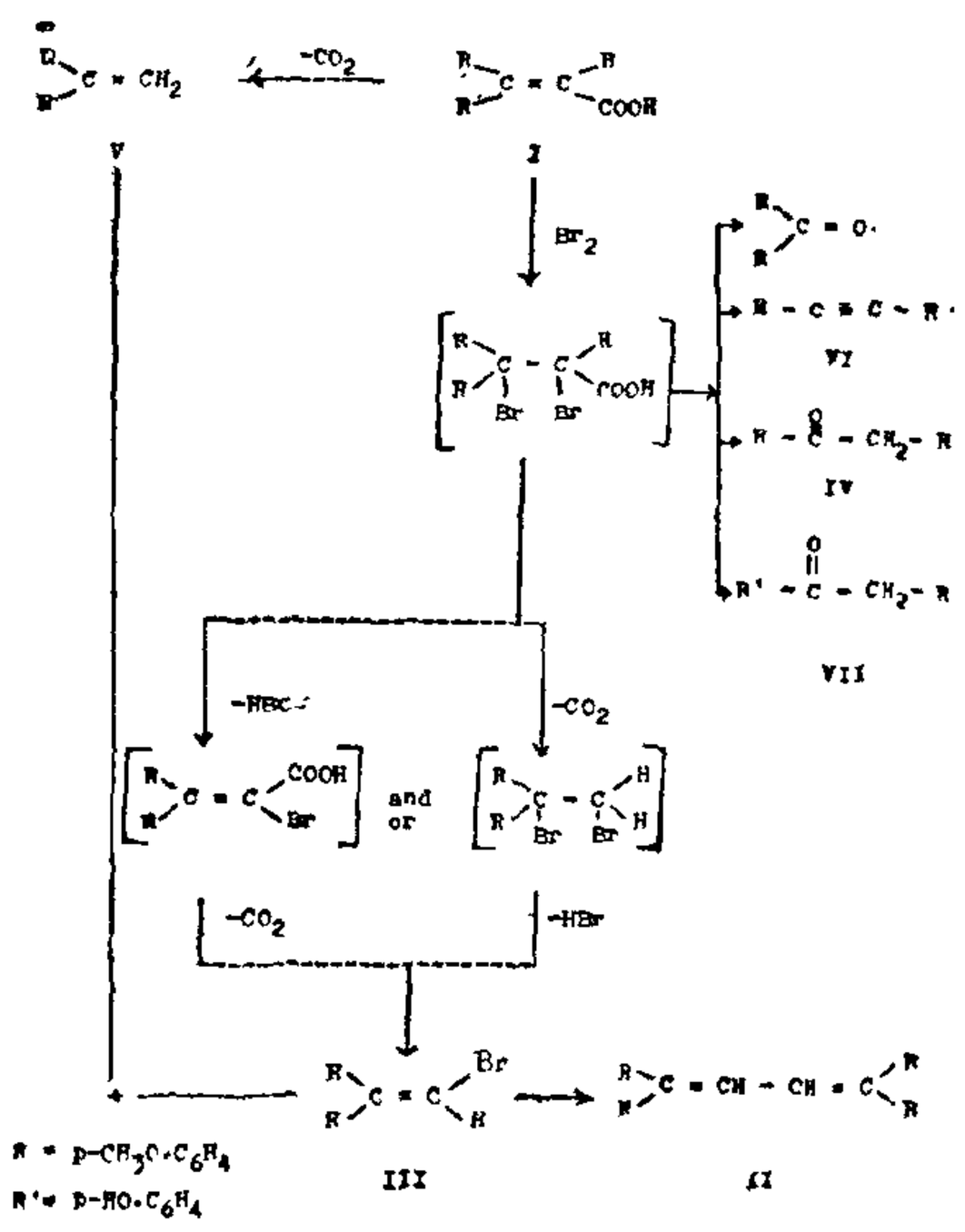
REARRANGEMENT REACTIONS OF 3,3-DI-p-METHOXYPHENYLPROPENOIC ACID ON BROMINATION IN DIFFERENT SOLVENTS

SADEK ELSAYED ABDOU* AND ALFY B. SAKLA
Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

ABSTRACT

Bromination of 3,3-di-*p*-methoxyphenylpropenoic acid in different solvents led to the formation of a number of products among which may be mentioned : 1,1,4,4-tetra-*p*-methoxyphenyl-buta-1, 3-diene, 4,4′-dimethoxyphenylacetylene, 4-methoxybenzyl-4′-methoxyphenyl kentone, 1,1-di-*p*-methoxyphenylethylene and its 2-bromo-derivative. The reaction products were influenced by the nature of the solvent as well as the reaction conditions.

PREVIOUS work by different investigators[1–5] has shown that the nucleophilic reagents effect elimination rearrangement of various 1,1-diaryl-2-halogenoethylenes to the corresponding diarylacetylenes. Factors such as the nature of the substituent in the benzene nuclei, the halogen of the side chain, and of the reagent[6] have been observed to influence this reaction. We now report on the rearrangement reactions resulting from the bromination of 3,3-di-*p*-methoxyphenylpropenoic acid I in different solvents. It was found that the reaction products and their relative quantities depend on the solvent used as well as the reaction conditions. Bromination of the acid I in chloroform or in benzene at room temperature gave 1,1,4,4-tetra-*p*-methoxyphenylbuta-1,3-diene II, 4,4′-dimethoxybenzophenone and 2-bromo-1,1-di-*p*-methoxyphenylethylene III. Bromination in ethylene glycol at $-10°$ C gave the buta-1,3-diene II and the 2-bromoethylene III only. On the other hand, when the experiment was repeated at the boiling point of the solvent for 1 min, the 2-bromoethylene III was not obtained but instead, 4-methoxybenzyl-4′-methoxyphenyl ketone IV and 1,1-di-*p*-methoxyphenylethylene V were isolated. It is remarkable to note that the acid I itself was recovered completely unchanged after reflux in ethylene glycol for 1 hour. When the reaction was conducted in alkaline reagents 4,4′-dimethoxyphenylacetylene[7] VI was isolated together with the demethylated product namely, 4-hydroxyphenyl-4′-methoxybenzyl ketone VII. The formation of II from III and V finds support and can easily be explained by the free radical reaction mechanism previously reported by W. Tadros *et al.*[8]



EXPERIMENTAL PROCEDURE

(a) Preparation of the acid I :

This was prepared according to the method of Klem and Bower[9]. It separated from 95% ethanol with m.p. 146° C.

b) Bromination of I in chloroform

A solution of bromine (0·8 g ; 0·005 mole) in chloroform (10 ml) was added to a solution of the acid I (1·42 g, 0·005 mole) in the same solvent (0 ml). The colour of bromine discharged and the solution acquired rapidly an olive-green colour. The solvent was recovered at room temperature under reduced pressure using the water-pump. The residue thus obtained was crystallised from 95% ethanol. The ethanol insoluble fraction was filtered off and crystallised from glacial acetic acid to give 1,1,4,4,-tetra-*p*-methoxyphenylbuta-1,3-diene II (0·5 g; 41·6%) with m.p. and mixed[10] m.p. 205° C. (Found: C, 80·30; H, 6·30. Calc. for $C_{32}H_{30}O_4$: C, 80·34; H, 6·27%). The ethanolic mother-liquor gave on cooling 4,4′-

* For correspondence.

dimethoxybenzophenone (0·3 g; 25%) with m.p. and mixed[11] m.p. 142° C. (Found: C, 74·40; H, 5·70. Calc. for $C_{15}H_{14}O_3$: C, 74·39; H, 5·75%). Further concentration and cooling gave 2-bromo-1,1-di-*p*-methoxyphenylethylne III (0·44 g; 21%) with m.p. and mixed[12] m.p. 84° C. (Found: C, 60·20; H, 4·70; Br, 25·00. Calc. for $C_{16}H_{15}BrO_2$: C, 60·19; H, 4·70; Br, 25·08%).

(c) Bromination of I in benzene

On repeating experiment (*b*) using benzene (20 ml), the following compounds were obtained: 1,1,4,4-tetra-*p*-methoxyphenylbuta-1,3-diene[10] (0·03 g; 25%) 4,4'-dimethoxybenzophenone[11] (0·33 g 27%) and 2-bromo-1,1-di-*p*-methoxyphenylethylene[12] (42%).

(d) Bromination of I in ethanol

The repitition of experiment (*b*) in ehtanol (20 ml) gave: 2-bromo-1,1-di-*p*-methoxyphenylethylene[12] (51%) and 1,1-di-*p*-methoxyphenylethylene V (0·3g; 33%) with m.p. and mixed[13] m.p. 142° C. (Found: C, 80·00; H, 6·62. Calc. for $C_{16}H_{16}O_2$: C, 80·00; H, 6·66%).

(e) Bromination of I in ethylene glycol

(i) Bromine (0·8 g) was added to a solution of the acid I in ethylene glycol (1·42 g/20 ml) at −10° C, and the whole was left at this temperature for 1 hr. The residue obtained after dilution with cold water was then crystallised from 95% ethanol. The ethanol-insoluble portion was recrystallised from glacial acetic acid to give the buta-1,3-diene II (16·6%). The ethanolic mother-liquor gave on cooling the 2-bromoethylene III (52%).

(ii) Operating experiment (i) at the boiling point of the solvent (195° C) for 1 min. gave the following products: the buta-1,3-diene[10] II (26·6%), the ethylene[13] V (33·6%) and 4-methoxybenzyl-4'-methoxyphenyl ketone IV (25%) with m.p. and mixed[14] m.p. 110–111° C (Found: C, 75·20; H, 6·20. Calc. for $C_{16}H_{16}O_3$: C, 75·01; H, 6·25%).

(iii) The acid I (1·42 g) in ethylene glycol (10 ml) was treated with bromine (0·8 g) and the whole was directly poured over a solution of sodium 2-hydroxyethoxide (sodium, 0·57 g; 0·025 atom; ethylene glycol, 10 ml). The reaction mixture was heated to boiling for 1 min and then diluted with cold water. The residue thus obtained was fractionated from 95% ethanol to give: 4,4'-dimethoxyphenylacetylene VI (40%) with m.p. and mixed[15] m.p. 142–3° C. (Found: C, 80·80; H, 5·90. Calc. for $C_{16}H_{14}O_2$: C, 80·67; H, 5·88%) and 4-methoxybenzyl-4'-methoxyphenyl ketone IV (20%). Acidification of the alkaline filtrate (HCl) gave the demethylated product 4-hydroxyphenyl-4'-methoxybenzyl ketone VII which on recrystallisation from a little ethanol had m.p. and mixed[15] m.p. 175° C. (Found: C, 74·3; H, 6·0. Calc. for $C_{15}H_{14}O_3$: C, 74·4; H, 5·8%).

(f) Bromination of I in ether followed by NaOEt

A solution of I (1·42 g) in diethyl ether (10 ml) was treated with a solution of bromine 0·8 g) in the same solvent (10 ml) and the whole was directly boiled with a solution of sodium ethoxide (sodium, 0·57 g; ethanol, 20 ml) for 1 min. The residue thus obtained was fractionated from 95% ethanol to give: the acetylene VI (4%), 4,4'-dimethoxybenzophenone (55%) and the 2-bromoethylene[12] III (25%). Acidification of the alkaline filtrate (HCl) gave 4-hydroxyphenyl-4'-methoxybenzyl ketone VII (6%).

1. Tadros, W., Sakla, A. B. and Ishak, M. S., *J. Chem. Soc.*, 1958, p. 4210.
2. Fritch, P., *Annalen*, 1894, **279**, 319.
3. Wiechell, H., *Ibid.*, 1894, **279**, 337.
4. Harris, E. E. and Frankforter, G. B., *J. Am. Chem. Soc.*, 1926, **48**, 3144.
5. Tadros, W., Sakla, A. B. and Armanious, E. R., *J. Chem. Soc.*, 1963, p. 4218.
6. Pritchard, J. G. and Bothner-By, A. A., *J. Phys. Chem.*, 1660, **64**, 1271.
7. Tadros, W., Sakla, A. B. and Helmy, A. A. A., *J. Chem. Soc.*, 1965, p. 3994.
8. —, — and Abdou, S. E., *Ibid.*, Perkin I, 1972, p. 2839.
9. Klem, L. H. and Bower, G. M., *J. Org. Chem.*, 1958, **23**, 344.
10. Bergmann, F., Szmuszkowicz, J. and Dimant, E., *J. Am. Chem. Soc.*, 1949, **71**, 2968.
11. Jones, B., *J. Chem. Soc.*, 1936, p. 1854.
12. Bergmann, F. and Szmuszkowicz, J., *J. Am. Chem. Soc.*, 1947, **69**, 1777.
13. Pfeiffer, P. and Wisinger, R., *Annalen*, 1928, **461**, 132.
14. Tadros, W., Sakla, A. B., Ishak, M. S. and Armanious, E. R., *J. Chem. Soc.*, 1963, p. 4527.
15. —, Ekladius, L. and Sakla, A. B., *Ibid.*, 1954, p. 2351.