, and *p*-chloro-compounds were not depressed in m. p. when admixed with authentic samples (for the chloro-compound, see Tadros [9]). 1 : 1 : 4 : 4-Tetra-*p*-bromophenylbuta-1 : 3-diene was obtained as pale yellow crystals, m. p. 262° (Brand and Krücke-Amelung [4] gave m. p. 265—266°) (Found : C, 50·2; H, 2·4; Br, 47·2. Calc. for $C_{28}H_{18}Br_4$: C, 49·9; H, 2·7; Br, 47·5%).

*Reaction between Di-*p*-alkoxyphenylvinyl Bromides and Anthrone.*—(*a*) A mixture of di-*p*-methoxy- (0·638 g., 2 mol.) or -ethoxy-phenylvinyl bromide (0·694 g., 2 mol.) and anthrone (0·194 g., 1 mol.) was heated on the water-bath for 7 min., melting and becoming violet-red. The product was digested with carbon disulphide. The undissolved fraction crystallised from acetone from which 9 : 9′-dianthronyl [10] separated as colourless crystals, m. p. 250—255° showing no depression when admixed with an authentic sample [11] (Found : C, 87·0; H, 4·4. Calc. for $C_{18}H_{18}O_2$: C, 87·0; H, 4·7%). 1 : 1 : 4 : 4-Tetra-*p*-methoxy- or -ethoxy-phenylbuta-1 : 3-diene separated from carbon disulphide showing no depression when admixed with authentic samples. The butadiene was filtered off, light petroleum (b. p. 50—70°) was added to the filtrate, and the 9-bromoanthrone thus obtained was recrystallised from carbon disulphide–light petroleum as almost colourless crystals, m. p. 148° showing no depression when admixed with an authentic sample.[12]

(*b*) Experiments (*a*) were repeated with acetic acid as solvent (3 min.). The reaction took place on boiling. On cooling, a mixture of the butadiene and 9 : 9′-dianthronyl was precipitated. These were separated by digestion with carbon disulphide as above. The acetic acid mother-liquor was diluted with cold water and the precipitate was filtered off. On fractional crystallisation of the precipitate from carbon disulphide–light petroleum, 9-bromoanthrone was isolated.

Effect of Direct Sunlight on 1 : 1-*Di-*p*-chloro- and -*p*-bromo-phenylvinyl Bromide.*—On exposure to direct sunlight, di-*p*-chloro- or -bromo-phenylvinyl bromide (0·5 g.) in solution in acetic acid or carbon tetrachloride (10 c.c.) was oxidised to 4 : 4′-dichloro- (m. p. and mixed m. p. 144°) and 4 : 4′-dibromo-benzophenone (m. p. and mixed m. p. 173°) respectively. The solution became yellow, pale brown, brownish-red, and finally dark orange (within 6—10 weeks depending on season of exposure), reaction then being almost complete.

Effect of Direct Sunlight on 1 : 1-*Di-*p*-alkoxyphenylvinyl Bromides in Nitrogen or Carbon Dioxide.*—A solution of di-*p*-methoxy- or -ethoxy-phenylvinyl bromide (1 g.) in acetic acid (10 c.c.) was sealed in a Pyrex tube under nitrogen or carbon dioxide and exposed to direct sunlight for 3 months, acquiring a pale brown colour within 24 hr., gradually darkening, and becoming finally dark brown. A precipitate (0·4 g.) separated and was filtered off. This proved to be 1 : 1 : 4 : 4-tetra-*p*-alkoxyphenylbuta-1 : 3-diene showing no depression in m. p. when mixed with authentic samples. When the acetic acid mother-liquor was diluted, dealkylated products separated.

Ozonolysis.—The butadienes gave glyoxal and the corresponding ketones, the procedure being similar to that previously reported.[1] Compounds obtained were 4 : 4′-diethylthiobenzophenone, m. p. and mixed m. p. 116—118°, 4 : 4′-dimethylbenzophenone, m. p. and mixed m. p. 95°, and 4 : 4′-dibromobenzophenone, m. p. and mixed m. p. 173°.

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[*Received, December 2nd*, 1955.]

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[9] Tadros, *J.*, 1954, 2966.

[10] Bell and Waring, *J.*, 1949, 267.

[11] Dimroth, *Ber.*, 1901, **34**, 219; Beilstein's Handbuch, 1925, Vol. VII, p. 846.

[12] Goldmann, *Ber.*, 1887, **20**, 2436; Meyer, *Annalen*, 1911, **379**, 37; Barnett, Cook, and Matthews, *J.*, 1923, 1994.