526. *Reactions with Asymmetric Diarylethylenes. Part VI.* Reduction of 2-Bromo-*1,1-*di-*p-*alkoxyphenylethylenes by Thiophenols, and Addition of These Thiols to* 1,1-*Di-*p-*alkoxyphenylethylenes.*

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1,1-Di-*p*-alkoxyphenyl-2-bromoethylenes are reduced by thiophenols to products whose nature depends on the substituents present in the thiophenols.

Thiophenols add to 1,1-di-*p*-alkoxyphenylethylenes in a reaction catalysed by hydrogen bromide. The stability of the products depends on the substituent in the thiophenol.

Reaction between anthrone and 1,1-di-*p*-alkoxyphenyl-2-bromoethylenes gives a number of compounds including dianthronyl, the 1,1-di-*p*-alkoxyphenylethylene, and the 1,1,4,4-tetra-*p*-alkoxyphenylbuta-1,3-diene.[1] When anthrone was replaced by thiophenol, the bromo-compound was reduced to the 1,1-dialkoxyethylene but the nature of the products was influenced by the relative quantities of the reactants. With 2 mol. of thiophenol, the main products were the ethylene, diphenyl disulphide, and hydrogen bromide:

$$(p\text{-RO}\cdot C_6H_4)_2\cdot C{:}CHBr + 2PhSH \longrightarrow (p\text{-RO}\cdot C_6H_4)_2\cdot C{:}CH_2 + HBr + Ph_2S_2$$

With one mol., the main product was 1,1,4,4-tetra-*p*-alkoxyphenylbuta-1,3-diene; only 0·5 mol. of the bromoethylene was reduced to the ethylene, $Ar_2C{:}CH_2$, leaving the other 0·5 mol. to react with this ethylene to give the butadiene according to the mechanism reported earlier.[1]

On extending the work to substituted thiophenols, it was found that the reaction was influenced by both the nature and the position of the substituent. With 2 mol. of toluene-*m*-thiol, the reaction proceeded as shown above. On the other hand, on boiling a solution of 2-bromo-1,1-di-*p*-methoxyphenylethylene and toluene-*p*-thiol in acetic acid, small quantities of 1,1,4,4-tetra-*p*-methoxyphenylbuta-1,3-diene and 4,4′-dimethoxystilbene were obtained under these conditions. Further study is being carried out to throw light

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* Part V, *J.*, 1958, 4210.

[1] Tadros and Sakla, *J.*, 1957, 3210.

on the formation of the stilbene. It may be mentioned, however, that 4,4'-dimethoxystilbene was formed from 2-bromo-1,1-di-*p*-methoxyphenylethane [2] in boiling acetic acid. The same stilbene was readily obtained from the bromoethane in boiling ethylene glycol in the presence or absence of silver acetate. *p*-Nitrobenzenethiol and 2-bromo-1,1-di-*p*-methoxyphenylethylene gave 1,1-di-*p*-methoxyphenyl-1-*p*-nitrophenylthioethane, both reduction and addition occurring. This thio-compound was readily obtained by interaction between *p*-nitrobenzenethiol and 1,1-di-*p*-methoxyphenylethylene.

The addition took place also with other thiophenols and was found to be catalysed by hydrogen bromide. Whereas the nitroarylthioethane was stable, 1,1-di-*p*-methoxy(or ethoxy)phenyl-1-phenylthioethane was unstable, darkening on storage; when treated with a mixture of hydrochloric and acetic acid or with alcoholic potassium hydroxide, it partly regenerated the ethylene. 1,1-Di-*p*-methoxyphenyl-1-*p*-tolylthioethane was more stable than the 1-phenylthioethane, but less so than the nitro-compound.

An attempt to condense 2-bromo-1,1-di-*p*-methoxyphenylethane with thiophenol or *p*-nitrobenzenethiol was unsuccessful. A small quantity of 4,4'-dimethoxystilbene was formed in acetic acid; 1,1-di-*p*-methoxyphenylethylene was obtained on treating the 2-bromoethane with sodium thiophenoxide in alcohol.

EXPERIMENTAL

Reactions between 1,1-*Di*-p-*alkoxyphenyl*-2-*bromoethylenes and Thiophenols.*—(a) *Reactions with thiophenol in boiling acetic acid.* (i) This is exemplified by the following: A solution of 2-bromo-1,1-di-*p*-methoxyphenylethylene (3·19 g.) and thiophenol (2·2 g.) in acetic acid (50 c.c.) was refluxed for 1 min. The solution, which became olive-green, was diluted with cold water, and the product was extracted with ether. The ethereal solution was washed with water, 5% aqueous sodium hydroxide, and again water. Ether was distilled off and the residue recrystallised from alcohol from which colourless 1,1-di-*p*-methoxyphenylethylene (1·1 g.) separated, having m. p. and mixed m. p. with an authentic sample [3] 140—142°. The alcoholic mother-liquor, on storage, gave diphenyl disulphide (0·8 g.), which on recrystallisation from alcohol had m. p. 59—60° alone or mixed with an authentic sample.[4] (ii) A solution of 2-bromo-1,1-di-*p*-ethoxyphenylethylene (2 g.) and thiophenol (1·27 g.) in acetic acid (30 c.c.) gave 1,1-di-*p*-ethoxyphenylethylene (0·6 g.), m. p. and mixed m. p. with an authentic sample [5] 142°, and diphenyl disulphide (0·22 g.). (iii) A solution of 2-bromo-1,1-di-*p*-butoxyphenylethylene (2 g.) and thiophenol (1·08 g.) in acetic acid (30 c.c.) gave 1,1-di-*p*-butoxyphenylethylene (0·6 g.), m. p. and mixed m. p. with an authentic sample [1] 125°, and diphenyl disulphide (0·3 g.).

(b) *Reaction at room temperature.* A mixture of the bromomethoxy-compound (0·64 g.) and thiophenol (0·22 g.) in acetic acid (10 c.c.) was left at room temperature for 10 days. The solution acquired an olive-green colour and a precipitate was gradually formed. On recrystallisation, this precipitate gave 1,1,4,4-tetra-*p*-methoxyphenylbuta-1,3-diene [6] (0·15 g.), m. p. and mixed m. p. 206—207°.

(c) *Reaction between* 2-*bromo*-1,1-*di*-p-*methoxyphenylethylene and toluene*-m-*thiol.* Repetition of experiment (a, i) with 2-bromo-1,1-di-*p*-methoxyphenylethylene (1 g.) and toluene-*m*-thiol (0·78 g.) in acetic acid (20 c.c.) gave 1,1-di-*p*-methoxyphenylethylene (0·35 g.) and di-*m*-tolyl disulphide,[7] an oil.

(d) *Reaction between* 2-*bromo*-1,1-*di*-p-*methoxyphenylethylene and toluene*-p-*thiol.* A solution of the bromo-compound (1 g.) and toluene-*p*-thiol (0·78 g.) in acetic acid (15 c.c.) was refluxed for 3 min. The green solution was diluted with cold water and extracted with ether, and the ethereal solution was washed with alkali and water. Ether was distilled off and the residue recrystallised from alcohol from which 4,4'-dimethoxystilbene (0·049 g.) separated, having m. p. and mixed m. p. with an authentic sample [8] 210°. The alcoholic mother-liquor gave, on

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[2] Harris and Frankforter, *J. Amer. Chem. Soc.*, 1926, **48**, 3144.
[3] Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 144.
[4] Vogt, *Annalen*, 1861, **119**, 142.
[5] Tadros and Aziz, *J.*, 1951, 2553.
[6] Bergmann, Szmuszkowicz, and Diamant, *J. Amer. Chem. Soc.*, 1949, **71**, 2968.
[7] Hübner and Post, *Annalen*, 1873, **169**, 1.
[8] Tadros and Ekladius, *Nature*, 1950, **166**, 525; Tadros, Ekladius, and Sakla, *J.*, 1954, 2351.

storage, 1,1,4,4-tetra-*p*-methoxyphenylbuta-1,3-diene (0·02 g.), m. p. and mixed m. p. 204—205°. The bromo-compound was partly recovered together with other products; the reaction is being studied in more detail.

(e) *Reaction between* 2-*bromo*-1,1-*di*-p-*methoxyphenylethylene and* p-*nitrobenzenethiol.* A mixture of the bromo-compound (1 g.) and *p*-nitrobenzenethiol (0·48 g.) in acetic acid (30 c.c.) was left overnight at room temperature. The solution became olive-green and a precipitate was formed. This precipitate was filtered off and recrystallised from acetic acid, from which yellow di-*p*-nitrophenyl disulphide (0·15 g.) separated, having m. p. and mixed m. p. with an authentic sample [9] 180—181°. The main olive-green mother-liquor was diluted with water and extracted with ether. The ethereal solution was washed with water and alkali, and the ether was distilled off. The residue, recrystallised from alcohol, gave yellow 1,1-*di*-p-*methoxyphenyl*-1-p-*nitrophenylthioethane* (0·22 g.), m. p. 135° (Found: C, 67·2; H, 5·6; N, 3·3; S, 8·2. $C_{22}H_{21}NO_4S$ requires C, 66·8; H, 5·3; N, 3·5; S, 8·1%).

Addition of Thiophenols to 1,1-*Di*-p-*methoxy*(*or ethoxy*)*phenylethylene.*—(a) (i) A mixture of 1,1-di-*p*-methoxyphenylethylene (1 g.) and thiophenol (0·45 g.) in acetic acid containing hydrogen bromide (25 c.c. to which was added 0·3 c.c. of acid saturated with hydrogen bromide) was refluxed for 3 min. The olive-green solution was diluted with cold water and extracted with ether. The ethereal solution was washed with alkali and water and evaporated. The residue, recrystallised from methyl alcohol, gave colourless 1,1-*di*-p-*methoxyphenyl*-1-*phenylthioethane* (0·3 g.), m. p. 75—76° (Found: C, 75·0; H, 6·3; S, 9·4. $C_{22}H_{22}O_2S$ requires C, 75·4; H, 6·3; S, 9·1%). (ii) The corresponding diethoxyethylene (1 g.) and thiophenol (0·41 g.) gave colourless 1,1-*di*-p-*ethoxyphenyl*-1-*phenylthioethane* (0·3 g.), m. p. 115° (Found: C, 76·0; H, 5·5; S, 8·6. $C_{24}H_{26}O_2S$ requires C, 76·2; H, 6·9; S, 8·5%).

(b) *Addition of toluene*-p-*thiol to the dimethoxyethylene.* By reaction as in section (a, i), toluene-*p*-thiol (0·51 g.) gave colourless 1,1-*di*-p-*methoxyphenyl*-1-p-*methylphenylthioethane* (0·25 g.), m. p. 65° (Found: C, 75·8; H, 6·9; S, 8·7. $C_{23}H_{24}O_2S$ requires C, 75·8; H, 6·6; S, 8·8%). In the absence of hydrogen bromide, neither the thiophenol nor the toluene-*p*-thiol added to the ethylene.

(c) *Addition of* p-*nitrobenzenethiol to the dimethoxyphenylethylene.* A mixture of the ethylene (1 g.) and *p*-nitrobenzenethiol (0·63 g.) in acetic acid containing hydrogen bromide (50 c.c. to which was added 0·6 c.c. of acid saturated with hydrogen bromide) was refluxed for 3 min., then left to cool. Di-*p*-nitrophenyl disulphide (0·2 g.), m. p. and mixed m. p. 181°, separated first. The mother-liquor was diluted with water, the product was extracted with ether, and the ethereal solution was washed with alkali and water. Ether was distilled off and the residue recrystallised from alcohol, from which 1,1-di-*p*-methoxyphenyl-1-*p*-nitrophenylthioethane separated as yellow crystals (0·25 g.) showing no depression in the m. p. (135°) on admixture with an authentic sample. In the absence of the hydrogen bromide, the nitrothioethane was obtained but it required a longer time (30 min.) to obtain the same yield.

Effect of Acid and Alkali on 1,1-*Di*-p-*methoxyphenyl*-1-*phenylthioethane.*—(*a*) A solution of the sulphur compound (0·2 g.) in acetic (10 c.c.) and concentrated hydrochloric (1 c.c.) acid was refluxed for 30 min. The olive-green solution deposited, on cooling, 1,1-di-*p*-methoxyphenylethylene (0·05 g.), m. p. and mixed m. p. 141—142°.

(*b*) A mixture of the sulphur compound (0·25 g.) and potassium hydroxide (0·3 g.) in alcohol (25 c.c.) was refluxed on the water-bath for 2 hr. On cooling, the dimethoxyethylene (0·05 g.) separated as colourless crystals, m. p. and mixed m. p. 142°.

Attempt to Condense 2-*Bromo*-1,1-*di*-p-*methoxyphenylethane with Thiophenol.*—(*a*) A solution of the 2-bromoethane (2 g.) and thiophenol (0·68 g.) in acetic acid (40 c.c.) was refluxed for 3 min. On cooling, colourless 4,4′-dimethoxystilbene (0·21 g.), m. p. and mixed m. p. 209—210°, separated. No condensation product could be obtained.

(*b*) A mixture of the 2-bromoethane (2 g.) and thiophenol (0·68 g.) in alcoholic sodium ethoxide (0·143 g. of sodium dissolved in 60 c.c. of alcohol) was refluxed for 1 hr. The alcoholic solution was concentrated, diluted with water, and extracted with ether. Ether was distilled off and the residue, recrystallised from alcohol, gave dimethoxyethylene, having m. p. and mixed m. p. 141—142°.

(*c*) The preceding experiment but with the 2-bromo-ethoxy-ethane gave no condensation product and the ethoxy-ethylene, m. p. and mixed m. p. 142°, was formed.

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[9] Wohlfahrt, *J. prakt. Chem.*, 1902, **66**, 551.

Conversion of 2-*Bromo*-1,1-*di*-p-*methoxyphenylethane into* 4,4′-*Dimethoxystilbene*.—(*a*) A solution of the 2-bromoethane (1 g.) in acetic acid (20 c.c.) was refluxed for 3 min. On cooling, 4,4′-dimethoxystilbene (0·1 g.), m. p. and mixed m. p. 210°, was obtained. Prolonging the time of boiling increased the yield of stilbene (0·19 g. after 30 min.; 0·23 g. after 90 min.). The reaction is being studied in more detail.

(*b*) A solution of the 2-bromoethane (0·5 g.) in ethylene glycol (15 c.c.) was refluxed for 30 min. On cooling, 4,4′-dimethoxystilbene (0·15 g.), m. p. and mixed m. p. 209°, was obtained.

(c) The preceding experiment but with silver acetate (0·52 g.) and 2-bromoethane (1 g.) in ethylene glycol (30 c.c.) gave a product (0·2 g.), m. p. 188°. This gave, on recrystallisation from acetic acid, the dimethoxystilbene (0·15 g.), m. p. and mixed m. p. 210°.

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