628. *Butadienes and Related Compounds. Part IV.*[1] *A Study of the Mechanism of Formation of* 1 : 1 : 4 : 4-*Tetra-arylbuta*-1 : 3-*dienes.*

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Evidence has been gathered that butadienes are formed from 2 : 2-di-(*p*-substituted phenyl)vinyl bromides in the presence of hydrogen chloride or bromide after addition according to the Markownikoff rule. The butadienes are readily formed from the corresponding vinyl chlorides in the presence of hydrogen bromide but not of hydrogen chloride.

Solvents such as alcohol, carbon tetrachloride, benzene, and acetic anhydride do not favour the reaction between the ethylenes and vinyl bromides to give the butadienes. Addition of acetic anhydride to acetic acid increases the induction period and decreases the yield.

2 : 2-Di-*p*-alkoxyphenylvinyl bromides are readily reduced by anthrone to the ethylenes, whereas the chlorides are not reduced except in the presence of a halogen acid. Together with the ethylenes, the corresponding butadienes and 9 : 9′-dianthronyl are formed as main products, different reactions leading to the formation of the last two products.

When two vinyl bromides, especially in the presence of a halogen acid, or a vinyl bromide and an ethylene with a different alkoxyl group, are heated together in the solid state or in acetic acid, three butadienes are formed.

A free-radical mechanism is suggested for the formation of the butadienes.

HYDROGEN BROMIDE [1a] and chloride [1c] have been shown to promote the formation of 1 : 1 : 4 : 4-tetra-arylbuta-1 : 3-dienes from 2 : 2-diarylvinyl halides, whereas dilution [1b] of the acetic acid used as solvent has the reverse effect. Addition of acetic anhydride to the ethylene and vinyl bromide in acetic acid increased the induction period, the reaction being prevented when the acetic acid was completely replaced by anhydride. At least two factors (besides others such as temperature, polarisability of the reagents, the rate of addition of acids, etc.) probably operate: (*a*) electrophilic addition of the acid (Ad_E) [2] to the vinyl bromide before the reaction, and (*b*) formation of the butadiene after this addition. The addition of acetic anhydride would remove the water present (2%), this being apparently associated with limitation in the ionisation of the acetic acid.[3] Hall and Voge [4] noted that acetic anhydride possessed weak conductivity which was attributed by Gillespie [5] to an ionic self-dissociation to acetylium and acetate ions:

$$(CH_3{\cdot}CO)_2O \rightleftharpoons CH_3{\cdot}CO^+ + CH_3{\cdot}CO_2^-$$

It seems that the degree of ionisation is too small to affect factor (*a*) or that the presence of a proton (or hydroxonium ion [6]) is necessary. On saturation of the acetic anhydride with hydrogen bromide, the reaction (even with the vinyl bromide alone) proceeded readily. The halogen acid apparently adds to the vinyl bromide before formation of the butadiene, to give 1 : 1-di-*p*-alkoxyphenyl-2 : 2- (A) or -1 : 2-dibromoethane (B) in accordance with the Markownikoff rule. Formation of (A) was excluded when 1 : 1-dibromo-2 : 2-di-*p*-methoxy(or ethoxy)phenylethane [7] proved to be stable in boiling acetic acid, even in the presence of hydrogen chloride or bromide; the alternative product (B), obtained on

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[1] Parts I—III, (*a*) Tadros and Aziz, *J.*, 1951, 2553; (*b*) Tadros, *J.*, 1954, 2966; (*c*) Tadros, Sakla, and Akhnookh, *J.*, 1956, 2701.

[2] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons, Ltd., London, 1953, p. 646.

[3] Kohlrausch's data for the ionisation of acetic acid at different dilutions; Landolt, Börnstein, Roth, and Scheel, " Physikalisch-chemische Tabellen," Part II, Julius Springer, Berlin, 1923, p. 1075.

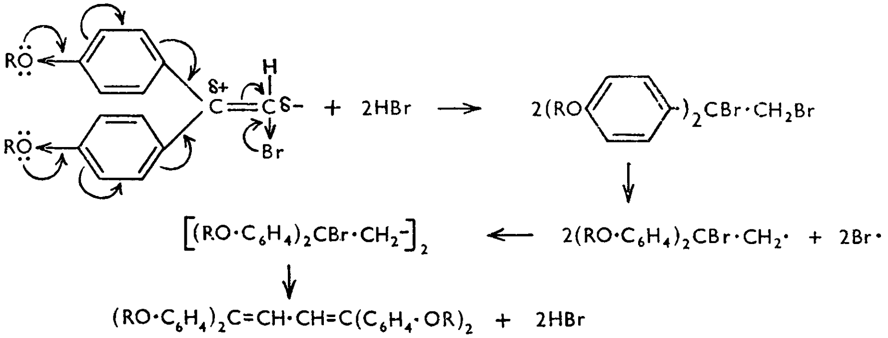
[4] Hall and Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 239.

[5] Gillespie, *J.*, 1950, 2997.

[6] Ref. 2, p. 651.

[7] Harris and Frankforter, *J. Amer. Chem. Soc.*, 1926, **48**, 3144.

addition of bromine to the ethylene, was unstable, readily giving rise to the vinyl bromide or the butadiene according to conditions. When the alkoxyarylvinyl bromide was left in an atmosphere of hydrogen chloride or bromide at room temperature, it gradually (faster with hydrogen bromide) became semisolid, giving back the vinyl bromide on treatment with alcohol or forming the butadiene when heated on the water-bath. 1 : 2-Dibromo-1 : 1-di-*p*-ethylthiophenylethane was more stable than the alkoxy-compounds, being formed when 2 : 2-di-*p*-ethylthiophenylvinyl bromide was treated with hydrogen bromide in acetic acid, showing beyond doubt that the addition of the halogen acid took place according to the Markownikoff rule. When a solution of 2 : 2-di-*p*-alkoxyphenylvinyl bromide, alone or with the corresponding 1 : 1-di-*p*-alkoxyphenylethylene, in alcohol, benzene, or carbon tetrachloride was refluxed for 12—15 hr., the butadiene was not formed, apparently owing to the absence of the necessary addition of Ad_E. The rôle played by the halogen acids in the formation of the butadienes from the vinyl halides may be represented in the light of present electronic theory by the annexed scheme.



The addition of hydrogen bromide (and of other halogen acids such as hydrogen chloride) as shown implies that electron density around the carbon atom β to the aryl group should be greater than that around the α-carbon atom. It may be assumed that a stage of " homopolarisability " would be reached at which the intermediate addition compound would undergo homolytic fission in acetic acid or in the solid state, to give two bromine atoms and two free radicals. The latter would dimerise and two molecules of halogen acid would subsequently be eliminated with formation of the butadiene. In the case of 1 : 1-dibromo-2 : 2-di-*p*-methoxy(or ethoxy)phenylethane, the electron density round the α- and β-carbon atoms seems not to favour the ready elimination of the halogen acid to give the vinyl bromide or the conversion into the butadiene; and therefore once these compounds were synthesised, they were more stable than their isomers.

Evidence that formation of free radicals precedes that of the butadienes was sought in the reaction between 2 : 2-di-*p*-alkoxyphenylvinyl bromides and anthrone.[1c] On studying this reaction further, it was found that refluxing a solution of the vinyl bromide (I) and anthrone (II) in acetic acid for only 20 seconds gives 1 : 1-di-*p*-alkoxyphenylethylene (III), 1 : 1 : 4 : 4-tetra-*p*-alkoxyphenylbuta-1 : 3-diene (V), and 9 : 9′-dianthronyl (VI) as main products, with minute quantities of other compounds, which seem to have been formed partly during fractionation and recrystallisation. A preliminary study showed that one of these compounds had m. p. 236—238° with analytical data corresponding to hydroxydianthronyl for which m. p. 219—249° with sintering at 180° was given.[9] An ionic mechanism should have given only a condensation product between the vinyl bromide and anthrone. The formation of the ethylene (III) indicated a reduction, but it should be emphasised that the presence of bromine had some bearing on this reducing property,

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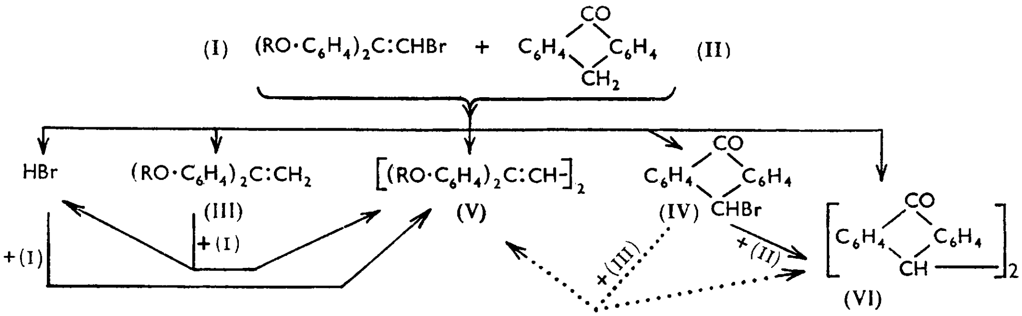
[8] Cf. ref. 1*c*.

[9] Scalera, Hardy, Hardy, and Joyce, *J. Amer. Chem. Soc.*, 1951, **73**, 3094.

since the vinyl chloride was reduced only in presence of a halogen acid (see below). It was interesting that the nitro-group was reduced by anthrone, as reported by Ingram.[10]

When equimolecular quantities of anthrone (II) and 9-bromoanthrone (IV) (or 9-chloroanthrone [11]) were refluxed in acetic acid, 9 : 9′-dianthronyl (VI) was obtained, perhaps by a condensation or by a free-radical reaction. When a solution of equimolecular quantities of 9-bromoanthrone (IV) and 1 : 1-di-*p*-methoxy(or ethoxy)phenylethylene (III) was refluxed, 9 : 9′-dianthronyl (VI) and the corresponding butadiene were the main products; the formation of 9 : 9′-dianthronyl may be attributed to transient existence of the anthronyl radical. That 9-bromoanthrone may form such a transient free radical, which would dimerise to 9 : 9′-dianthronyl, was suggested by Barnett *et al.*[12] With regard the formation of the butadiene a number of reactions may be involved: (*a*) Interaction between the vinyl bromide (I) and 1 : 1-di-*p*-methoxy(or ethoxy)phenylethylene (III) formed; (*b*) hydrogen bromide [formed on reduction of the vinyl bromide with anthrone or in reaction (*a*) together with the butadiene], acting on the vinyl bromide; and (*c*) interaction of 9-bromoanthrone (IV) and the ethylene (III). Reactions (*a*) and (*b*) have been reported,[1a] and (*c*) was mentioned above (reaction 2). It may be noted that cross-dimerisation of the anthronyl and vinyl radicals seemed not to occur. The products previously reported [1c] and the above reactions may be represented by the annexed general scheme.



The ethylene, which would be formed only in the presence of a halogen acid on the interaction of the vinyl chloride and anthrone (anthrone not being affected by hydrogen chloride or bromide), was apparently produced by reduction of the vinyl chloride–halogen acid addition compound with subsequent loss of the halogen acid. In the presence of hydrogen bromide 9-chloroanthrone was obtained. The ready formation of the butadiene from the vinyl bromide (in contrast to the vinyl chloride) was apparently related to the lower energy of activation for homolytic fission of the C–Br than of the C–Cl bond.[13] Formation of the vinyl chloride, together with the butadiene, when the vinyl bromide was dissolved in acetic acid saturated with hydrogen chloride [1c] was apparently due to a concurrent reaction involving electrophilic substitution (chlorine probably replacing the bromine in the halogen acid addition compound), followed by dehydrochlorination. The effect of temperature [1a, 14] (see Table) was further corroborated.

When two vinyl bromides, especially in the presence of hydrogen bromide, were heated together in the solid state or in solution in acetic acid, three butadienes were formed. These were, however, obtained more readily and in better yields when a mixture of the vinyl bromide and the ethylene (with two different alkoxyl groups) was used, indicating that the ethylene played some part in the reaction. An ionic condensation would have given, as a sole product, the mixed butadiene and hydrogen bromide, and not three butadienes.

[10] Ingram, *J.*, 1950, 2246.
[11] Matthews, *J.*, 1926, 236.
[12] Barnett, Cook, and Matthews, *J.*, 1923, 1994.
[13] Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308.
[14] Bergmann, Szmuskowicz, and Dimant, *J. Amer. Chem. Soc.*, 1949, **71**, 2968.

Hydrogen bromide has been shown[15] to have no effect on 1 : 1-di-*p*-methoxyphenylethylene; other ethylenes also were not affected, except for the development of a green colour, when in solution in acetic acid saturated with hydrogen bromide. The butadiene corresponding to the ethylene could have been formed only by the action of bromine liberated from the vinyl bromide. The ionic mechanism postulated by Bergmann *et al.*[14] seemed not to be favoured because 1 : 1-di-*p*-alkoxyphenylethylene failed to condense with 2 : 2-di-*p*-alkoxyphenylvinyl chloride; and, according to their probable mechanism, the addition of hydrogen bromide should take place contrary to the Markownikoff rule, whereas the present findings showed that the addition follows the Markownikoff rule. The formation of three butadienes from mixtures of the vinyl bromides in the presence of hydrogen chloride or bromide, especially in the solid state, was probably due to transient free-radical formation ($Ar_2CHal{\cdot}CH_2{\cdot}$) after the addition of the halogen acid. It was shown[1c] that the butadiene was formed on irradiating a solution of 2 : 2-di-*p*-methoxy(or ethoxy)phenylvinyl bromide in acetic acid in an atmosphere of nitrogen or carbon dioxide; the same result has now been obtained in absence of a solvent.

The structure of the new butadienes was confirmed by ozonolysis.

EXPERIMENTAL

1 : 1-*Di*-p-n-*butoxyphenylethylene*.—4 : 4′-Di-*p*-*n*-butoxybenzophenone[16] (16·3 g.) in ether (250 c.c.) was added to methylmagnesium iodide (from magnesium, 3 g., and methyl iodide, 17·7 g.) in ether (150 c.c.) with stirring, during 2 hr., and the whole was set aside overnight. The mixture was decomposed with aqueous ammonium chloride and extracted with ether. The *ethylene*, crystallised from alcohol, had m. p. 125° (Found: C, 81·5; H, 8·5. $C_{22}H_{28}O_2$ requires C, 81·3; H, 8·6%).

2 : 2-*Di*-p-*alkoxyphenylvinyl Bromides*.—These were obtained by adding 1 mol. of bromine in chloroform, carbon tetrachloride, or ether to the ethylene in the same solvent[1c], and crystallised from alcohol. 2 : 2-*Di*-p-iso*propoxy*- (Found: C, 64·0; H, 5·9; Br, 22·0. $C_{20}H_{23}O_2Br$ requires C, 64·0; H, 6·1; Br, 21·4%) and 2 : 2-*di*-p-n-*butoxy-phenylvinyl bromide* (Found: C, 65·4; H, 6·5; Br, 20·0. $C_{22}H_{27}O_2Br$ requires C, 65·5; H, 6·7; Br, 19·9%) had m. p. 46—47° and 54° respectively. All 2 : 2-di-*p*-substituted phenylvinyl bromides required for the present work were purified from any contaminating hydrogen bromide by refluxing them for an hour with alcoholic potassium hydroxide (5 g. of vinyl bromide, 2 g. of potassium hydroxide, and 50 c.c. of alcohol); the solution was diluted, and the precipitate filtered off, washed with water, and recrystallised from alcohol.

1 : 1 : 4 : 4-*Tetra*-p-*alkoxyphenylbuta*-1 : 3-*dienes*.—(a) 1 : 1 : 4 : 4-*Tetra*-p-n-*butoxyphenylbuta*-1 : 3-*diene*. (i) A solution of bromine (0·16 g., 0·5 mol.) in glacial acetic acid (2 c.c.) was added to a warm solution of 1 : 1-di-*p*-*n*-butoxyphenylethylene (0·648 g., 1 mol.) in the same solvent (10 c.c.) and refluxed for 5 min. On cooling, the *butadiene* (0·45 g.) separated and was obtained from acetic acid as colourless or straw-yellow crystals, m. p. 185—186° (Found: C, 82·0; H, 8·1. $C_{44}H_{54}O_4$ requires C, 81·8; H, 8·4%). (ii) It was also obtained (0·9 g.) on refluxing a solution of 1 : 1-di-*p*-*n*-butoxyphenylethylene (0·648 g., 1 mol.) and 2 : 2-di-*p*-*n*-butoxyphenylvinyl bromide (0·806 g., 1 mol.) in glacial acetic acid (10 c.c.) for 5 min. (iii) It was obtained (0·9 g.) within 20—25 min. when the mixture used in experiment (ii) was heated on the water-bath without a solvent. (iv) A solution of 2 : 2-di-*p*-*n*-butoxyphenylvinyl bromide (1 g.) in acetic acid saturated with hydrogen bromide (10 c.c.) was refluxed for 10 min., whereby the butadiene (0·4 g.) was obtained. (v) Heating the vinyl bromide (1 g.) in an atmosphere of hydrogen bromide on the water-bath gave the butadiene (0·2 g.).

(b) 1 : 1-*Di*-p-*methoxyphenyl*-4 : 4-*di*-p-n-*propoxyphenylbuta*-1 : 3-*diene*. (i) A solution of 1 : 1-di-*p*-methoxyphenylethylene (0·48 g., 1 mol.) and 2 : 2-di-*p*-*n*-propoxyphenylvinyl bromide (0·75 g., 1 mol.) in 98% acetic acid (10 c.c.) was boiled for 3—4 min. A few drops of water were added and, after cooling, the mixture of butadienes (0·9 g.) was filtered off. The components were separated by repeated fractional recrystallisation from carbon disulphide–light petroleum (b. p. 50—70°) or alcohol and finally from acetic acid. Thus were obtained

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[15] Bergmann and Szmuskowicz, *ibid.*, 1947, **69**, 1777.
[16] Jones, *J.*, **1936**, 1854.

1 : 1 : 4 : 4-tetra-*p*-*n*-propoxy-, 198°, and 1 : 1 : 4 : 4-tetra-*p*-methoxy-phenylbuta-1 : 3-diene, m. p. 204—205°, showing no depression when admixed with authentic samples, and 1 : 1-*di*-p-*methoxyphenyl*-4 : 4-*di*-p-n-*propoxyphenylbuta*-1 : 3-*diene* as colourless or pale yellow crystals, m. p. 142° (depressed when admixed with 1 : 1-di-*p*-methoxyphenylethylene) (Found : C, 80·8; H, 7·0. $C_{36}H_{38}O_4$ requires C, 80·9; H, 7·1%); the last compound melted incompletely at 142° when mixed with 1 : 1 : 4 : 4-tetra-*p*-methoxy- or -propoxy-butadiene. (ii) The same result was obtained on repeating the experiment (10—12 minutes' boiling) with 1 : 1-di-*p*-*n*-propoxyphenylethylene (0·592 g., 1 mol.) and 2 : 2-di-*p*-methoxyphenylvinyl bromide (0·64 g., 1 mol.). (iii) Heating mixtures as in (i) and (ii) without acetic acid, on the water-bath for 20—25 min., gave the same products. (iv) A solution of 2 : 2-di-*p*-methoxy- (0·64 g., 1 mol.) and 2 : 2-di-*p*-*n*-propoxy-phenylvinyl bromide (0·75 g., 1 mol.) in acetic acid saturated with hydrogen bromide (10 c.c.) was boiled for 10 min. A mixture of butadienes (*ca.* 0·4 g.) was obtained and fractionated as above. (v) The bromides as in (iv) were heated on the water-bath in a tube filled with gaseous hydrogen bromide. The products were freed from hydrogen bromide by treatment with warm alcohol and fractionally recrystallised from acetic acid.

(c) 1 : 1-Di-*p*-methoxyphenyl-4 : 4-di-*p*-*iso*propoxyphenylbuta-1 : 3-diene, previously prepared[1b] by method (b, ii) above, was also obtained by methods b, i, iii, iv, and v; 1 : 1 : 4 : 4-tetra-*p*-methoxy- and -*iso*propoxy-phenylbuta-1 : 3-diene were also formed.

(d) The following new butadienes were obtained as colourless or pale yellow crystals, each together with two others, when 0·002 mol. of an ethylene and a vinyl bromide or two vinyl bromides with two different alkoxyl groups were treated according to methods b, i, ii, iii, iv, and v; 1 : 1-*di*-p-*ethoxyphenyl*-4 : 4-*di*-p-*methoxyphenylbuta*-1 : 3-*diene* (1), m. p. 155° (Found : C, 80·2; H, 6·5. $C_{34}H_{34}O_4$ requires C, 80·6; H, 6·7%); 1 : 1-*di*-p-n-*butoxyphenyl*-4 : 4-*di*-p-*methoxyphenylbuta*-1 : 3-*diene* (2), m. p. 151° (Found : C, 81·2; H, 7·2. $C_{38}H_{42}O_4$ requires C, 81·1; H, 7·5%); and 1 : 1-*di*-p-*ethoxyphenyl*-4 : 4-*di*-p-*propoxyphenylbuta*-1 : 3-*diene* (3), m. p. 162° (Found : C, 81·5; H, 7·7. $C_{38}H_{42}O_4$ requires C, 81·1; H, 7·5%). Together with (2), 1 : 1 : 4 : 4-tetra-*p*-methoxy-, m. p. 204—205°, -*p*-*n*-butoxy-, m. p. 185—186°, and with (3) 1 : 1 : 4 : 4-tetra-*p*-ethoxy-, m. p. 207°, and -*p*-*iso*propoxy-, m. p. 187—188,° -phenylbuta-1 : 3-diene were obtained. In case of compound (1), the small quantities of 1 : 1 : 4 : 4-tetra-*p*-methoxy- and -*p*-ethoxy-phenylbuta-1 : 3-diene could not be readily isolated : the mixture had m. p. 185—186° not depressed when admixed with an equal amount of authentic samples of the two butadienes, m. p. 189—190°.

Reactions with Solid 1 : 1-*Di*-(p-*substituted phenylethylene*) *and the Corresponding Vinyl Chloride or Bromide, or Each of the Last Two Alone ; and the Effect of Solvent.*—Results of reactions between the ethylene and the vinyl chloride or bromide using 0·002 mol. [1 : 1-di-*p*-methoxy- (0·48 g.), -ethoxy- (0·536 g.), -*n*-propoxy- or -*iso*propoxy- (0·592 g.), or -*n*-butoxy- (0·648 g.) -phenylethylene; 2 : 2-di-*p*-methoxy- (0·549 g.) or -ethoxy- (0·605 g.) -phenylvinyl chloride; 2 : 2-di-*p*-methoxy- (0·64 g.), -*p*-ethoxy- (0·694 g.), -*n*- or -*iso*propoxy- (0·75 g.), or -*n*-butoxy- (0·806 g.) -phenylvinyl bromide; or the vinyl halide alone (0·5 g.)] are shown in the Table.

In all reactions between the ethylenes and vinyl bromides, a brown or an olive-green colour developed during the formation of the butadiene. The volume of solvent, whenever used, was 10 c.c.

Experiments with 2 : 2-*Dibromo*-1 : 1-*di*-p-*methoxy*(*or ethoxy*)*phenylethane*.[7]—When a solution of 2 : 2-dibromo-1 : 1-di-*p*-methoxyphenylethane, m. p. 122° (or the ethoxy-analogue, m. p. 104°) (1 g.), in glacial acetic acid (10 c.c.) (pure or saturated with hydrogen bromide) was refluxed for 30 min., the ethane was recovered unchanged.

Addition of Hydrogen Bromide to 2 : 2-*Di*-p-*ethylthiophenylvinyl Bromide*.[1c]—When 2 : 2-di-*p*-ethylthiophenylvinyl bromide (0·5 g.) in acetic acid saturated with hydrogen bromide (10 c.c.) was kept at 20° for 3 hr., the colour changed from yellow to green and then olive-green. The precipitate obtained on cooling was filtered off, washed with a little acetic acid, and recrystallied from warm acetic acid, to give 1 : 1 : 4 : 4-tetra-*p*-ethylthiophenylbuta-1 : 3-diene, m. p. and mixed m. p. 156°. The acetic acid mother-liquors were diluted with water, and the precipitate was filtered off. It was recrystallised from little alcohol, whereby 1 : 2-dibromo-1 : 1-di-*p*-ethylthiophenylethane, m. p. 100° showing no depression when admixed with an authentic sample[1c], separated. The alcoholic mother-liquor gave on concentration a product, m. p. 85—90°, apparently a mixture of the ethane and a minute quantity of unchanged vinyl bromide, the m. p. being slightly increased when admixed with the ethane.

Reactions with Anthrone and its 9-Chloro- or 9-Bromo-derivative.—(a) *Reactions between 2 : 2-di-*p*-methoxy(or ethoxy)phenylvinyl chloride and anthrone.* (i) When a solution of 2 : 2-di-*p*-methoxyphenylvinyl chloride (1·37 g.) (or the ethoxy-analogue, 1·56 g., 2 mol.) and anthrone (0·485 g., 1 mol.) was refluxed for 30 min., the colour became yellow, and, on cooling, unchanged anthrone, m. p. and mixed m. p. 155°, separated. Unchanged vinyl chloride (m. p. 78° for methoxy-, and 76° for ethoxy-, not depressed when admixed with authentic samples) was obtained on recrystallisation from alcohol of the precipitate formed on dilution of the acetic acid mother-liquor.

Solvent (if any)	Temp.	Reaction period	R in *p*-OR	Butadiene (g.)
(I) *Ethylene and vinyl chloride*				
Solid	100°	2 hr.	Me or Et	0
98% AcOH	B. p.	9 hr.	Me or Et	0
98% AcOH *	B. p.	5 min.	Me or Et	0·5
98% AcOH *	B. p.	15 min.	Me or Et	0·15
(II) *Ethylene and vinyl bromide*				
Solid ‡	100°	25—30 min.	Me or Et	0·75
,,	,,	,,	Pr^n or Pr^i	0·8
,,	,,	,,	Bu^n	0·9
EtOH	B. p.	15 hr.	Me or Et	0
CCl_4 or C_6H_6	B. p.	12 hr.	Me or Et	0
Ac_2O	B. p.	6 hr.	Me or Et	0
Ac_2O *	B. p.	5 min.	Me or Et	0·4
98% AcOH §	B. p.	15—20 min.	Me or Et	0·75
,,	B. p.	,,	Pr^n or Pr^i	0·8
,,	B. p.	,,	Bu^n	0·92
80% AcOH	B. p.	1 hr.	Me	0·25
,, *	B. p.	1 hr.	Me	0·50
98% AcOH	30—35°	9 days	Me	0
,,	30—35	11 days	Me	0·75
98% AcOH (8 c.c.) + Ac_2O) (2 c.c.)	B. p.	2 hr.	Me	0·3
,, *	B. p.	5 min.	Me	0·6
(III) *Vinyl chloride alone*				
Solid	100°	5 hr.	Me or Et	0
Solid *	100	15 min.	Me or Et	0·15
Solid †	100	5 hr.	Me or Et	0
98% AcOH	B. p.	5 hr.	Me or Et	0
,, *	B. p.	5 min.	Me or Et	0·2
,, †	B. p.	5 hr.	Me or Et	0
(IV) *Vinyl bromide alone*				
Solid	100°	6 hr.	Me or Et	0·12
Solid *	100	15 min.	Me or Et	0·17
Solid †	100	15 min.	Me or Et	0·15
98% AcOH	B. p.	1·5—2 hr.	Me or Et	0·1
,, *	B. p.	5 min.	Me or Et	0·12
,, †	B. p.	5 min.	Me or Et	0·1

* Reactions with solid in atmosphere of hydrogen bromide or in solvent saturated with the same acid.

† Reactions carried out in the presence of hydrogen chloride.

‡ The same results were obtained within 5 min. in an atmosphere of hydrogen bromide.

§ The same result was obtained within 1—2 min. in the presence of hydrogen bromide.

(ii) Experiment (i) was repeated with acetic acid saturated with hydrogen bromide. The solution which was rose-red changed on boiling (5 min.) to red, dark red, and then dark olive-green. It was left to cool to room temperature and the yellowish-brown precipitate (A) was filtered off and washed with a few c.c. of acetic acid. This precipitate was digested with a few c.c. of carbon disulphide; the insoluble fraction, when recrystallised from acetone, gave 9 : 9′-dianthronyl, m. p. and mixed m. p. 265° (0·15 g.) (Found: C, 87·2; H, 4·8. Calc. for $C_{28}H_{18}O_2$: C, 87·0; H, 4·7%). The acetone mother-liquor gave a minute quantity of a yellow substance, m. p. >300°, to be studied later. The carbon disulphide mother-liquor gave, on cooling, 1 : 1 : 4 : 4-tetra-*p*-methoxy(or ethoxy)phenylbuta-1 : 3-diene (*ca.* 0·45 g.). The mother-liquor from fraction (A) was diluted with a few drops of water, and the dark green solution was left in the ice-chest for 2—3 hr. The precipitate (B) thus formed was filtered off and recrystallised from alcohol, whereby 1 : 1-di-*p*-methoxy- (m. p. and mixed m. p. 144°) (Found: C, 79·6; H, 6·7. Calc. for $C_{16}H_{16}O_2$: C, 80·0; H, 6·7%) or -ethoxy-phenylethylene (m. p. and mixed m. p. 142°) (0·11 g.) was obtained. The mother-liquor from (B) was diluted with water until turbidity occurred and the solution left overnight in the ice-chest. The precipitate (C) was filtered off and dried on porous plate. It was digested with a few c.c. of carbon disulphide and the minute quantity (0·05 g.) of 9 : 9′-dianthronyl, m. p. 250°, was filtered off. The carbon disulphide mother-liquor was treated with light petroleum (b. p. 50—60°) until turbidity occurred, and was left in the ice-chest for 2—3 hr. A brownish-green precipitate (0·035 g.) which melted from 135° to 185° and requires further investigation was filtered off. The filtrate was treated with a few drops of light petroleum and then decanted from a minute quantity of an oil thus formed. More light petroleum was added to the decanted liquid and the whole was left overnight at 0°. A yellow substance which sintered at 170° and melted at

200° was obtained. This was recrystallised from benzene or xylene, whereby a minute quantity of pale yellow crystals containing chlorine and having m. p. 229° (not depressed when admixed with 9-chloroanthrone [11]) was obtained. (Zahn [17] gave m. p. 234°. Dufraisse and Gérard [18] reported that 9-chloroanthrone had m. p. 165° and that the compound obtained by Matthews with m. p. 225° was chlorodianthronyl but they gave no analytical data. However, the compound with m. p. 225° prepared by Matthews's method proved by analysis, when freshly prepared, to be 9-chloroanthrone. On storage the value for chlorine decreased gradually until it corresponded to that of chlorodianthronyl with only a slight difference in m. p. This is being further studied.) The benzene or xylene mother-liquor was evaporated almost to dryness and the residue recrystallised from little alcohol, giving *ca.* 50 mg. of butadiene. The filtrate from (C) was diluted with more water, and the precipitate (D) was filtered off and dried on porous plate. Recrystallisation from a little carbon disulphide gave a minute quantity of a substance, m. p. >280°, requiring further study.

(iii) Experiment (i) was repeated with acetic acid saturated with hydrogen chloride, boiling for 5 min. only. The solution was left to cool to room temperature and the product (A) was filtered off. It was recrystallised from acetone, giving 9 : 9′-dianthronyl (0·23 g.), m. p. and mixed m. p. 264—265° (Found : C, 86·6; H, 5·0%). The filtrate from (A) was treated with a few drops of water until it became turbid and was left in the ice-chest for 2—3 hr. The precipitate (B) was filtered off and recrystallised from alcohol, whereby 1 : 1-di-*p*-methoxyphenylethylene (0·1 g.), m. p. and mixed m. p. 144° (or the ethoxy-analogue, m. p. and mixed m. p. 142°), separated. The filtrate from (B) was diluted with water, and the precipitate (C) was recrystallised from alcohol, giving unchanged 2 : 2-di-*p*-methoxyphenylvinyl chloride, m. p. 78° (or the ethoxy-compound, m. p. 76°).

(iv) On repetition of experiment (iii) with boiling for 15 min., the solution changed from faint yellow to green and the same products were obtained, together with the corresponding butadiene (*ca.* 0·12 g.) which was separated from 9 : 9′-dianthronyl by digestion with carbon disulphide as mentioned above.

(b) *Reaction between* 2 : 2-*di*-p-*methoxy*(*or ethoxy*)*phenylvinyl bromide and anthrone.* A mixture of 2 : 2-di-*p*-methoxyphenylvinyl bromide (0·638 g., 2 mol.) (or the ethoxy-analogue, 0·694 g., 2 mol.) and anthrone (0·194 g., 1 mol.) was added to boiling acetic acid (10 c.c.) and boiling continued for 20 sec. The solution was cooled and the precipitate (A) was filtered off. This was fractionated by digestion with carbon disulphide. Recrystallisation of the insoluble fraction from acetone gave 9 : 9′-dianthronyl (0·12 g.), m. p. and mixed m. p. 264—265°. Light petroleum (b. p. 50—60°) was added to the carbon disulphide mother-liquor, and the precipitate, m. p. 200°, was recrystallised from acetic acid to give the butadiene (methoxy-, m. p. 204—205°; ethoxy-, m. p. 207°; no depression in mixed m. p.s; *ca.* 0·3 g.). The green filtrate from (A) was diluted with water until it became turbid and was left in the ice-chest for 2—3 hr. The precipitate (B) was filtered off and recrystallised from alcohol. The first fraction (0·05 g.), which separated while the solution was still warm, proved to be a butadiene, and, on cooling, 1 : 1-di-*p*-methoxyphenylethylene, m. p. 144° (0·1 g.) (or the ethoxy-analogue, m. p. 142°) (no depressions in mixed m. p.s), was obtained. The filtrate from (B) was diluted with water and left in the ice-chest overnight. The precipitate was filtered off and dried on porous plate. It recrystallised from carbon disulphide as pale yellow crystals, m. p. 236—238° (unchanged on recrystallisation from acetic acid). Analytical data indicated hydroxydianthrone [9] (Found : C, 83·7; H, 4·5. Calc. for $C_{28}H_{18}O_3$: C, 83·6; H, 4·5%). Light petroleum (b. p. 50—60°) was added to the carbon disulphide mother-liquor, giving a minute quantity of brown crystals, m. p. 182°. When recrystallised from alcohol, a substance, m. p. 192°, was obtained and showed considerable depression in m. p. (172—174°) when admixed with the butadiene, and requires further study.

(c) *Reaction between anthrone and* 9-*chloroanthrone.* On refluxing a solution of anthrone (0·388 g., 1 mol.) and freshly prepared 9-chloroanthrone [11] (0·457 g., 1 mol.) in acetic acid (10 c.c.) for 5 min., 9 : 9′-dianthronyl (0·5 g.) was obtained. It separated from acetone as colourless crystals, m. p. and mixed m. p. 264—265° (Found : C, 87·0; H, 4·8%).

(d) *Reaction between anthrone and* 9-*bromoanthrone.* When a solution of anthrone (0·388 g., 1 mol.) and freshly prepared 9-bromoanthrone (0·546 g., 1 mol.) in acetic acid (10 c.c.) was refluxed for 5 min., the colour became pale orange-yellow and a precipitate separated. The

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[17] Zahn, *Ber.*, 1934, **67**, 2063.

[18] Dufraisse and Gérard, *Bull. Soc. chim. France*, 1937, **4**, 2052.

whole was left to cool and the precipitate was filtered off. When recrystallised from acetone, 9 : 9′-dianthronyl (0·5 g.), m. p. and mixed m. p. 255°, was obtained (Found : C, 87·0; H, 4·7%).

(e) No reaction took place when anthrone alone (1 g.) in solution in acetic acid (10 c.c.) saturated with hydrogen chloride or bromide was refluxed for 30 min.

(f) *Reaction between* 9-*bromoanthrone and* 1 : 1-*di*-p-*methoxy*(*or ethoxy*)*phenylethylene.* When a solution of 1 : 1-di-*p*-methoxyphenylethylene (0·96 g., 1 mol.) (or the ethoxy-compound, 1·07 g., 1 mol.) and 9-bromoanthrone (1·092 g., 1 mol.) in glacial acetic acid (10 c.c.) was boiled, an olive-green colour developed immediately. The reaction was stopped after 5 min., 5 c.c. of water were added, and the precipitate thus formed was filtered off, and dried on porous plate. It was digested with carbon disulphide, and the insoluble portion was recrystallised from acetone, from which 9 : 9′-dianthronyl (0·5 g.) separated (m. p. and mixed m. p. 264—265°). The carbon disulphide mother-liquor gave, on cooling, the corresponding diene (*ca.* 0·5 g.).

Effect of Sunlight on Solid 2 : 2-*Di*-p-*alkoxyphenylvinyl Bromides in Nitrogen or Carbon Dioxide.*—When solid 2 : 2-di-*p*-methoxyphenylvinyl bromide (or the ethoxy-, *n*-propoxy-, *iso*propoxy-, or *n*-butoxy-analogue, 0·5 g.) was exposed in a sealed Pyrex tube in atmosphere of nitrogen or carbon dioxide to direct sunlight for 1 month, the corresponding diene (*ca.* 25%) was obtained.

Ozonolysis.—The butadienes gave glyoxal and the corresponding ketones, the procedure being similar to that previously reported.[1a] The *p*-*n*-butoxy-butadiene gave 4 : 4′-di-*n*-butoxybenzophenone, m. p. and mixed m. p. 118°. The 1 : 1-di-*p*-methoxy-4 : 4-di-*p*-ethoxy-, 1 : 1-di-*p*-methoxy-4 : 4-di-*p*-*n*-propoxy-, and 1 : 1-di-*p*-*n*-butoxy-4 : 4-di-*p*-methoxy-butadienes gave in each case 4 : 4′-dimethoxybenzophenone, m. p. 142°, together with 4 : 4′-diethoxy-, m. p. 131°, 4 : 4-di-*n*-propoxy-, m. p. 127°, and 4 : 4′-di-*n*-butoxy-benzophenone, m. p. 118° respectively; the 1 : 1-di-*p*-ethoxy-4 : 4-di-*p*-*iso*propoxybutadiene gave 4 : 4′-diethoxy- and 4 : 4′-di*iso*propoxy-benzophenone, m. p. 72°. Ketones were separated by fractional recrystallisation from dilute alcohol, and m. p.s were not depressed on admixture with authentic samples.

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