527. *Reactions with Asymmetric Diarylethylenes. Part VII.* A New Synthetic Route to Tetra-arylallenes.*

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Diphenylmethyl chloride or bromide added readily to asymmetric diarylethylenes, giving tetra-arylpropenes. With bromine these afforded tetra-aryl-2-bromopropenes whose structure was confirmed by ozonolysis and which with alcoholic potassium hydrioxide afforded tetra-arylallenes.

Triphenylmethyl chloride also added to the asymmetric diarylethylenes, giving penta-arylpropenes.

We report a new synthetic route to tetra-arylallenes. Diphenylmethyl chloride or bromide added to asymmetric diarylethylenes, to give a product which underwent dehydrohalogenation readily with the formation of tetra-arylpropenes (I). These propenes were also obtained on passing hydrogen chloride or hydrogen bromide through a benzene solution of diphenylmethanol and the ethylene,[3] diphenylmethyl chloride or bromide being apparently formed before initiation of the reaction. Triphenylmethyl chloride also added to the ethylenes, giving the penta-aryl propenes. The simplest member of the series, tetraphenylpropene (I; R = H) was obtained earlier by Vorländer and Siebert [1a] and by Straus and Ehrenstein.[2]

Treating the tetra-arylpropenes with bromine gave bromo-compounds (II) whose structure was confirmed by ozonolysis; and the bromo-compounds with alcoholic potassium hydroxide gave the tetra-arylallenes (III). These reactions were effected by starting from 1,1-diphenylethylene and its di-*p*-methoxy-, -ethoxy-, -propoxy-, and -isopropoxy-derivatives. Tetraphenylallene itself has been obtained previously [1a,3] but three of the four derivatives which we prepared are new.

$$\mathrm{Ar_2C{:}CH_2 + Ph_2CHX \longrightarrow [Ar_2CX{\cdot}CH_2{\cdot}CHPh_2] \longrightarrow Ar_2C{:}CH{\cdot}CHPh_2\ (I) \longrightarrow}$$

$$\mathrm{[Ar_2CBr{\cdot}CHBr{\cdot}CHPh_2] \longrightarrow \underset{(II)}{Ar_2C{:}CBr{\cdot}CHPh_2} \longrightarrow \underset{(III)}{Ar_2C{:}C{:}CPh_2}}$$

In an attempt to add diphenylmethyl bromide to 2-bromo-1,1-diphenylethylene the latter was recovered unchanged and diphenylmethyl ethyl ether was formed on treating the reaction mixture with ethyl alcohol.

In tests on groups of 5 ovariectomised mice (average wt., 25 g.), tetraphenylallene and

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* Part VI, preceding paper.

[1] (*a*) Vorländer and Siebert, *Ber.*, 1906, **39**, 1024; (*b*) Vorländer and Weinstein, *Ber.*, 1923, **56**, 1122.

[2] Straus and Ehrenstein, *Annalen*, 1925, **442**, 93.

[3] Staudinger and Meyer, *Helv. Chim. Acta*, 1922, **5**, 656; Vorländer, Osterburg, and Meyer, *Ber.*, 1923, **56**, 1136; Ziegler and Ochs, *Ber.*, 1922, **55**, 2257; Maitland and Mills, *J.*, 1936, 987; Ziegler, *Annalen*, 1923, **434**, 34; Bergmann, Hoffmann, and Meyer, *J. prakt. Chem.*, 1932, **135**, 245.

1,1-di-*p*-methoxyphenyl-3,3-diphenylprop-1-ene and its 2-bromo-derivative (5 mg. in 0·4 c.c. of olive oil, injected subcutaneously during 2 days) showed practically no activity.

EXPERIMENTAL

1,1,3,3-*Tetra-arylpropenes*.—This is exemplified by the preparation of tetraphenylpropene. (*a*) A solution of diphenylmethyl bromide (2·47 g., 0·01 mole) or chloride (2·02 g.), and 1,1-diphenylethylene (1·8 g., 0·01 mole) in dry benzene (30 c.c.) was refluxed on the water-bath for 6 hr., becoming yellow and then green with evolution of halogen acid. Benzene was distilled, and the residue was digested for 30 min. with potassium hydroxide (1 g.) in alcohol (30 c.c.). The mixture was cooled, diluted with water (50 c.c.), and extracted with ether and the extract was washed with water. The ether was distilled off and the residue recrystallised from alcohol from which 1,1,3,3-tetraphenylpropene [1a] (2·1 g.) separated as colourless crystals, m. p. 127° (Found: C, 93·5; H, 6·4. Calc. for $C_{27}H_{22}$: C, 93·6; H, 6·4%). The treatment with alkali was merely precautionary because, as just indicated, the intermediate lost halogen acid spontaneously in the hot reaction mixture.

(*b*) Experiment (*a*) was repeated without use of a solvent, the mixture being heated in a boiling-water bath for 6 hr. and the product treated with alcoholic potassium hydroxide as above. 1,1,3,3-Tetraphenylpropene (2 g.) (from alcohol) had m. p. and mixed m. p. 127°.

(*c*) Hydrogen chloride or bromide gas was passed for 1 hr. through a boiling solution of diphenylmethanol (1·84 g., 0·01 mole) and 1,1-diphenylethylene (1·8 g., 0·01 mole) in dry benzene, then boiling was continued for further 5 hr., the same changes in colour as in (*a*) occurring; 1,1,3,3-tetraphenylpropene (2·1 g.) was obtained.

The following propenes similarly prepared; they crystallised from alcohol in 60—65% yield). 1,1-*Di*-p-*methoxyphenyl*-3,3-*diphenylprop*-1-*ene*, m. p. 86—88° (Found: C, 85·8; H, 6·6. $C_{29}H_{26}O_2$ requires C, 85·7; H, 6·4%); 1,1-*di*-p-*ethoxyphenyl*-3,3-*diphenylprop*-1-*ene*, m. p. 88—91° (Found: C, 85·5; H, 7·0. $C_{31}H_{30}O_2$ requires C, 85·7; H, 6·9%); 3,3-*diphenyl*-1,1-*di*-p-*propoxyphenylprop*-1-*ene* softens at 92° and melts at 96° (Found: C, 85·4; H, 7·0. $C_{33}H_{34}O_2$ requires C, 85·7; H, 7·4%); 3,3-*diphenyl*-1,1-*di*-p-*isopropoxyphenylprop*-1-*ene* softens at 97° and melts at 110° (Found: C, 85·5; H, 7·3%). Longer heating improved the yield only slightly, the 1,1-di-*p*-alkoxyphenylethylene being partly recovered and diphenylmethyl ethyl ether formed

1,1-*Di*-p-*methoxy*(*or ethoxy*)*phenyl*-3,3,3-*triphenylprop*-1-*ene*.—(*a*) Triphenylmethyl chloride (2·78 g., 0·01 mole) and 1,1-di-*p*-methoxyphenylethylene (2·4 g., 0·01 mole) or the ethoxyphenylethylene (2·68 g.) in dry benzene (30 c.c.) were refluxed for 3 hr. Hydrogen chloride was evolved and the colour changed from orange to green. Benzene was distilled off and a solution of the residue with potassium hydroxide (1 g.) in alcohol (30 c.c.) was refluxed for 30 min., then diluted with water (50 c.c.), cooled, and filtered. The solid was washed with water and recrystallised from alcohol, from which colourless 1,1-*di*-p-*methoxyphenyl*-3,3,3-*triphenylprop*-1-*ene* (1·6 g.), m. p. 137—138°, separated (Found: C, 87·0; H, 6·5. $C_{35}H_{30}O_2$ requires C, 87·1; H, 6·2%). 1,1-*Di*-p-*ethoxyphenyl*-3,3,3-*triphenylprop*-1-*ene* (yield 1·7 g.) had m. p. 136—137° (Found: C, 87·0; H, 6·4. $C_{37}H_{34}O_2$ requires C, 87·1; H, 6·7%).

(*b*) Experiment (*a*) was repeated but without the solvent. The mixture was heated in a boiling-water bath for 3 hr., melting and becoming yellow and then green with evolution of hydrogen chloride. The product was refluxed with alcoholic potassium hydroxide as in (*a*). 1,1-Di-*p*-methoxy(or ethoxy)phenyl-3,3,3-triphenylprop-1-ene was obtained. Increasing the time of reaction by 1 hr. only slightly improved the yield. The alcoholic mother-liquors gave unchanged dialkoxyethylene and a triphenylmethyl ethyl ether, m. p. and mixed m. p. 78° (cf. ref. 4).

1,1,3,3-*Tetra-aryl-2-bromopropenes*.—To the tetra-arylpropene (0·01 mole) in ether (30 c.c.), bromine (1·6 g., 0·01 mole) in ether (10 c.c.) was added. After evaporation the residue was recrystallised from alcohol–acetone (2 : 1). Thus were obtained as colourless crystals in almost quantitative yield: 2-bromo-1,1,3,3-tetraphenylpropene,[1a, b] m. p. 124° (Found: C, 76·1; H, 4·8; Br, 18·4. Calc. for $C_{27}H_{21}Br$: C, 76·2; H, 4·9; Br, 18·8%); 2-*bromo*-1,1-*di*-p-*methoxy*-, m. p. 96—97° (Found: C, 71·4; H, 5·0; Br, 16·8. $C_{29}H_{25}BrO_2$ requires C, 71·7; H, 5·2; Br, 16·5%), and 2-*bromo*-1,1-*di*-p-*ethoxy-phenyl*-3,3-*diphenylprop*-1-*ene*, m. p. 116—117° (Found: C,

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[4] Hemilian, *Ber.*, 1874, 7, 1203.

72·2; H, 5·7; Br, 16·1. $C_{31}H_{29}BrO_2$ requires C, 72·5; H, 5·7; Br, 15·6%); 2-*bromo*-3,3-*diphenyl*-1,1-*di*-p-*propoxy*-, m. p. 80—82° (Found: C, 72·7; H, 6·1; Br, 15·2. $C_{33}H_{33}BrO_2$ requires C, 73·2; H, 6·1; Br, 14·8%), and -*isopropoxy-phenylprop*-1-*ene*, m. p. 129—130° (Found: C, 72·9; H, 6·1; Br, 15·2%).

*Ozonolysis of Tetra-aryl-*2-*bromopropenes.*—A stream of ozonised oxygen (*ca.* 3%) was passed through a cold solution of the tetra-aryl-2-bromopropene (0·5 g.) in carbon tetrachloride (30 c.c.) for 48 hr. Raney nickel sludge (*ca.* 5 g.) in distilled water was added and the mixture heated on the water-bath until carbon tetrachloride was recovered. The mixture was decanted and treated with 10% aqueous sodium hydroxide. The undissolved material was extracted with ether, the extract was washed with water and evaporated, and the residue recrystallised from alcohol to give benzophenone or the corresponding 4,4′-dialkoxybenzophenone (dimethoxy-, m. p. 142°; diethoxy-, m. p. 131°; dipropoxy-, m. p. 127°; di-isopropoxy-, m. p. 72°), showing no depression of the m. p. when mixed with authentic samples.[5] On acidification, the alkaline mother-liquor gave diphenylacetic acid, m. p. and mixed m. p. 144—145°.

Tetra-arylallenes.—This is exemplified by the preparation of tetraphenylallene. 2-Bromo-1,1,3,3-tetraphenylpropene (1 g.) and potassium hydroxide (2 g.) in alcohol (30 c.c.) were refluxed for 1 hr., then cooled and diluted with water (50 c.c.). The solid was washed with water and recrystallised from alcohol–acetone (2 : 1). It had m. p. 165° and was tetraphenylallene [1a] (yield almost quantitative) (Found: C, 93·8; H, 5·7. Calc. for $C_{27}H_{20}$: C, 94·2; H, 5·8%). Similarly were obtained in almost quantitative yield: 1,1-di-*p*-methoxyphenyl-3,3-diphenylallene, m. p. 104° (cf. Ziegler and Ochs [3]) (Found: C, 85·6; H, 6·0. Calc. for $C_{29}H_{24}O_2$: C, 86·1; H, 5·9%); 1,1-*di*-p-*ethoxyphenyl*-3,3-*diphenyallene*, m. p. 109° (Found: C, 85·6; H, 6·4. $C_{31}H_{28}O_2$ requires C, 86·1; H, 6·5%); 3,3-*diphenyl*-1,1-*di*-p-*propoxyphenylallene*, m. p. 73—74° (Found: C, 85·6; H, 7·1. $C_{33}H_{32}O_2$ requires C, 86·1; H, 7·0%); and 3,3-*diphenyl*-1,1-*di*-p-*isopropoxyphenylallene*, m. p. 102—103° (Found: C, 85·7; H, 6·8%).

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[5] Jones, *J.*, 1936, 1854.