SECTION C
Organic Chemistry

Reactions with Asymmetric Diarylethanes and Diarylethylenes. Part XIII.[1] Rearrangements of 1,1-Dihalogeno-2,2-diarylethanes and the Corresponding 1-Halogenoethylenes in Boiling Ethylene Glycol, Alone or in the Presence of Sodium 2-Hydroxyethoxide

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1,1-Dihalogeno-2,2-di-*p*-tolylethane in boiling ethylene glycol (98%) gave the corresponding 1-halogenoethylene, the corresponding stilbene, the cyclic acetal 1,1-ethylenedioxy-2,2-di-*p*-tolylethane, 4,4′-dimethyldeoxybenzoin, di-*p*-tolylacetaldehyde, and 4,4′-dimethylbenzophenone. The last three compounds are also formed when a solution of the acetal in acidified ethylene glycol (98%) is boiled. The 1-halogenoethylene gave the deoxybenzoin and a trace of 1,1-di-*p*-tolylethylene in boiling ethylene glycol. 1,1-Dichloro-2,2-bis-*p*-bromophenyl-(or 2,2-bis-*p*-chlorophenyl)-ethane underwent partial dehydrochlorination.

1,1-Dihalogeno-2,2-di-*p*-tolylethane, and the corresponding 1-halogenoethylene, with sodium 2-hydroxyethoxide in boiling ethylene glycol (98%) gave di-*p*-tolylacetylene and traces of the cyclic acetal and ditolylacetic acid. 1,1-Dichloro-2,2-bis-*p*-bromo-(or 2,2-bis-*p*-chloro)-phenylethane, and the 1-chloroethylene gave the cyclic acetal, 1,1-bis-*p*-chlorophenyl-2-(2-hydroxyethoxy)ethylene, bis-*p*-chlorophenylacetic acid, and bis-*p*-chlorophenylmethane. The 1-bromoethylene gave in addition a trace of bis-*p*-bromo-(or chloro)-phenylacetylene.

1,1-DIHALOGENO-2,2-BIS-*p*-ALKOXYPHENYLETHANES (I; R = MeO or EtO) * are converted in boiling ethylene glycol (98%) into the corresponding stilbene (II; R = MeO or EtO), and the cyclic acetal (III; R = MeO or EtO); longer heating gives the corresponding aldehyde (IV; R = MeO or EtO), deoxybenzoin (V; R = MeO or EtO), and the 4,4′-disubstituted benzophenone.[2]

We now show that 1,1-dihalogeno-2,2-di-*p*-tolylethanes (I; R = Me, X = Br or Cl) in boiling ethylene glycol (98%) give the same types of product. After short reaction times 1-halogeno-2,2-di-*p*-tolylethylenes (VI; R = Me, X = Br or Cl) could also be isolated; longer heating was accompanied by rearrangement of these products (VI) to give 4,4′-dimethyldeoxybenzoin (V; R = Me, see Table 1). The occurrence of this rearrangement is supported by the fact that 1-halogeno-2,2-di-*p*-tolyethylenes (VI; R = Me, X = Br or Cl) gave, in boiling ethylene glycol, 4,4′-dimethyldeoxybenzoin (V; R = Me) and a trace of 1,1-di-*p*-tolyethylene. Replacement of the alkoxy-group by methyl apparently suppresses the reactivity, since the 1-halogeno-2,2-bis-*p*-alkoxyphenylethylenes (VI; R = MeO or EtO) could not be isolated [2] from the corresponding reaction. As noted in previous studies,[2-4] a bromine atom in the side chain is much more reactive than a chlorine atom.

The acetals (III) are formed by reaction between the ethanes (I) and ethylene glycol. 1,1-Ethylenedioxy-2,2-di-*p*-tolylethane (III; R = Me) in boiling ethylene glycol (98%) containing hydrogen bromide or chloride is converted into 4,4′-dimethyldiphenylacetaldehyde (IV; R = Me), 4,4′-dimethyldeoxybenzoin (V; R = Me), and 4,4′-dimethylbenzophenone. The deoxybenzoin (V) can therefore be formed by two different routes: (*a*) rearrangement of the 1-halogenoethylenes (VI) [*cf.*[3] the reaction with 1-halogeno-2,2-bis-*p*-alkoxyphenylethylenes (VI; R = MeO or EtO, X = Br or Cl)] and (*b*) an aldehyde–ketone rearrangement [5,6] of the aldehyde (IV).

4,4′-Dimethylstilbene (II; R = Me) is apparently formed by rearrangement of 1-halogeno-2,2-di-*p*-tolylethane (VIII), the latter being formed by reduction of one of the two halogen atoms. In support of this mechanism (*a*) 1-halogeno-2,2-di-*p*-tolylethylene rearranges to 4,4′-dimethyldeoxybenzoin (see previously), (*b*) 1-halogeno-2,2-di-*p*-methoxyphenylethane (VII; R = MeO) is readily converted into the stilbene [7] (II; R = MeO), and (*c*) 1-chloro-2,2-di-*p*-chlorophenylethane (VII; R = Cl) rearranges to 4,4′-dichlorostilbene (II; R = Cl); this reaction was ascribed [8] to a Wagner–Meerwein rearrangement.

When the *p*-substituent was bromine or chlorine, the 1,1-dichloroethane underwent dehydrochlorination on

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* In the Discussion section locants for substituents are assigned so as to cause least confusion in the argument. The correct locants are given in the Experimental section.

[1] Part XII, A. B. Sakla, W. Tadros, and A. A. Helmy, *J. Chem. Soc.* (*C*), 1969, 1044.

[2] W. Tadros, A. B. Sakla, and M. K. Khalil, *J. Chem. Soc.* (*C*), 1966, 373.

[3] W. Tadros, A. B. Sakla, M. S. Ishak, and E. R. Armanious, *J. Chem. Soc.*, 1963, 4527.

[4] W. Tadros, A. B. Sakla, A. A. A. Helmy, and M. K. Khalil, *J. Chem. Soc.*, 1965, 3994.

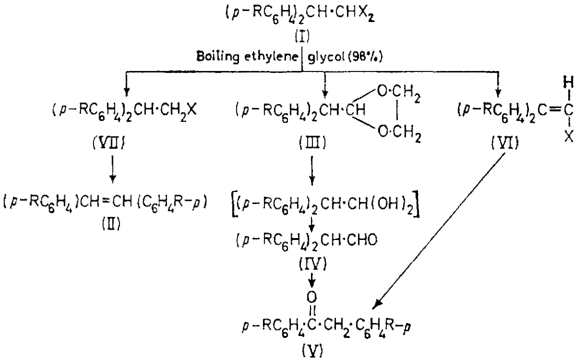
[5] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell and Son, London, 1953, p. 479.

[6] C. J. Collins, *Quart. Rev.*, 1960, **14**, 357.

[7] W. Tadros and G. Aziz, *J. Chem. Soc.*, 1961, 2684.

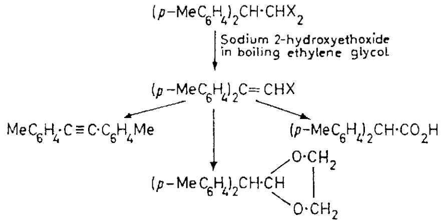
[8] J. Forrest, O. Stephenson, and W. A. Waters, *J. Chem. Soc.*, 1946, 333.

prolonged heating to give the 1-chloroethylene (VI; R = Br or Cl). 1-Bromo-2,2-bis-*p*-chlorophenylethylene was stable in boiling ethylene glycol even in the presence of acid.[3]



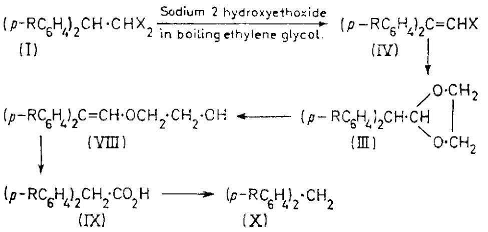
1,1-Dihalogeno-2,2-bis-*p*-alkoxyphenylethanes[2] (I; R = MeO or EtO) gave, with sodium 2-hydroxyethoxide in boiling ethylene glycol, the corresponding diarylacetylenes, apparently through the intermediate 1-halogenoethylene[9] (VI; R = MeO or EtO).

When similarly treated, 1,1-dihalogeno-2,2-di-*p*-tolylethanes (I; R = Me, X = Br or Cl) or the corresponding 1-halogenoethylenes (VI; R = Me, X = Br or Cl) gave di-*p*-tolylacetylene together with traces of 1,1-ethylenedioxy-2,2-di-*p*-tolylethane (III; R = Me) and di-*p*-tolylacetic acid (Table 2).



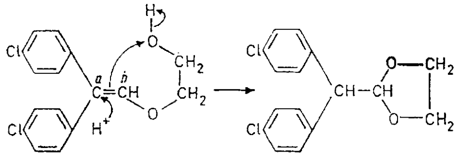
Riemschneider and his co-workers[10] reported that 1,1-dichloro-2,2-bis-*p*-halogenophenylethane (I; R = Br or Cl, X = Cl), with barium hydroxide in ethylene glycol, gave the cyclic acetal (III; R = Br or Cl). We have stated[11] that 1-bromo-2,2-bis-*p*-chlorophenylethylene (VI; R = Cl, X = Br), with sodium 2-hydroxyethoxide in boiling ethylene glycol, gives 1,1-bis-*p*-chlorophenyl-2-(2-hydroxyethoxy)ethylene (VIII; R = Cl) with, at most, a trace of bis-*p*-chlorophenylacetylene.

In repetition of this work, both the acetal (III; R = Br or Cl) and the ether (VIII; R = Br or Cl) (related acetals and ethers possess similar m.p.s, see Table 3) could be isolated, together with bis-*p*-halogenophenylacetic acid (IX; R = Br or Cl) and bis-*p*-halogenophenylmethane (X; R = Br or Cl). Bis-*p*-halogenophenylacetylene was also obtained with the 1-bromoethylenes (VI; R = Br or Cl, X = Br). The yields of the acetal (III; R = Br or Cl), the ether (VIII; R = Br or Cl), the acid (IX), and the methane (X) depend on the reaction period; those of the first three compounds decreased, while that of the methane (X) (apparently through decarboxylation [1]) increased with time (Table 3). The formation of acetals as products of attack of alkoxide ion on activated vinylic halides has already been reported.[12-15] It seems that the reaction involves addition of the 2-hydroxyethoxide ion to carbon 1 of the 1-halogenoethylene (VI; R = Br or Cl) with simultaneous ring closure and liberation of the halogen acid (neutralised by the alkali) and introduction of a proton on carbon 2, to give the cyclic acetal (III; R = Br or Cl). However, the cyclic acetal was converted by sodium 2-hydroxyethoxide in boiling ethylene glycol (98%) into the corresponding ether (VIII; R = Br or Cl), showing that the former was formed first (Table 4). The mechanisms of these reactions (Scheme) await further study.



SCHEME When X = Br, a trace of the acetylene is also isolated

The ethers (VIII) have been readily converted with concentrated hydrochloric acid into the corresponding cyclic acetals (III; R = Br or Cl). This would require that in the ether (VIII; R = Br or Cl) the electron density on carbon *b* should be higher than that on carbon *a*, otherwise the dioxan would have been formed.



(III) (also p-Br)

Oxidation of the acetals (III; R = Me, Br, or Cl) or the ethers (VIII; R = Br or Cl) with potassium dichromate gave the corresponding benzophenone. The structures of the cyclic acetals (III) were proved by synthesis from the corresponding aldehyde (IV) and ethylene glycol in the presence of hydrogen chloride, and by their i.r. spectra, which showed the four characteristic absorption bands in the 1200—1000 cm.$^{-1}$

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[9] W. Tadros, A. B. Sakla, and M. S. Ishak, *J. Chem. Soc.*, 1958, 4210.

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[13] N. K. Kochetkov, *Uspekhi Khim.*, 1955, **24**, 32 (*Chem. Abs.*, 1955, **49**, 7544c).

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region.[16a,17] The structure of the ethers (VIII; R = Br or Cl) was proved (*a*) by the formation of the acetyl derivatives, and (*b*) by the i.r. spectra, which showed the characteristic vinyl ether bands between 1652 and 1611 cm.$^{-1}$.[16b]

EXPERIMENTAL

1,1-*Dihalogeno*-2,2-*diarylethanes*.—These were prepared by condensation of the corresponding hydrocarbon (toluene, chlorobenzene, or bromobenzene) and dichloroacetaldehyde diethyl acetal or dibromoacetaldehyde. They separated from 95% ethanol as colourless crystals; 1,1-dibromo-2,2-di-*p*-tolyethane [18] had m.p. 95—96°; 1,1-dichloro-2,2-di-*p*-tolyethane [19] had m.p. 80—81°; 1,1-bis-*p*-bromophenyl-2,2-dichloroethane [20] had m.p. 133°; and 1,1-dichloro-2,2-bis-*p*-chlorophenylethane [20] had m.p. 110°.

1,1-*Diaryl*-2-*halogenoethylenes*.—There were prepared by (*a*) dehydrohalogenation of the corresponding 1,1-dihalogeno-2,2-diarylethanes or (*b*) bromination or chlorination of the corresponding asymmetric diarylethylene. They were recrystallised from 95% ethanol, from which they separated as colourless crystals; 2-bromo-1,1-di-*p*-tolylethylene [21] had m.p. 67°; 2-bromo-1,1-bis-*p*-bromophenylethylene [22] had m.p. 104°; 2-bromo-1,1-bis-*p*-chlorophenylethylene [22] had m.p. 76°; 2-chloro-1,1-di-*p*-tolylphenylethylene [19] had m.p. 67°; 1,1-bis-*p*-bromophenyl-2-chloroethylene [23] had m.p. 107—108°; and 2-chloro-1,1-bis-*p*-chlorophenylethylene [24] had m.p. 65°.

Reactions of 1,1-*Dihalogeno*-2,2-*bis*-p-*substituted Phenylethanes and the Corresponding* 1-*Halogenoethylenes in Boiling Ethylene Glycol*.—(a) *Di*-p-*tolyl compounds* (Table 1). The procedure and the products are exemplified by the following. A solution of 1,1-dichloro-2,2-di-*p*-tolylethane (10 g.) in ethylene glycol (150 c.c.) was boiled for 12 hr., cooled, diluted with water, and extracted with ether. Evaporation of the extract and fractional recrystallisation of the residue from ethanol gave di-*p*-tolylstilbene (0·2 g.), m.p. and mixed [25] m.p. 176—177° (from 95% ethanol), then 1,1-ethylenedioxy-2,2-di-*p*-tolylethane (6·1 g.), m.p. and mixed m.p. with an authentic sample [1] 99° (Found: C, 80·4; H, 7·8. Calc. for $C_{18}H_{20}O_2$: C, 80·5; H, 7·5%). The ethanolic mother liquor, when chilled, deposited di-*p*-tolyldeoxybenzoin (0·9 g.), m.p. and mixed [19] m.p. 102° (95% ethanol). Concentration of the remaining mother liquor gave di-*p*-tolylbenzophenone (0·1 g.), m.p. and mixed [26] m.p. 94°. The filtrate, when cooled, yielded di-*p*-tolylacetaldehyde, identified as the semicarbazone, m.p. and mixed m.p. with an authentic sample [27] 185° (0·2 g.).

(b) *Bis*-p-*bromo*-(or *chloro*-)*compounds*. (i) 1,1-Bis-*p*-bromophenyl-2,2-dichloroethane (2·0 g.) in ethylene glycol (30 c.c.) was boiled for 12 hr., cooled, diluted with water, and extracted with ether. Evaporation of the extract and recrystallisation of the residue from ethanol gave unchanged starting material (0·8 g.), m.p. and mixed [20] m.p. 133°, and 1,1-bis-*p*-bromophenyl-2-chloroethylene (0·8 g.), m.p. and mixed [23] m.p. 107—108°.

(ii) A similar experiment with 1,1-dichloro-2,2-bis-*p*-chlorophenylethane (2·0 g.) gave unchanged starting material (0·7 g.), m.p. and mixed [20] m.p. 110°, and 2-chloro-1,1-bis-*p*-chlorophenylethylene (0·8 g.), m.p. and mixed [24] m.p. 65°.

Reactions with Sodium 2-*Hydroxyethoxide in Boiling Ethylene Glycol*.—(a) *Di*-p-*tolyl compounds*. (Table 2). The procedure is exemplified as follows. A mixture of 1,1-dibromo-2,2-di-*p*-tolylethane (3·68 g., 0·01 mole) and sodium 2-hydroxyethoxide in ethylene glycol [sodium (1·38 g., 0·06 g. atom) in ethylene glycol (50 c.c.)] was boiled for 2 hr., cooled, diluted with water, and extracted with ether. The extract was evaporated and the residue was fractionally crystallised from ethanol to give di-*p*-tolylacetylene (1·8 g.), m.p. and mixed [19] m.p. 136°, and 1,1-ethylenedioxy-2,2-di-p-tolylethane (0·05 g.), m.p. and mixed m.p. 99°. Acidification of the alkaline solution gave di-*p*-tolylacetic acid (0·05 g.), which separated as colourless crystals (from 50% ethanol), m.p. and mixed [26] m.p. 144°. When the experiment was repeated with 2-halogeno-1,1-di-*p*-tolylethylene (0·01 mole) the same products were obtained.

(b) *Bis*-p-*bromo*-(or p-*chloro*-)*compounds* (Table 3). This is exemplified by the following. A mixture of 1,1-dichloro-2,2-bis-*p*-chlorophenylethane (9·6 g., 0·03 mole) and sodium 2-hydroxyethoxide in ethylene glycol [sodium (4·14 g., 0·18 g. atom) in ethylene glycol (150 c.c.)] was boiled for 3 hr., cooled, diluted with water, and extracted with ether. The extract was washed with water and ether was distilled off. Fractional crystallisation of the residue from 95% ethanol gave 1,1-bis-*p*-chlorophenyl-2,2-ethylenedioxyethane (4·3 g.), m.p. and mixed m.p. with an authentic sample [10] 94° (Found: C, 62·1; H, 4·7; Cl, 22·7. Calc. for $C_{16}H_{14}Cl_2O_2$: C, 62·1; H, 4·5; Cl, 23·0%), and bis-*p*-chlorophenylmethane (1·8 g.), m.p. and mixed [28] m.p. 55°. The ethanolic mother liquor was concentrated and the oily product thus obtained was recrystallised from petroleum (b.p. 40—60°) to give 1,1-bis-*p*-chlorophenyl-2-(2-hydroxyethoxy)ethylene (0·5 g.), m.p. and mixed m.p. with an authentic sample [1] 90° (Found: C, 62·2; H, 4·6; Cl, 22·8. Calc. for $C_{16}H_{14}Cl_2O_2$: C, 62·1; H, 4·5; Cl, 23·0%). Acidification of the ether-extracted alkaline solution with hydrochloric acid gave bis-*p*-chlorophenylacetic acid (0·05 g.), which separated from 50% ethanol as colourless crystals, m.p. and mixed [29] m.p. 164—166°.

Reactions of Bis-p-*bromo*-(or *chloro*-)*compounds with Barium Hydroxide in Boiling Ethylene Glycol*.—(i) A mixture of 1,1-bis-*p*-bromophenyl-2,2-dichloroethane (10 g.) and barium hydroxide (19·0 g.) in ethylene glycol (200 c.c.) was heated at 210—220° for 16 hr., cooled, diluted with water, acidified with hydrochloric acid (Congo Red), and extracted with ether. The extract was dried (Na_2SO_4) and

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[17] K. Nakanishi, 'Infrared Absorption Spectroscopy,' Holden-Day, San Francisco, 1964, p. 36.

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[20] R. Riemschneider, *Pharmazie*, Ergänzungsband, 1947, I, Beiheft 2, 77.

[21] R. Anschütz and H. Hilbert, *Ber.*, 1924, **57**, 1697.

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

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[25] G. Goldschmiedt and E. Hepp, *Ber.*, 1873, **6**, 1504.

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[27] R. Stoermer, *Ber.*, 1906, **39**, 2288.

[28] P. J. Montagne, *Rec. Trav. chim.*, 1907, **25**, 379; *Chem. Zentralblatte*, 1907, **1**, 475.

[29] O. Grummitt, A. Buck, and R. Egan, *Org. Synth.*, 1946, **26**, 21.

evaporated and the residue was recrystallised from 95% ethanol, to give 1,1-bis-*p*-bromophenyl-2,2-ethylenedioxyethane (7·5 g.) as colourless crystals, m.p. and mixed [10] m.p. 104°. Concentration of the ethanolic mother liquor gave an oil, which was recrystallised from petroleum (b.p. 40—60°) to give 1,1-*bis*-p-*bromophenyl*-2-(2-*hydroxyethoxy*)*ethylene* (0·6 g.), m.p. 105—106° (Found: C, 47·8; H, 3·8; Br, 40·5. $C_{16}H_{14}Br_2O_2$ requires C, 48·2; H, 3·5; Br, 40·2%).

(ii) Similar treatment of 1,1-dichloro-2,2-bis-*p*-chlorophenylethane (5·0 g.) and barium hydroxide (10 g.) in ethylene glycol (100 c.c.) for 20 hr. gave 1,1-bis-*p*-chlorophenyl-2,2-ethylenedioxyethane (3·9 g.), m.p. and mixed [10] m.p. 94°, and 1,1-bis-*p*-chlorophenyl-2-(2-hydroxyethoxy)-ethylene (0·3 g.), m.p. and mixed [1] m.p. 90°.

Reactions of 1,1-*Ethylenedioxy*-2,2-*bis*-p-*substituted Phenylethanes in Acid*.—(i) A solution of 1,1-bis-*p*-bromophenyl-2,2-ethylenedioxyethane (1·0 g.) in 20% hydrochloric acid (50 c.c.) was boiled for 5 hr., diluted with water, and extracted with ether. The extract was washed with water, aqueous sodium carbonate (10%), and water, and dried (Na_2SO_4). The residue after evaporation was recrystallised from methanol to give 4,4′-dibromobenzophenone (0·4 g.), m.p. and mixed [30] m.p. 172—173°, and bis-4-bromophenylacetaldehyde (0·1 g.), m.p. and mixed [10] m.p. 170° (Found: C, 47·5; H, 3·0; Br, 45·4. Calc. for $C_{14}H_{10}Br_2O$: C, 47·5; H, 2·8; Br, 45·2%).

TABLE 1

Reactions of 1,1-dihalogeno-2,2-di-*p*-tolylethanes (I; R = Me) and the corresponding 1-halogenoethylenes (VI; R = Me) in boiling ethylene glycol (30 c.c.)

Starting material (2 g.)	X	Reaction period	Products (%) (II) [c]	(III) [d]	(IV) [e]	(V) [f]	(VI) [g]	Benzophenone [h]	Ethylene
(I) [a]	Br	15 min.	9	62			6		Trace
(I)	Br	2 hr.	9	55	8	8		4	1
(I) [b]	Cl	6 hr.	3	45	5	Trace	9	1	1
(I)	Cl	12 hr.	3	64	6	11		2	2
(VI) [a]	Br	15 min.				58	20		7
(VI)	Br	2 hr.				83			14
(VI) [b]	Cl	6 hr.				54	20		6
(VI)	Cl	12 hr.				76			13

[a] When boiling was stopped after 1 min. the starting material was mainly recovered unchanged. [b] When boiling was stopped after 3 hr. the starting material was mainly recovered unchanged. [c] (II; R = Me), m.p. and mixed m.p. with an authentic sample [25] 176—177°. [d] (III; R = Me), m.p. and mixed m.p. with an authentic sample [1] 99°. [e] (IV; R = Me), identified as its semicarbazone, m.p. and mixed m.p. with an authentic sample [27] 185°. [f] (V; R = Me), m.p. and mixed [19] m.p. 102°. [g] (VI; R = Me, X = Br), m.p. and mixed [21] m.p. 67°; (X = Cl) m.p. and mixed [19] m.p. 67°. [h] 4,4′-Dimethylbenzophenone had m.p. and mixed [26] m.p. 94°. [i] 1,1-Di-*p*-tolylethylene had m.p. and mixed [21] m.p. 60°.

(ii) A similar experiment with the bis-*p*-chlorophenyl compound (2·0 g.) gave 4,4′-dichlorobenzophenone (0·8 g.), m.p. and mixed [31] m.p. 145°, and bis-4-chlorophenylacetaldehyde (0·2 g.), m.p. and mixed [10] m.p. 147° (Found: C, 63·0; H, 3·9; Cl, 26·5. Calc. for $C_{14}H_{10}Cl_2O$: C, 63·4; H, 3·8; Cl, 26·8%).

(iii) A solution of 1,1-ethylenedioxy-2,2-di-*p*-tolyethane (1·34 g., 0·005 mole) in ethylene glycol (30 c.c.) containing 6% hydrogen bromide (or saturated with hydrogen chloride) was boiled for 6 hr. The products were 4,4′-dimethyldeoxybenzoin (0·45 g.), m.p. and mixed [19] m.p. 102°, 4,4′-dimethylbenzophenone (0·1 g.), m.p. and mixed [26] m.p. 94°, and di-*p*-tolylacetaldehyde, identified as the semicarbazone (0·4 g.), m.p. and mixed [27] m.p. 185°. Heating for 10 hr. in ethylene glycol alone gave largely unchanged acetal.

(iv) A repeat of experiment (iii) in 80% acetic acid (30 c.c.) gave mainly 4,4′-dimethylbenzophenone (0·7 g.) and di-*p*-tolylacetaldehyde, identified as the semicarbazone (0·4 g.). In glacial acetic acid and acetic anhydride (2 : 1; 50 c.c.), the acetal was mainly recovered unchanged.

Reactions of 1,1-*Ethylenedioxy*-2,2-*bis*-p-*substituted phenylethanes and* 1,1-*Bis*-p-*bromo*- (or p-*chloro*)*phenyl*-2-(2-*hydroxyethoxy*)*ethylenes in Alkali*.—The procedure was similar to that used for the reactions with sodium 2-hydroxyethoxide, and the results are shown in Table 4.

Acetylation of 1,1-*Bis*-p-*bromo*-(or p-*chloro*-)*phenyl*-2-(2-*hydroxyethoxy*)*ethylenes*.—A solution of the bromo-compound (1·0 g.) in acetic anhydride (30 c.c.) was boiled for 10 min., cooled, diluted with water, and extracted with ether. The extract was washed with water and dried (Na_2SO_4). The residue after evaporation was recrystallised from 95% ethanol to give 2-(2-*acetoxyethoxy*)-1,1-*bis*-p-*bromophenylethylene* (0·6 g.), m.p. 73° (Found: C, 49·3; H, 3·7; Br, 36·7. $C_{18}H_{16}Br_2O_3$ requires C, 49·1; H, 3·6;

TABLE 2

Reactions of 1,1-dihalogeno-2,2-di-*p*-tolylethanes (I; R = Me) and the corresponding 1-halogenoethylenes (VI; R = Me) with sodium 2-hydroxyethoxide [sodium (1·38 g., 0·06 g. atom) in boiling ethylene glycol (50 c.c.)]

Starting material (0·01 mole)	X	Reaction period (hr.)	Products (%) (VI) [a]	(III) [b]	Acetylene [c]	Acid [d]
(I)	Br	1	21	Trace	49	1
(I)	Br	2		2	73	2
(I)	Cl	1	83			
(I)	Cl	3	64	Trace	5	1
(I)	Cl	10		2	78	2
(VI)	Br	1	25	Trace	44	1
(VI)	Br	2		2	73	2
(VI)	Cl	1	85			
(VI)	Cl	3	64	Trace	5	1
(VI)	Cl	10		2	82	2

[a] (VI; R = Me, X = Br), m.p. and mixed m.p. with an authentic sample [21] 67°; (X = Cl), m.p. and mixed m.p. with an authentic sample [19] 67°. [b] M.p. and mixed m.p. with an authentic sample [1] 99°. [c] M.p. and mixed m.p. with an authentic sample of di-*p*-tolylacetylene [19] 136°. [d] M.p. and mixed with an authentic sample of di-*p*-tolylacetic acid [26] 144°.

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[30] H. Hoffmann, *Annalen*, 1891, **264**, 160.

[31] M. Dittrich, *Annalen*, 1891, **264**, 174.

TABLE 3

Reactions of 1,1-dichloro-2,2-bis-*p*-bromo-(and *p*-chloro-)phenylethanes (I; R = Br or Cl, X = Cl, (0·01 mole) and the corresponding 1-halogenoethylenes (VI; R = Br or Cl, X = Br or Cl) (0·005 mole) with sodium 2-hydroxyethoxide in boiling ethylene glycol

Starting material			Reaction period	Products (%)					
	R	X		(VI)[c]	(III)[d]	(VIII)[e]	Acetylene[f]	Acid[g]	Methane[h]
(I)[a]	Br	Cl	30 min.	91					
(I)	Br	Cl	3 hr.		63	5		1	9
(I)	Br	Cl	10 hr.						73
(I)	Cl	Cl	30 min.	89					
(I)	Cl	Cl	3 hr.		46	5		1	25
(I)	Cl	Cl	10 hr.						79
(VI)[b]	Br	Br	15 min.	74	10			Trace	
(VI)	Br	Br	5 hr.		55	5	1	1	9
(VI)	Br	Cl	3 hr.		45	5		1	21
(VI)	Br	Cl	10 hr.						75
(VI)	Cl	Br	15 min.	79	10			Trace	
(VI)	Cl	Br	5 hr.		53	7	1	1	23
(VI)	Cl	Cl	3 hr.		47	7		1	25
(VI)	Cl	Cl	10 hr.						75

[a] Sodium (0·06 g. atom) in ethylene glycol (50 c.c.). [b] Sodium (0·025 g. atom) in ethylene glycol (15 c.c.). [c] (VI; R = Br, X = Cl), m.p. and mixed[23] m.p. 107—108°; (VI; R = Cl, X = Cl), m.p. and mixed[24] m.p. 65°; (VI; R = Br, X = Br), m.p. and mixed[22] m.p. 104° (IV; R = Cl, X = Br), m.p. and mixed[22] m.p. 76°. [d] (III; R = Br), m.p. and mixed[10] m.p. 104° (Found: C, 48·6; H, 3·7; Br, 39·8. Calc. for $C_{16}H_{14}Br_2O_2$: C, 48·2; H, 3·5; Br, 40·2%); (III; R = Cl), m.p. and mixed m.p.[1] 94° [e] (VIII; R = Br), m.p. 105—106°; (VIII; R = Cl), m.p. and mixed m.p.[1] 90°. [f] Bis-*p*-bromophenylacetylene, m.p. and mixed (H. J. Barber and R. Slack, *J. Chem. Soc.*, 1944, 612) m.p. 182—184° (Found: Br, 47·6. Calc. for $C_{14}H_{18}Br_2$: Br, 47·6%); bis-*p*-chlorophenylacetylene, m.p. and mixed (J. Kenner and E. Witham, *J. Chem. Soc.*, 1910, **97**, 1960) m.p. 175—176° (Found: Cl, 28·7. Calc. for $C_{14}H_{18}Cl_2$: Cl, 28·7%). [g] Bis-*p*-bromophenylacetic acid, m.p. and mixed (H. Bilts, *Ber.*, 1910, **43**, 1815) m.p. 187—188°; bis-*p*-chlorophenylacetic acid, m.p. and mixed[29] m.p. 164—166°. [h] Bis-*p*-bromophenylmethane, m.p. and mixed (N. E. Goldthwaite, *Amer. Chem. J.*, 1903, **30**, 447; *Chem. Zentr.*, 1904, **1**, 376) m.p. 64° (Found: C, 48·1; H, 3·3; Br, 48·7. Calc. for $C_{13}H_{10}Br_2$: C, 47·9; H, 3·1; Br, 49·1%); bis-*p*-chlorophenylmethane, m.p. and mixed[28] m.p. 55° (Found: C, 66·0; H, 4·1; Cl, 30·1. Calc. for $C_{13}H_{10}Cl_2$: C, 65·8; H, 4·2; Cl, 30·0%).

Br, 36·4%). A similar experiment with the chloro-compound gave 2-(2-*acetoxyethoxy*)-1,1-*bis*-p-*chlorophenylethylene*, m.p. 80° (Found: C, 61·3; H, 4·7; Cl, 20·1. $C_{18}H_{16}Cl_2O_3$ requires C, 61·5; H, 4·6; Cl, 20·2%).

Conversion of 1,1-*Bis*-p-*bromo*-(*or* p-*chloro*-)*phenyl*-2-(2-*hydroxyethoxy*)*ethylene into the Corresponding* 1,1-*Bis*-p-*bromo*-(*or* p-*chloro*)*phenyl*-2,2-*ethylenedioxyethane*.—The hydroxy-ether (1·0 g.) in concentrated hydrochloric acid (20 c.c.) was boiled for 5 min., cooled, diluted with water, and extracted with ether. The extract was washed with water, aqueous sodium carbonate, and water again, and dried (Na_2SO_4). Evaporation followed by recrystallisation of the residue from ethanol gave the acetal (0·6 g.), m.p. and mixed[10] m.p. 104°. A similar experiment with the chloro-compound (1·0 g.) gave the chloro-acetal (0·6 g.), m.p. and mixed[1] m.p. 94°.

Preparation of Bis-4-*chlorophenylacetaldehyde*.[32]—(i) *Bis*-4-*chlorophenyl*-N-*methylacetanilide*. A mixture of bis-4-chlorophenylacetic acid[29] (9·3 g., 0·033 mole) and phosphorus pentachloride (6·8 g., 0·033 mole) was heated on a water-bath till evolution of hydrogen chloride ceased (3 hr.). Phosphoryl chloride was distilled off under reduced pressure. The residue was cooled, methylaniline (3·6 g., 0·033 mole) was added, and the whole was heated on a water-bath for 2 hr. The mixture was cooled, diluted with water, and extracted with ether. The extract was washed with aqueous sodium carbonate (10%) and water, and evaporated. The residue was steam-distilled to remove excess of methylaniline and recrystallised from ethanol–acetone (1 : 1) to give the *acetanilide* (10 g.), m.p. 105° (Found: C, 68·0; H, 4·6; Cl, 19·0; N, 3·7. $C_{21}H_{17}Cl_2NO$ requires C, 68·1; H, 4·6; Cl, 19·2; N, 3·8%).

(ii) To a solution of the anilide (3·71 g., 0·01 mole) in dry ether (50 c.c.), lithium aluminium hydride (0·114 g., 0·003 mole) was added in portions with stirring. The mixture was left at room temperature for 3 hr., then poured

TABLE 4

Reactions of 1,1-ethylenedioxy-2,2-bis-*p*-substituted phenylethanes (III) (0·01 mole) and 1,1-bis-*p*-bromo(or *p*-chloro)phenyl-2-(2-hydroxyethoxy)ethylenes (VIII) (0·001 mole) with sodium 2-hydroxyethoxide in boiling ethylene glycol

Starting material		Reaction period (hr.)	Products (%)			
	R		(III)[c]	(VIII)[d]	Acid[e]	Methane[f]
(III)[a]	Me	12	95			
(III)	Br	1	50	20	Trace	
(III)	Br	3	37	30	3	5
(III)	Br	10				90
(III)	Cl	1	52	19	Trace	
(III)	Cl	3	36	29	4	6
(III)	Cl	10				90
(VIII)[b]	Br	0·25		63	14	
(VIII)	Br	1			Trace	61
(VIII)	Cl	0·25		65	14	
(VIII)	Br	1			Trace	63

[a] Sodium (0·06 g. atom) in ethylene glycol (50 c.c.). [b] Sodium (0·006 g. atom) in ethylene glycol (15 c.c.). [c] (III; R = Br), m.p. and mixed[10] m.p. 104°; (III); R = Cl), m.p. and mixed m.p.[1] 94°; (III; R = Me), m.p. and mixed m.p.[1] 99°. [d] (VIII; R = Br); m.p. and mixed m.p. 105—106°; (VIII; R = Cl), m.p. and mixed m.p.[1] 90°. [e] Bis-*p*-bromophenylacetic acid, m.p. and mixed m.p. with an authentic sample (H. Bilts, *Ber.*, 1910, **43**, 1815) 187—188°; bis-*p*-chlorophenylacetic acid, m.p. and mixed m.p. with an authentic sample[29] 164—166°. [f] Bis-*p*-bromophenylmethane, m.p. and mixed m.p. (N. E. Goldthwaite, *Amer. Chem. J.*, 1903, **30**, 447; *Chem. Zentr.*, 1904, **1**, 376) 64°; bis-*p*-chlorophenylmethane, m.p. and mixed m.p.[28] 55°.

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[32] F. Weygand and E. Eberhardt, *Angew. Chem.*, 1953, **65**, 525.

into cold 2N-hydrochloric acid (50 c.c.) and extracted with ether. The residue after evaporation was steam-distilled to remove the methylaniline. The residue was recrystallised from methanol to give bis-4-chlorophenylacetaldehyde (1·2 g.) as colourless crystals, m.p. and mixed[10] m.p. 147° (Found: C, 63·1; H, 3·9; Cl, 26·6. Calc. for $C_{14}H_{10}Cl_2O$: C, 63·4; H, 3·8; Cl, 26·8%).

Preparation of 1,1-*Bis*-p-*bromo*- (*and* p-*chloro*-)*phenyl*-2,2-*ethylenedioxyethane from the Corresponding Aldehyde.*—Bis-*p*-bromophenylacetaldehyde (0·2 g.) in ethylene glycol containing hydrogen chloride (5%; 40 c.c.) was left at room temperature for 7 days. The mixture was diluted with water; the precipitate was filtered off and recrystallised from 95% ethanol to give the bromo-acetal, m.p. and mixed[10] m.p. 104° (Found: C, 48·6; H, 3·8; Br, 39·8. Calc. for $C_{16}H_{14}Br_2O_2$: C, 48·2; H, 3·5; Br, 40·2%). Similarly prepared, the chloro-acetal had m.p. and mixed[1,10] m.p. 94° (Found: C, 62·1; H, 4·7; Cl, 22·8. Calc. for $C_{16}H_{14}Cl_2O_2$: C, 62·1; H, 4·5; Cl, 23·0%).

These acetals were also obtained, together with the corresponding benzophenones, when the aldehyde (1 g.) in ethylene glycol (30 c.c.) containing hydrogen chloride (5%) was heated under reflux for 10 min.

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