

52. Preparation of $\alpha\zeta$ -Diphenylhexatriene and 1:4-Diphenylbenzene from Cinnamaldehyde.

By ALEXANDER SCHÖNBERG and ABDEL FATTAH ALY ISMAIL.

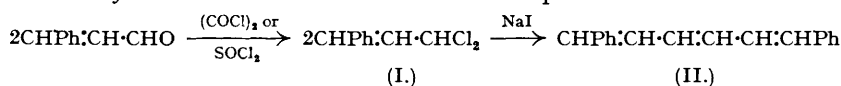
Cinnamaldehyde was allowed to react with thionyl chloride or oxalyl chloride and the product (I) was treated with sodium iodide; $\alpha\zeta$ -diphenylhexatriene (II) was formed directly and also a product which on distillation yielded 1:4-diphenylbenzene (V).

THE preparation of $\alpha\zeta$ -diphenylhexatriene (II) has previously been effected by various methods, none of which was satisfactory as regards yield, and in most cases a number of intermediate products were formed from the initial material, cinnamaldehyde. Smedley (J., 1908, **93**, 373) condensed cinnamaldehyde with sodium phenylisocrotonate and obtained (II); from 35 g. of phenylisocrotonic acid, 2 g. of the hydrocarbon were obtained.

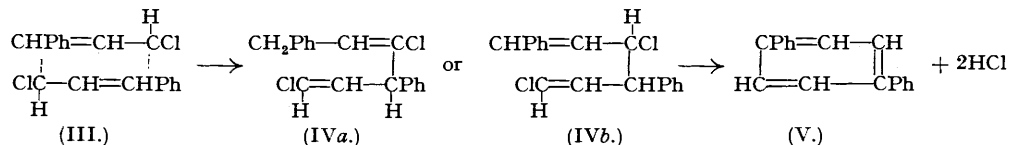
Farmer, Laroia, Switz, and Thorpe (J., 1927, 2955) used *s*-distyrylethylene glycol, which may be obtained in 10–12% yield from cinnamaldehyde. The next step, which further decreased the yield, as it proceeded by no means quantitatively, was the formation of dibromo- $\alpha\zeta$ -diphenylhexatriene, from which the hydrocarbon (II) was obtained in 60–65% yield by the action of zinc dust.

Kuhn and Winterstein (*Helv. Chim. Acta*, 1928, **11**, 87) prepared (II) by the action of potassium iodide in acetone on dibromo- $\alpha\zeta$ -diphenylhexatriene.

Styryldichloromethane (I), easily obtainable from cinnamaldehyde, is an obvious starting material for the preparation of (II). It was indeed used by Kuhn and Winterstein (*loc. cit.*), who treated it with zinc dust in alcohol, but obtained a very poor yield (quoted from *Centr.*, 1928, **I**, 1401; we could not consult the original paper). We found that, if the crude product (I) obtained by the action of thionyl chloride or oxalyl chloride on cinnamaldehyde is treated with sodium iodide in acetone, $\alpha\zeta$ -diphenylhexatriene (II) is formed, in addition to a product which on distillation yields 1:4-diphenylbenzene (V). By this method, it is now possible to obtain (II) and (V) in reasonable yields without isolation of intermediate products.



Kuhn and Winterstein (*Ber.*, 1927, **60**, 432) have obtained 1:4-diphenylbenzene (V), and discussed two explanations for its formation. In our case, too, several explanations are possible; one may assume, for example, that by the action of sodium iodide on (I) the compound (III) is formed, which has the nature of a free radical; two of these radicals may add to each other to form (IVa) or (IVb), which on pyrolysis yields 1:4-diphenylbenzene (V):



EXPERIMENTAL.

$\alpha\zeta$ -Diphenylhexatriene (II).—Freshly distilled cinnamaldehyde (30 g.) was refluxed with thionyl chloride (100 c.c.) or, preferably, oxalyl chloride (42 g.) (Staudinger, *Ber.*, 1909, **42**, 3975) for 10 hours (calcium chloride guard-tube). (Thionyl chloride is more accessible than oxalyl chloride, but the latter seems to yield purer products.) The excess of the reagent was then driven off in a vacuum, and the oily product dissolved in acetone (100 c.c.) and poured into a solution of sodium iodide (100 g.) in acetone (750 c.c.); the acetone used was free from alcohol and water. The mixture was refluxed (mechanical stirrer) for 4 hours, sodium chloride being precipitated, and then cooled, and the precipitate collected and washed several times with acetone. The filtrate and washings were evaporated to about 400 c.c. and cooled in ice. The precipitated green crystals were collected, and the acetone solution diluted with ice-water (about 400 c.c.); sulphur dioxide was passed through the mixture till the colour of the iodine was discharged; the dark semi-solid (A) was separated by decantation from the aqueous acetone solution (B) and treated with ether (about 100 c.c.). The solid (C) dispersed in the ethereal mixture was filtered off (2 g. of crude $\alpha\zeta$ -diphenylhexatriene); the ethereal filtrate was added to (B), and the whole shaken with ether (about 500 c.c.). The ethereal layer was washed successively with excess of sodium bicarbonate solution, water, 20% sodium thiosulphate solution (100 c.c.), and water, dried over sodium sulphate, and evaporated on the water-pump to about 100 c.c.; the yellow crystals (D) which separated on cooling were filtered off (1.1 g. of almost pure $\alpha\zeta$ -diphenylhexatriene). From the ethereal filtrate an additional quantity of less pure substance (E) was isolated by slow concentration, cooling and filtration, leaving a dark ethereal solution (F). C, D, and E crystallised from acetone in yellow plates (2.2 g.), m. p. 200°, not depressed by two authentic samples prepared according to Kuhn and Winterstein (*Helv. Chim. Acta*, 1928, **11**, 87), and Farmer, Laroia, Switz, and Thorpe (*loc. cit.*) (Found: C, 92.6; H, 7.0. Calc. for $\text{C}_{18}\text{H}_{16}$: C, 93.1; H, 6.9%).

1:4-Diphenylbenzene (V).—Solution (F) (in a 50 c.c. short-necked Claisen flask) was freed from ether, and the residue heated at about 150° (bath temp.) with occasional stirring for 1 hour, hydrogen chloride being evolved; the residue was distilled (direct flame) under about 45 mm. and the fraction distilling at about 250° (compare Schmidt and Schultz, *Annalen*, 1880, **203**, 124) was collected as a light brown oil, which soon solidified. It separated from benzene (2 vols.)—alcohol (1 vol.) in colourless crystals (2.9 g.), m. p. 209–210°, not depressed by authentic 1:4-diphenylbenzene (Kuhn and Winterstein, *Ber.*, 1927, **60**, 432) (Found: C, 93.9; H, 6.0. Calc. for $\text{C}_{18}\text{H}_{14}$: C, 93.9; H, 6.1%).