740. *Reactions with Asymmetrical Diarylethylenes and Diarylethanes. Part X.*[1] *A New Synthesis of 4,4′-Dialkoxy-diphenylacetylenes, -deoxybenzoins, and -benzils*

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1,1-Di-*p*-alkoxyphenyl-2,2-dibromo- and -2-bromo-2-chloro-ethylenes, and -2,2,2-tribromo-ethanes were converted by sodium 2-hydroxyethoxide in boiling ethylene glycol into the corresponding acetylene. 1,1-Di-*p*-alkoxyphenyl-2-halogenoethylene was also isolated and was apparently an intermediate. 2,2-Dichloroethylenes did not give the acetylene, and 2,2,2-trichloroethanes gave 2,2-dichloroethylenes.

4,4′-Dialkoxydeoxybenzoins and 4,4′-dialkoxybenzils were the main products when solutions of 1,1,-di-*p*-alkoxyphenyl-2,2-dibromoethylenes and -2,2,2-tribromoethanes in ethylene glycol were heated to boiling. The formation of the deoxybenzoin preceded that of benzil rendering the solution acidic with hydrogen bromide.

Similarly were converted into the above products 1,1-di-*p*-alkoxyphenyl-2-bromo-2-chloroethylenes and -2,2,2-trichloroethanes when ethylene glycol was acidified with hydrogen bromide.

Harris and Frankforter[2] reported the conversion of 1,1-di-*p*-alkoxyphenyl-2,2-dihalogenoethylenes into 4,4′-dialkoxyphenylacetylenes by powdered sodium in benzene or alcoholic sodium ethoxide at 180—200°; the 2,2,2-trihalogenoethanes and metallic sodium in boiling benzene gave the corresponding 4,4′-dialkoxystilbenes. We found that when mixtures of 1,1-di-*p*-alkoxyphenyl-2,2-dibromoethylenes or the -2,2,2-tribromoethanes and sodium 2-hydroxyethoxide in ethylene glycol were heated to boiling for 1½ hr., the acetylenes were obtained together with 1,1-di-*p*-alkoxyphenyl-2-bromoethylenes. If heating were continued for longer (3—5 hr.) as previously reported,[3a,b] further conversion of the intermediate 2-bromoethylenes into acetylenes would take place. The dimethoxy-compound underwent partial dealkylation; on acidification of the alkaline solution, *p*-hydroxyphenyl-4′-methoxybenzyl ketone[3a] was obtained. 1,1-Di-*p*-alkoxyphenyl-2-bromo-2-chloroethylenes gave the corresponding 1,1-di-*p*-alkoxyphenyl-2-chloroethylenes,

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[1] Part IX, W. Tadros, A. B. Sakla, M. S. Ishak, and (Miss) E. R. Armanious, *J.*, 1963, 4527.

[2] E. E. Harris and G. B. Frankforter, *J. Amer. Chem. Soc.*, 1926, **48**, 3144.

[3] (*a*) W. Tadros, A. B. Sakla, and M. S. Ishak, *J.*, 1958, 4210; (*b*) W. Tadros, A. B. Sakla, M. S. Ishak, and (Miss) E. R. Armanious, *J.*, 1963, 4218.

showing a preferential reduction of the bromine atom. Heating for longer gave the acetylene.[3]

The 2,2,2-trichloroethanes and 2,2-dichloroethylenes were not converted under the experimental conditions cited into the acetylene, giving a further example of the reactivity of bromine compared with chlorine,[1] the former changing only to the 2,2-dichloroethylenes.

When a solution of 1,1-di-*p*-alkoxyphenyl-2,2-dibromoethylene in ethylene glycol was heated to boiling (1 hr.), the corresponding 4,4′-dialkoxydeoxybenzoin and 4,4′-dialkoxybenzil were obtained. When similarly treated in ethylene glycol acidified with hydrogen bromide, 1,1-di-*p*-alkoxyphenyl-2-bromo-2-chloroethylene gave the above ketones together with 1,1-di-*p*-alkoxyphenyl-2-chloroethylene. The formation of the deoxybenzoins was apparently mediated by 2-monohalogenoethylenes, the monobromo- being converted more readily than the monochloro-compound.[1] When boiling was stopped after 15 min., the dibromoethylene was mainly recovered together with little deoxybenzoin, the medium becoming acidic with hydrogen bromide; acidification of the ethylene glycol with hydrogen bromide reduced the reaction time. The tribromoethanes gave the deoxybenzoin and benzil more readily than the trichloroethanes, which required acidification with hydrogen bromide. The mechanisms of the above reactions are being investigated.

EXPERIMENTAL

*2-Bromo-2-chloro-*1,1*-di-*p*-alkoxyphenylethylenes.*—(*a*) *2-Bromo-2-chloro-*1,1*-di-*p*-methoxyphenylethylene.* (i) A solution of bromine (3·2 g., 0·02 mole) in ether (5 c.c.), was added to a solution of 2-chloro-1,1-di-*p*-methoxyphenylethylene [4] (5·5 g., 0·02 mole) in ether (100 c.c.). The solvent was distilled off, and the residue was recrystallised from alcohol from which *2-bromo-2-chloro-*1,1*-di-*p*-methoxyphenylethylene* (6·0 g.) separated as colourless crystals, m. p. 102—103° (Found: C, 54·8; H, 4·3; Br, 22·2; Cl, 10·0. $C_{16}H_{14}BrClO_2$ requires C, 54·3; H, 3·9; Br, 22·6; Cl, 10·0%).

(ii) To a solution of 2-bromo-1,1-di-*p*-methoxyphenylethylene [5] (6·4 g., 0·02 mole) in carbon tetrachloride (50 c.c.) a solution of sulphuryl chloride (2·7 g., 0·02 mole) in the same solvent (10 c.c.) was added. A vigorous reaction took place at room temperature and was complete within 15 min. The solvent was removed on the water-bath, and the residue was recrystallised from alcohol from which 2-bromo-2-chloro-1,1-di-*p*-methoxyphenylethylene separated with m. p. and mixed m. p. with product (i) above 102—103° (6·2 g.).

(*b*) *2-Bromo-2-chloro-*1,1*-di-*p*-ethoxyphenylethylene.* Similarly prepared by (i) bromination of 2-chloro-1,1-di-*p*-ethoxyphenylethylene [4] (6·05 g., 0·02 mole) with bromine (3·2 g., 0·02 mole) in ether (10 c.c.) and by (ii) chlorination of 2-bromo-1,1-di-*p*-ethoxyphenylethylene [9] (6·94 g., 0·02 mole) with sulphuryl chloride (2·7 g., 0·02 mole) in ether (10 c.c.), *2-bromo-2-chloro-*1,1*-di-*p*-ethoxyphenylethylene* separated from alcohol as colourless crystals, m. p. 115° (Found: C, 56·1; H, 4·7; Br, 21·4; Cl, 9·0. $C_{18}H_{18}BrClO_2$ requires C, 56·6; H, 4·7; Br, 21·0; Cl, 9·3%).

Reactions of 1,1*-Di-*p*-alkoxyphenyl-*2,2*-dihalogenoethylenes and -*2,2,2*-trihalogenoethanes with Sodium* 2*-Hydroxyethoxide in Boiling Ethylene Glycol* [Table 1 (*A* and *B*)].—The procedure and the products obtained are exemplified by the following: 2,2-Dibromo-1,1-di-*p*-methoxyphenylethylene [2,8] (2·0 g., 0·005 mole) and a solution from sodium (0·46 g., 0·02 g.-atom) in ethylene glycol (30 c.c.) were boiled for 1½ hr. The solution which became reddish-brown was diluted with water and the product was extracted with ether. Ether was recovered and the residue was recrystallised from alcohol from which 4,4′-dimethoxyphenylacetylene separated after repeated recrystallisation (0·5 g.) as colourless crystals, m. p. and mixed m. p.[3] 142—143°. Concentration of the mother-liquor gave unchanged dibromide, m. p. and mixed m. p.[2,8] 91° (0·1 g.), and 2-bromo-1,1-di-*p*-methoxyphenylethylene (0·1 g.), m. p. and mixed m. p.[5] 84°. Acidification of the alkaline solution with hydrochloric acid gave 4-hydroxyphenyl 4′-methoxybenzyl ketone, recrystallised from alcohol (0·1 g.), with m. p. 175° not depressed when mixed with an authentic sample.[6]

Reactions of 1,1*-Di-*p*-alkoxyphenyl-*2,2*-dihalogenoethylenes and -*2,2,2*-trihalogenoethanes in Boiling Ethylene Glycol* [Table 2 (*A* and *B*)].—The procedure is exemplified as follows: A

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

[5] F. Bergmann and J. Szmuszkowicz, *J. Amer. Chem. Soc.*, 1947, **69**, 1777.

[6] W. Tadros, L. Ekladius, and A. B. Sakla, *J.*, 1954, 2351.

TABLE 1 (*A*)

$(p\text{-RO}\cdot\text{C}_6\text{H}_4)_2\text{C}{=}\text{C}<^{\text{X}^a}_{\text{X}'}$					Concn. of reagent				Reaction products									
					Sodium		Ethylene glycol	Reaction period	Unchanged compound			$p\text{-RO}\cdot\text{C}_6\text{H}_4\cdot\text{C}{\equiv}\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OR-}p$			$(p\text{-RO}\cdot\text{C}_6\text{H}_4)_2\text{C}{=}\text{C}<^{\text{X}}_{\text{H}}$			
R	X	X′	g.	mole.	g.	g.-Atom	(c.c.)	(hr.)	g.	%	M. p. and mixed m. p.	g.	%	M. p. and mixed m. p.	X	g.	%	M. p. and mixed m. p.
CH_3[b]	Br	Br	2·0	0·005	0·46	0·02	30	1½	0·1	5	91°[2,8]	0·5	42	142—143°[3]	Br	0·1	7	84°[5]
C_2H_5	Br	Br	2·15	0·005	0·46	0·02	30	1½	0·4	20	118[2,8]	0·4	30	162—163[3]	Br	0·1	6	64[9]
CH_3	Br	Cl	1·77	0·005	0·23	0·01	15	2	—	—	—	—	—	—	Cl[c]	1·1	80	78[4]
CH_3[d]	Br	Cl	1·77	0·005	0·57	0·025	15	5	—	—	—	0·1	9	142—143[3]	Cl	0·3	22	78[4]
C_2H_5	Br	Cl	1·9	0·005	0·23	0·01	15	2	—	—	—	—	—	—	Cl[e]	1·2	80	76[4]
C_2H_5	Br	Cl	1·9	0·005	0·57	0·025	15	5	—	—	—	0·5	38	162—163[3]	Cl	0·2	16	76[4]

TABLE 1 (*B*)

$(p\text{-RO}\cdot\text{C}_6\text{H}_4)_2\overset{\text{H}}{\text{C}}\text{—CX}_3$				Concn. of reagent				Reaction products								
				Sodium		Ethylene glycol	Reaction period	$p\text{-RO}\cdot\text{C}_6\text{H}_4\cdot\text{C}{\equiv}\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OR-}p$			$(p\text{-RO}\cdot\text{C}_6\text{H}_4)_2\text{C}{=}\text{C}<^{\text{H}}_{\text{X}}$			$(p\text{-RO}\cdot\text{C}_6\text{H}_4)_2\text{C}{=}\text{CX}_2$		
R	X	g.	mole.	g.	g.-Atom	(c.c.)	(hr.)	g.	%	M. p. and mixed m. p.	g.	%	M. p. and mixed m. p.	g.	%	M. p. and mixed m. p.
CH_3[b]	Br	2·4	0·005	0·69	0·03	30	1½	0·5	42	142—143°[3]	0·1	7	84°[5]	0·1	5	91°[2,8]
C_2H_5	Br	2·54	0·005	0·69	0·03	30	1½	0·5	38	162—163[3]	0·1	7	64[9]	0·3	14	118[2,8]
CH_3	Cl	1·7	0·005	0·69	0·03	30	1½	—	—	—	—	—	—	1·2	80	110[2,7]
C_2H_5	Cl	1·9	0·005	0·69	0·03	30	1½	—	—	—	—	—	—	1·6	94	106—107[2,7]

[a] 2,2,-Dichloro-1,1-di-*p*-methoxyphenylethylene,[2,7] m. p. 110° (1·5 g.; 0·005 mole) gave on heating for 5 hr. with sodium (0·46 g.; 0·02 atom) in ethylene glycol (30 c.c.), unchanged material (0·5 g.), and demethylated product which gave on methylation the same dichloroethylene, m. p. and mixed m. p.[2,7] 110°. When the experiment was repeated with 2,2-dichloro-1,1-di-*p*-ethoxyphenylethylene,[2,7] m. p. 106—107° (1·7 g.; 0·005 mole), the compound was mainly recovered unchanged. [b] On acidifying the alkaline filtrate with HCl and recrystallising the precipitate from little alcohol, 4-hydroxyphenyl 4′-methoxybenzyl ketone (0·1 g.) with m. p. 175°, not depressed when mixed with an authentic sample,[6] was obtained. [c] Found: C, 69·9; H, 5·8; Cl, 12·6. Calc. for $\text{C}_{16}\text{H}_{15}\text{ClO}_2$: C, 69·9; H, 5·5; Cl, 12·9%. [d] On acidifying the alkaline solution, 4-hydroxyphenyl 4′-methoxybenzyl ketone was obtained with m. p. and mixed m. p.[6] 175° (0·2 g., 17%). [e] Found: C, 71·6; H, 6·2; Cl, 11·5. Calc. for $\text{C}_{18}\text{H}_{19}\text{ClO}_2$: C, 71·4; H, 6·3; Cl, 11·7%.

TABLE 2 (*A*)

$(p\text{-RO}\cdot C_6H_4)_2C{=}CXX'$ [a]				Ethylene glycol	Reaction	Unchanged compound			$p\text{-RO}\cdot C_6H_4\cdot CO\cdot CH_2\cdot C_6H_4\cdot OR\text{-}p$			$(p\text{-RO}\cdot C_6H_4\cdot CO)_2$			$(p\text{-RO}\cdot C_6H_4)_2C{=}CHX$			
R	X	X′	g.	(c.c.)	period	g.	%	M. p. and mixed m. p.	g.	%	M. p. and mixed m. p.	g.	%	M. p. and mixed m. p.	X	g.	%	M. p. and mixed m. p.
CH_3	Br	Br	2	30	15 min.	1·6	80	91°[2,8]	0·2	16	110—111°[b,1]	—	—	—	—	—	—	—
CH_3	Br	Br	2	30	1 hr.	—	—	—	0·5	40	110—111	0·6	44	133[c,10]	—	—	—	—
CH_3	Br	Br	2	30 *	15 min.	—	—	—	0·6	46	110—111	0·6	44	133	—	—	—	—
C_2H_5	Br	Br	2	30	15 min.	1·6	80	118[2]	0·2	15	103—104[d,1]	—	—	—	—	—	—	—
C_2H_5	Br	Br	2	30	1 hr.	—	—	—	0·6	45	103—104	0·6	42	148—149[e,11]	—	—	—	—
C_2H_5	Br	Br	2	30 *	15 min.	—	—	—	0·7	51	103—104	0·6	42	148—149	—	—	—	—
CH_3	Cl	Br	2	30 *	1½ hr.	0·3	15	102—103	0·2	15	110—111	0·3	20	133	Cl	0·3	20	78°[4]
C_2H_5	Cl	Br	2	30 *	1½ hr.	0·3	14	115	0·2	14	103—104	0·4	25	148—149	Cl	0·4	25	76[4]

TABLE 2 (*B*)

$(p\text{-RO}\cdot C_6H_4)_2CH{-}CX_3$			Ethylene glycol	Reaction	$(p\text{-RO}\cdot C_6H_4)_2C{=}CX_2$			$p\text{-RO}\cdot C_6H_4\cdot CO\cdot CH_2\cdot C_6H_4\cdot OR\text{-}p$			$(p\text{-RO}\cdot C_6H_4\cdot CO)_2$		
R	X	g.	(c.c.)	period	g.	%	M. p. and mixed m. p.	g.	%	M. p. and mixed m. p.	g.	%	M. p. and mixed m. p.
CH_3	Br	2	30	15 min.	—	—	—	0·4	36	110—111°[1]	0·5	44	133°[10]
C_2H_5	Br	2	30	15 min.	—	—	—	0·5	44	103—104[1]	0·6	50	148—149[11]
CH_3	Cl	2	30	5 hr.	1·6	91	110°[2,7]	—	—	—	—	—	—
CH_3	Cl	2	30 *	5 hr.	1·0	55	110	0·1	7	110—111	0·2	13	133
C_2H_5	Cl	2	30	5 hr.	1·7	95	106—107[2,7]	—	—	—	—	—	—
C_2H_5	Cl	2	30 *	5 hr.	1·0	54	106—107	0·1	7	103—104	0·2	12	148—149

* Ethylene glycol containing hydrogen bromide (6·0%).

[a] When R = CH_3 or C_2H_5 and X = X′ = Br and heating for 1 min. in ethylene glycol; and when R = CH_3 or C_2H_5 and X = X′ = Cl and heating for 6 hr. in ethylene glycol alone or in the presence of HBr; and when R = CH_3 or C_2H_5 and X = Cl, X′ = Br and heating in ethylene glycol for 5 hr., the starting material was recovered unchanged. [b] Found: C, 74·8; H, 6·1. Calc. for $C_{16}H_{16}O_3$: C, 75·0; H, 6·2%. [c] Found: C, 71·0; H, 5·1. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%. [d] Found: C, 75·7; H, 6·9. Calc. for $C_{18}H_{20}O_3$: C, 76·1; H, 7·0%. [e] Found: C, 72·2; H, 6·1. Calc. for $C_{18}H_{18}O_4$: C, 72·5; H, 6·0%.

solution of 2,2-dibromo-1,1-di-*p*-methoxyphenylethylene [2,8] (2·0 g.) in ethylene glycol (30 c.c.) was refluxed for 1 hr., diluted with water, and extracted with ether. Ether was distilled off and the residue was recrystallised from alcohol. 4,4′-Dimethoxybenzil (0·6 g.) separated as pale yellow needles with m. p. and mixed m. p. with an authentic sample [10] 133° (Found: C, 71·0; H, 5·1. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%). On cooling the alcoholic mother-liquor 4,4′-dimethoxydeoxybenzoin [1] (0·5 g.) was obtained as colourless crystals with m. p. and mixed m. p. 110—111° (Found: C, 74·8; H, 6·1. Calc. for $C_{16}H_{16}O_3$: C, 75·0; H, 6·2%).

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