797. *Reactions with Diarylethylenes. Part VIII.*[1] *The Mechanism of Conversion of Some 2-Halogeno-1,1-diarylethylenes by Sodium 2-Hydroxyethoxide into Diarylacetylenes.*

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Both isomers of 2-bromo-1-*p*-methoxyphenyl-1-phenylethylene are converted by sodium 2-hydroxyethoxide in boiling ethylene glycol into *p*-methoxyphenylphenylacetylene. The use of [2-^{14}C]isomers showed that the *p*-methoxyphenyl group migrated predominantly in both cases. The product assigned the structure *p*-methoxyphenylphenylacetylene by Oréckhoff and Tiffeneau was a mixture of 4-methoxybenzyl phenyl ketone and 4-methoxystilbene.

2-Bromo-1,1-di-*p*-chlorophenylethylene did not undergo the rearrangement, the 2-2′-hydroxyethyl ether being formed instead of the acetylene, which indicates the influence of the substituents in the benzene nuclei on the rearrangement.

The mechanism of the elimination-rearrangement is discussed.

1-*p*-Hydroxyphenyl-1-phenylethylene is not œstrogenic.

PREVIOUS work has shown that the nucleophilic reagents sodium 2-hydroxyethoxide [1e] and ethoxide [2a-c,e] and potassium t-butoxide [3] and pentyloxide [2d] in the corresponding alcohol, powdered sodium in dry benzene,[2e] sodium and potassium amide [4] in liquid ammonia, n-butyl-lithium,[5a-c] and phenyl-lithium [5a,d] 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 and of the halogen in the side-chain, and, as pointed out by Pritchard and Bothner-By,[6] of the reagent have been observed to influence this reaction. Curtin and Flynn [5c] claimed the rearrangement of 2-bromo-1,1-di-*p*-chlorophenylethylene to di-(*p*-chlorophenyl)acetylene by n-butyl-lithium; we find, however, that this bromoethylene with sodium 2-hydroxyethoxide in boiling ethylene glycol gives 1,1-di-*p*-chlorophenyl-2-2′-hydroxyethoxyethylene with, at most, a trace of the acetylene. Oxidation of the ether gave 4,4′-dichlorobenzophenone.

[1] Part VII, Tadros, Sakla, and Helmy, *J.*, 1961, 2687. Parts I—V: (*a*) Tadros and Aziz, *J.*, 1951, 2553; (*b*) Tadros, *J.*, 1954, 2966; (*c*) Tadros, Sakla, and Akhnookh, *J.*, 1956, 2701; (*d*) Tadros and Sakla, *J.*, 1957, 3210; (*e*) Tadros, Sakla, and Ishak, *J.*, 1958, 4210.

[2] (*a*) Fritsch, *Annalen*, 1894, **279**, 319; (*b*) Buttenberg, *ibid.*, p. 324; (*c*) Wiechell, *ibid.*, p. 337; (*d*) Fritsch, *ibid.*, 1903, **329**, 37; (*e*) Harris and Frankforter, *J. Amer. Chem. Soc.*, 1926, **48**, 3144.

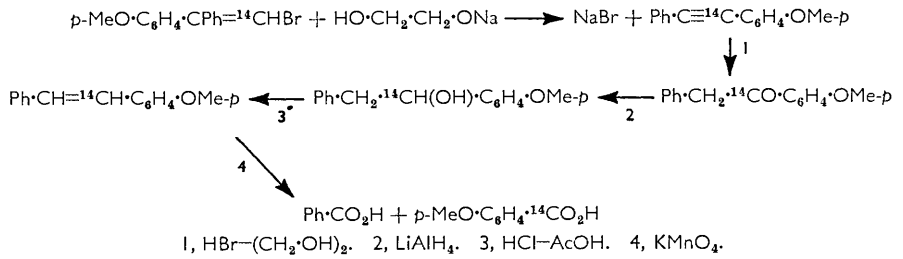
[3] Bothner-By, *J. Amer. Chem. Soc.*, 1955, **77**, 3293.

[4] (*a*) Coleman and Maxwell, *J. Amer. Chem. Soc.*, 1934, **56**, 132; (*b*) Coleman, Holst, and Maxwell, *ibid.*, 1936, **58**, 2310.

[5] (*a*) Curtin, Flynn, Nystrom, and Richardson, *Chem. and Ind.*, 1957, 1453; (*b*) Curtin, Flynn, and Nystrom, *J. Amer. Chem. Soc.*, 1958, **80**, 4599; (*c*) Curtin and Flynn, *ibid.*, 1959, **81**, 4714; (*d*) Curtin and Richardson, *ibid.*, p. 4719.

[6] Pritchard and Bothner-By, *J. Phys. Chem.*, 1960, **64**, 1271.

The two geometrical isomers [7] of 2-bromo-1-*p*-methoxyphenyl-1-phenylethylene were both converted by sodium 2-hydroxyethoxide in ethylene glycol into *p*-methoxyphenylphenylacetylene. Use of the two isomers of 2-bromo-1-*p*-methoxyphenyl-1-phenyl-[2-^{14}C]ethylene proved predominant migration in both cases of the *p*-methoxyphenyl group, this being proved by the reactions in the annexed scheme. The carbon-14 was mainly recovered in the anisic acid fraction. On acidification of the alkaline mother-liquor with hydrochloric acid, benzyl *p*-hydroxyphenyl ketone alone or together with



1, $HBr–(CH_2·OH)_2$. 2, $LiAlH_4$. 3, HCl–AcOH. 4, $KMnO_4$.

4-hydroxystilbene (depending on the concentration of the reagent) was obtained. On the other hand, stereospecificity was noted by Bothner-By [3] in the rearrangement of *cis*- and *trans*-2-bromo-1-*p*-bromophenyl-1-phenyl[1-^{14}C]ethylene with t-butyl-alcoholic potassium t-butoxide, and by Curtin *et al.*[5a–c] in the rearrangement of *cis*- and *trans*-2-bromo-1-*p*-chlorophenyl-1-phenyl[1-^{14}C]ethylene with n-butyl-lithium; these authors noted predominant migration of the aryl group *trans* to the halogen atom on rearrangement to the diarylacetylene.

Of two probable mechanisms, (*a*) prior abstraction of the proton from carbon-2, and (*b*) the removal of the halide ion leaving a carbon atom with a sextet of electrons, Coleman *et al.*[4b] preferred the latter. They cited (i) analogy with the mechanism given by Whitmore and Fleming [8] for the formation of trimethylethylene and t-pentyl acetate in the reaction of neopentyl iodide with silver acetate in acetic acid, and (ii) the formation of diphenylvinyl ethyl ether and diphenylacetylene from 2-chloro-1,1-diphenylethylene by alcoholic sodium ethoxide [2b] at *ca.* 200°. Though they did not explicitly state it, route (*b*) apparently requires formation of a carbonium ion with simultaneous rearrangement to the acetylene, and, whether the reaction follows the S_N1 or the S_N2 mechanism, it is to be expected that alongside with the acetylene some ether would be formed. However, in the reaction of the 1,1-di-*p*-alkoxyphenyl-2-halogenoethylenes [1e] or the two isomers of 2-bromo-1-*p*-methoxyphenyl-1-phenylethylene with sodium 2-hydroxyethoxide, we obtained the diarylacetylenes and no ether (the 2,2-di-*p*-alkoxyphenylvinyl ethers were prepared by another route to be reported later) could be isolated. Fritsch [2a] noted also that the only product of the reaction of 2-chloro-1,1-di-*p*-methyl(or methoxy or ethoxy)phenylethylene with alcoholic sodium ethoxide at 180—190° was the acetylene. In fact the absence of these ethers is to be expected in the light of the finding by Tadros, Sakla, and Helmy [1a] that hydrogen bromide adds to 1,1-di-*p*-alkoxyphenyl-2-halogenoethylenes according to Markownikoff's rule, *i.e.*, that the electron density on carbon-2 is greater than that on carbon-1. This makes approach of the nucleophile to the negatively charged carbon-2 improbable. Rearrangement by mechanism (*b*) therefore seems unlikely. With some difference in the detail, route (*a*) was favoured recently.[3,5a–d,6] Our views on this and other probable routes will be discussed later.

Oréckhoff and Tiffeneau [9] reported that *p*-methoxyphenylphenylacetylene of m. p. 89—90° was obtained on treating 1,2-dibromo-1-*p*-methoxyphenyl-2-phenylethane with boiling aqueous potassium carbonate. Our acetylene melted at 60°. We then found that

[7] Stoermer and Simon, *Ber.*, 1904, **37**, 4163.
[8] Whitemore and Fleming, *J.*, 1934, 1269.
[9] Oréckhoff and Tiffeneau, *Bull. Soc. chim. France*, 1925, **37**, 1410.

Oréckhoff and Tiffeneau's product was not the acetylene, but was a mixture of 4-methoxybenzyl phenyl ketone (m. p. 98°) and 4-methoxystilbene (m. p. 137°). A mixture of authentic samples of the two compounds had m. p. 89—90°. A solution of *p*-methoxyphenylphenylacetylene in boiling ethylene glycol containing hydrogen bromide gave the isomer, benzyl 4-methoxyphenyl ketone, m. p. 78°.

Curtin and Flynn [5c] recently noted a band at 915 cm.$^{-1}$ for diphenylacetylene. A parallel band at 920 cm.$^{-1}$ was shown by the di-*p*-ethoxyphenyl- and *p*-ethoxyphenyl-*p'*-methoxyphenyl-acetylene, and was especially strong for the di-*p*-ethoxy-compound. However, it was either missing or relatively weak when both *p*-alkoxy-substituents were methoxy, n-propoxy, isopropoxy, or n-butoxy. The band at 2190—2260 cm.$^{-1}$ was not shown by the above acetylenes (cf. Wotiz and Miller [10]).

1-*p*-Hydroxyphenyl-1-*p*-methoxyphenylethylene was prepared with the object of testing the compound for œstrogenic activity, 1,1-di-*p*-methoxyphenylethylene being known [1a] to be devoid of such activity. Tested on groups of 5 ovariectomised mice (average weight, 25 g.), the former compound (5 mg. in 0·4 c.c. of olive oil, injected subcutaneously in 4 doses on 2 days) showed practically no activity. The hydroxy-compound was obtained on partial dealkylation of 1,1-di-*p*-methoxyphenylethylene with sodium 2-hydroxyethoxide in ethylene glycol, or by heating a solution of 1-*p*-isopropoxyphenyl-1-*p*-methoxyphenylethylene in acetic acid containing hydrogen bromide.

Experimental

Infrared spectra measured on Perkin-Elmer model 21 spectrophotometer by Sadtler and Son, Research Labs., Philadelphia, Pennsylvania, U.S.A. Specimens were 0·5% mixtures in KBr discs (0·5 mm. thick).

4-*Isopropoxy*-4'-*methoxybenzophenone*.—Prepared by the standard method from 4-hydroxy-4'-methoxybenzophenone (2·28 g.), ethanolic sodium ethoxide (0·35 g. of sodium in 50 c.c. of alcohol), and isopropyl iodide (2·6 g.), this *ketone* had m. p. 60° (from alcohol) (Found: C, 75·2; H, 6·6. $C_{17}H_{18}O_3$ requires C, 75·6; H, 6·7%).

1-p-*Isopropoxyphenyl*-1-p-*methoxyphenylethylene*.—4-Isopropoxy-4'-methoxybenzophenone (27·0 g.) was added to a Grignard reagent (magnesium, 3·6 g.; methyl iodide, 21·3 g.; ether, 200 c.c.). Decomposition with aqueous ammonium chloride and extraction with ether gave the *ethylene* (20·5 g.), m. p. 85° (from alcohol) (Found: C, 80·1; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%).

1-p-*Hydroxyphenyl*-1-p-*methoxyphenylethylene*.—(*a*) A mixture of sodium 2-hydroxyethoxide in ethylene glycol [sodium (2·3 g.) in ethylene glycol (30 c.c.)] and 1,1-di-*p*-methoxyphenylethylene (6·0 g.) was boiled for 1 hr., cooled, and diluted with water, and the precipitate was filtered off and recrystallised from alcohol, to give unchanged 1,1-di-*p*-methoxyphenylethylene (3·6 g.), m. p. and mixed m. p. 142°. Acidification of the alkaline filtrate gave 1-*p*-hydroxyphenyl-1-*p*-methoxyphenylethylene (1·7 g.), m. p. 110° [from light petroleum (b. p. 100—120°)] (Found: C, 76·9; H, 6·6. $C_{15}H_{14}O_2,\frac{1}{2}H_2O$ requires C, 76·6; H, 6·4%). Repeated recrystallisation as above and drying over phosphorus pentoxide in a vacuum did not remove the water of crystallisation. Preparation of the acetoxy-derivative (see below) and its hydrolysis gave the same hydroxy-compound with the same analysis. Remethylation of the hydroxyethylene with dimethyl sulphate gave 1,1-di-*p*-methoxyphenylethylene.

(*b*) A solution of 1-*p*-isopropoxyphenyl-1-*p*-methoxyphenylethylene (5·0 g.) in acetic acid containing hydrogen bromide (20 c.c.) was boiled for 1 hr., then cooled, diluted with water, and extracted with ether. Ether was diluted off and the residue was treated with 5% aqueous sodium hydroxide. The insoluble fraction gave unchanged ethylene (3·4 g.). Acidification of the alkaline filtrate gave 1-*p*-hydroxyphenyl-1-*p*-methoxyphenylethylene (0·7 g.).

1-p-*Acetoxyphenyl*-1-p-*methoxyphenylethylene*.—Prepared by heating the hydroxyethylene (2·0 g.) in acetic anhydride (30 c.c.) for 30 min. and crystallised from alcohol, this *acetate* had m. p. 85° (Found: C, 76·6; H, 6·1. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%).

Reactions with Sodium-2-hydroxyethoxide in Ethylene Glycol.—(*a*) *1,1-Diaryl-2-halogenoethylenes*. (i) The procedure and products obtained are exemplified by the following: 2-Chloro-1,1-di-*p*-methoxyphenylethylene (1·37 g., 0·005 mole) and a solution from sodium (0·575 g.,

[10] Wotiz and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 3441.

0·025 g.-atom) in ethylene glycol (15 c.c.) were boiled for 3 hr., then cooled and diluted with water, and the precipitate was filtered off. 4,4′-Dimethoxytolane separated from alcohol (0·1 g.; m. p. and mixed m. p.[1e] 142—143°), with unchanged chloroethylene (0·3 g.; m. p. and mixed m. p. 77—78°). Acidification of the alkaline filtrate with hydrochloric acid gave 4-hydroxyphenyl 4′-methoxybenzyl ketone which on recrystallisation from a little alcohol had m. p. and mixed m. p.[11] 175° (0·35 g.) (Found: C, 74·2; H, 5·9. Calc. for $C_{15}H_{14}O_3$: C, 74·4; H, 5·8%).

(ii) On repeating experiment (i) with the two isomers of 2-bromo-1-*p*-methoxyphenyl-1-phenylethylene (m. p. 52° and 82°; 1·45 g.) and sodium 2-hydroxyethoxide in ethylene glycol (sodium, 0·23 g., in ethylene glycol, 15 c.c.), p-*methoxyphenylphenylacetylene*, m. p. 60° (from alcohol) (0·8 g.) (Found: C, 86·6; H, 6·1. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%), was similarly obtained. Acidification of the alkaline mother-liquor gave benzyl *p*-hydroxyphenyl ketone (from alcohol) (0·3 g.), m. p. and mixed m. p.[12] 146° (Found: C, 79·6; H, 5·7. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7%). When the quantity of sodium (2·5 times) and the time of heating were increased (5 hr.), in addition to the acetylene and ketone a small quantity of 4-hydroxystilbene (0·1 g.), m. p. 186° alone or when admixed with an authentic sample [13] was obtained.

(iii) A mixture of 2-bromo-1,1-di-*p*-chlorophenylethylene (1·64 g., 0·005 mole) and the reagent (0·23 g. of sodium in 15 c.c. of ethylene glycol) was refluxed for 5 hr. On dilution and recrystallisation of the precipitate from alcohol, 1,1-*di*-p-*chlorophenyl*-2-2′-*hydroxyethoxyethylene* separated (0·96 g.); it had m. p. 96° (Found: C, 62·1; H, 4·7; Cl, 22·7. $C_{16}H_{14}Cl_2O_2$ requires C, 62·1; H, 4·5; Cl, 23·0%). When heated for 3 hr., with a more concentrated solution of the reagent (sodium, 0·575 g., in ethylene glycol, 15 c.c.), this ether (1·54 g.) was recovered unchanged.

Oxidation of the ether. To a mixture of this ether (0·5 g.) and powdered potassium dichromate (1 g.) in glacial acetic acid (15 c.c.), concentrated sulphuric acid (0·5 c.c.) was added dropwise with shaking. Water (1 c.c.) was subsequently added and the mixture refluxed for 15 min., diluted with cold water, and extracted with ether. The ethereal layer was washed with water, aqueous sodium carbonate, and water again, and dried (Na_2SO_4), and ether was distilled off. Recrystallisation, from alcohol, of the residue gave 4,4′-dichlorobenzophenone, m. p. and mixed m. p.[14] 145°.

(*b*) p-*Methoxyphenylphenylacetylene*. The acetylene (1 g.) and the reagent (sodium, 0·23 g., in ethylene glycol, 15 c.c.) were boiled for 3 hr. Dilution with water gave unchanged acetylene (0·6 g.). Acidification of the alkaline filtrate gave benzyl 4-hydroxyphenyl ketone (0·3 g.), m. p. and mixed m. p. 146°. When the quantity of sodium was increased (to 0·575 g.) and heating was prolonged (to 5 hr.), unchanged acetylene (0·2 g.) was obtained. Acidification of the alkaline filtrate and fractionation of the precipitate gave benzyl *p*-hydroxyphenyl ketone (0·2 g.), m. p. and mixed m. p. 146°, and 4-hydroxystilbene (0·15 g.), m. p. and mixed m. p. 186°.

(*c*) *Benzyl* p-*Hydroxyphenyl ketone*. The ketone (1·05 g.) and the reagent (sodium 0·575 g., in ethylene glycol, 15 c.c.) were refluxed for 5 hr. Dilution and acidification of the alkaline mother-liquor and fractional crystallisation of the precipitate from dilute alcohol gave 4-hydroxystilbene (0·3 g.), m. p. and mixed m. p. 186°, and unchanged benzyl *p*-hydroxyphenyl ketone (0·5 g.), m. p. 146°.

(*d*) 4-*Methoxystilbene*. The stilbene [9] (1·05 g.) and the reagent (sodium, 0·23 g., in ethylene glycol, 15 c.c.) were refluxed for 3 hr. Dilution with water gave unchanged 4-methoxystilbene (0·5 g.) m. p. and mixed m. p. 136°. Acidification of the alkaline filtrate gave 4-hydroxystilbene (0·2 g.), m. p. and mixed m. p. 186°.

Action of Hydrogen Bromide in Ethylene Glycol on p-*Methoxyphenylphenylacetylene*.—A solution of the acetylene (0·5 g.) in ethylene glycol (15 c.c.) containing hydrogen bromide (6%) was refluxed for 3 hr., then cooled, diluted with water, and filtered. On recrystallisation the precipitate from alcohol gave benzyl *p*-methoxyphenyl ketone, m. p. and mixed m. p.[15] 78° (from alcohol) (0·4 g.) (Found: C, 79·6; H, 6·3. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%).

[11] Tadros, Ekladius, and Sakla, *J.*, 1954, 2351.
[12] Weisl, *Monatsh.*, 1905, **26**, 977.
[13] Hewitt, Lewcock, and Pope, *J.*, 1912, 604.
[14] Dittrich, *Annalen*, 1891, **264**, 174.
[15] Ney, *Ber.*, 1888, **21**, 2445.

Reactions with Compounds Labelled with Carbon-14.—[^{14}C]Methyliodide (0·5 mc) was diluted with normal methyl iodide (50 c.c.).

1-p-*Methoxyphenyl*-1-*phenyl*[2-^{14}C]*ethylene*.—4-Methoxybenzophenone (21·2 g.) was added to the Grignard reagent (magnesium, 3·5 g.; [^{14}C]methyl iodide, 21·3 g., and ether, 150 c.c.). Decomposition with aqueous ammonium chloride, extraction with ether, and recrystallisation from alcohol gave 1-*p*-methoxyphenyl-1-phenyl[2-^{14}C]ethylene (12·0 g.), m. p. and mixed m. p. 75°.

2-*Bromo*-1-p-*methoxyphenyl*-1-*phenyl*[2-^{14}C]*ethylene*.—The product from bromine (8·0 g.) and the labelled ethylene (10·5 g.) in ether (200 c.c.) was washed with 10% aqueous sodium hydroxide, followed by water, and after recovery, was heated on the water-bath with sodium hydroxide (3 g.) in alcohol (60 c.c.) for 30 min., diluted with water, cooled, and extracted with ether. The ethereal layer was washed with water and dried (Na_2SO_4), and ether was then distilled. The residue was fractionated from alcohol, to give the two isomers of 2-bromo-2-*p*-methoxyphenyl-1-phenyl[2-^{14}C]ethylene, m. p.s 52° and 82°.

The position of carbon-14. (i) A solution of sodium (0·23 g.) in ethylene glycol (15 c.c.) with labelled 2-bromo-1-*p*-methoxyphenyl-1-phenyl[2-^{14}C]ethylene, m. p. 52° or 82° (1·45 g.) gave the labelled acetylene (0·7 g.), m. p. 60°.

(ii) Benzyl *p*-methoxyphenylphenyl [^{14}C]ketone (1·2 g.) was obtained from the acetylene (1·5 g.) mentioned above.

(iii) To a solution of the benzyl *p*-methoxyphenyl [^{14}C]ketone (1 g.) in dry ether (100 c.c.), powdered lithium aluminium hydride (2 g.) was added gradually. The mixture was refluxed for 1 hr. and left overnight at room temperature. The excess of lithium aluminium hydride was decomposed with cold dilute acetic acid, and the product was extracted with ether. The ethereal layer was washed with aqueous sodium carbonate and water and dried (Na_2SO_4). Ether was removed and the residue crystallised from light petroleum (b. p. 50—70°) from which 1-*p*-methoxyphenyl-2-phenylethan-1-ol separated (0·8 g.), having m. p. and mixed m. p. [9] 58°.

(iv) 1-*p*-Methoxyphenyl-2-phenyl[1-^{14}C]ethylene was obtained by refluxing a solution of the preceding alcohol (0·5 g.) in ethylene glycol for 30 min. Crystallised (0·4 g.) from alcohol, it had m. p. and mixed m. p. 136°.

(v) A mixture of the labelled stilbene (0·5 g.) and potassium permanganate (1·0 g.) in acetone (50 c.c.) was refluxed for 2 hr. Acetone was distilled off and the residue was treated with a little hot distilled water. The solution was filtered and evaporated almost to dryness on the water-bath. The product was acidified with a little concentrated hydrochloric acid, and the whole was extracted with ether. Ether was removed and the residue crystallised from dilute alcohol, whereby *p*-anisic acid separated, having m. p. and mixed m. p. 179—180° (Found: C, 63·3; H, 5·2. Calc. for $C_8H_8O_3$: C, 63·2; H, 5·3%) The radioactivity of the acid obtained from the isomer with m. p. 52° was 0·262 μc/mmole and that obtained from the isomer with m. p. 82° was 0·267 μc/mmole. The mother-liquor was made slightly alkaline, and the solution was evaporated almost to dryness on the water-bath. The residue was acidified with a few drops of concentrated hydrochloric acid, and the precipitate was extracted with a little ether. Ether was distilled off, and the residue was treated with distilled water (1 c.c.). The small quantity of insoluble anisic acid was filtered off. On cooling, the filtrate deposited benzoic acid, m. p. and mixed m. p. 120° (Found: C, 69·0; H, 4·9. Calc. for $C_7H_6O_2$: C, 68·9; H, 4·9%). The activity of benzoic acid from the isomer with m. p. 52° was 0·0337 μc/mmole, and that from the isomer with m. p. 82° was 0·0131 μc/mmole

Oréckhoff and Tiffeneau's Product.[9]—As described by Oréckhoff and Tiffeneau, a suspension of 1,2-dibromo-1-*p*-methoxyphenyl-2-phenylethane (37·0 g.) in aqueous potassium carbonate (37·0 g. in 750 c.c.) was boiled for 4 hr., then cooled and extracted with ether. The ether was distilled off and the residue was fractionally recrystallised from alcohol. 4-Methoxystilbene (12·5 g.), m. p. and mixed m. p.[9] 136°, and 4-methoxybenzyl phenyl ketone (4·8 g.), m. p. and mixed m. p. 98°, were obtained.

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