521. *A Synthesis of Biphenyls*

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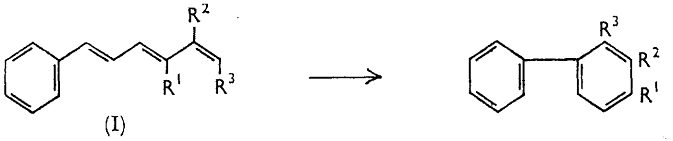
The pyrolysis of phenyl-trienes (I) yields cyclic dienes, and, in the presence of palladised charcoal, biphenyls. The phenyl-trienes were prepared as the *trans,cis,trans-* and *trans,trans,trans*-isomers by ordinary or modified Wittig reactions of cinnamylidenetriphenylphosphorane on αβ-unsaturated aldehydes or ketones. Very high yields of biphenyls were obtained from the *trans,cis,trans*-trienes.

The four most important methods of preparing unsymmetrical biphenyls have been reviewed.[1] The two most widely used reactions are the coupling of aryl diazonium salts with aromatic nuclei, and the reaction of an arylmagnesium halide with a cyclohexanone. Both reactions have their limitations.[1] The reaction described here, which can be used to prepare biphenyls differently substituted in each ring, can usefully supplement existing methods.

Trienes, when heated to 325—350° over alumina, form cyclic dienes, and, in particular, 1-phenylhexa-1,3,5-triene is reported to form 1-phenylcyclohexa-1,3-diene.[2] The required trienes were previously fairly inaccessible but the Wittig reaction of carbonyl compounds and ylides of phosphonium salts has made the required geometrical isomers relatively easy to obtain. In our work on the pyrolysis of polyenes [3] we found that trienes in which the sequence of double bonds is *trans,cis,trans* cyclised readily on distillation to give high yields of cyclic dienes. However, the all-*trans*-trienes are not so readily isomerised, and require a temperature of about 250°, giving lower yields of cyclic dienes. The competing reaction of self-condensation by Diels–Alder addition reduces the yields of the cyclic dienes. By heating the trienes *in vacuo* with a palladium–charcoal catalyst at 250° for 1 hr. we could convert the trienes directly into biphenyls. Temperatures of only 170—180° for 10—20 min. were sufficient for the *trans,cis,trans*-isomers. In the cases illustrated here, the ylide obtained from cinnamyltriphenylphosphonium bromide by treatment with n-butyl-lithium was condensed with an αβ-unsaturated aldehyde or ketone to yield a phenyl-triene (I) (see Table). The trienes (I) were then converted directly into the biphenyls (II) by heating with palladium–charcoal.



(I) (II)

Phenyl-triene (I)					
R^1	R^2	R^3	Isomer used *	Product	Yield (%)
H	H	H	*cis*	Biphenyl	95
H	H	Me	*cis*	2-Methylbiphenyl	96
			cis,trans		61
H	Me	Me	*cis*	2,3-Dimethylbiphenyl	98
			cis,trans		52
H	H	A	*cis,trans*	2-*p*-Methoxyphenylbiphenyl	77
Me	H	B	*cis,trans*	4-Methyl-2-(2,2,6-trimethylcyclohexyl)biphenyl	43

* *cis* or *trans* indicates the configuration in the centre of the triene chain.

A = *p*-Methoxyphenyl. B = 2,6,6-Trimethylcyclohexenyl.

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[1] W. E. Bachmann and R. A. Hoffman, *Org. Reactions*, 1944, **2**, 224.

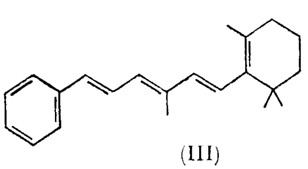
[2] G. F. Woods, N. C. Bolgiano, and D. E. Duggan, *J. Amer. Chem. Soc.*, 1955, **77**, 1800.

[3] F. S. Edmunds and R. A. W. Johnstone, preceding Paper.

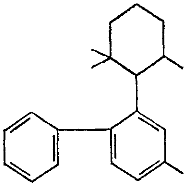
The trienes (I) were obtained normally as mixtures of the *trans,cis,trans*- and *trans,trans,trans*-isomers which were not separated, although the all-*trans*-isomer predominated. The isomers could be separated by chromatography on alumina, but in only one case was this done, the physical properties being in close agreement with those of other similar trienes.[4] Conjugation in the all-*trans*-trienes caused a shift in the infrared absorption of *trans*-disubstituted double bonds from the normal 960—970 to 990—995 $cm.^{-1}$

In one experiment, extended heating of the triene (I; $R^1 = H$; $R^2 = R^3 = Me$) without palladium–charcoal yielded a mixture of 4,5-dimethyl-6-phenylcyclohexa-1,3-diene and 5,6-dimethyl-1-phenylcyclohexa-1,3-diene which were separated by chromatography on alumina. The second evidently arose from the first by migration of the double bonds into conjugation with the benzene ring.

The synthesis was applied to the preparation of the biphenyl (IV), not readily accessible by the usual methods,[4] and to an *o*-terphenyl. Thus, β-ionone and the ylide of cinnamyltriphenylphosphonium bromide gave the tetraene (III) which, with palladium–charcoal afforded the biphenyl (IV). Although the conversion of the tetraene (III) into the biphenyl (IV) involves no dehydrogenation,[3] a better yield at a lower temperature was obtained in the presence of the catalyst which probably facilitated 1,3-hydrogen shifts. The Table lists the percentage yields of biphenyls obtained from the phenyl-trienes.



(III)



(IV)

In two cases, the phenyl-trienes (I) were prepared predominantly in the *trans,cis,trans*-form by the Shemyakin modification [5] of the Wittig reaction. Very high yields of biphenyls were obtained from these isomers of the phenyl-trienes. In some cases the yields of phenyl-triene (I) obtained by the Wittig reaction were not very satisfactory but most of the preparations were performed only once and no attempt was made to improve the yields of this step in the syntheses.

Recent work [6] indicates that the originally reported high yields of *cis*-olefin formed in the Shemyakin modification are suspect. In the cases described here, the *cis*-isomers were formed predominantly, but overall yields were lower than for the unmodified Wittig reactions.

EXPERIMENTAL

Preparation of the Phenyl-trienes (I).—Cinnamyltriphenylphosphonium bromide (1 mol.) (prepared from triphenylphosphine and cinnamyl bromide in benzene) in dry ether was treated with a solution of n-butyl-lithium (1 mol.) in ether. The solution was stirred under nitrogen for 1½—2 hr., to give a deep red solution. To this solution was added, with cooling, the αβ-unsaturated aldehyde or ketone (1·3 mol.) in ether. The mixture was stirred for 18 hr. at room temperature, filtered, and the ether distilled from the filtrate. The residue was placed on a column of neutral alumina (Brockmann grade I) and eluted with light petroleum (b. p. 40—60°), to give the phenyl-triene. By careful chromatography the *trans,cis,trans*-triene could be separated from the all-*trans*-isomer.

When the Shemyakin modification was used, the ylide of cinnamyltriphenylphosphonium bromide was prepared as above. Before addition of the αβ-unsaturated aldehyde or ketone, dry dimethylformamide (3 vol. to each 1 vol. of ether) was added, and then a solution of anhydrous lithium bromide (1 mol.) in dimethylformamide (1 vol.). The mixture was stirred for 10 min. before addition of a solution of the αβ-unsaturated aldehyde or ketone in dimethylformamide.

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[4] D. F. Schneider and C. F. Garbers, *J.*, 1964, 2465.

[5] L. D. Bergelson and M. M. Shemyakin, *Tetrahedron*, 1963, **19**, 149.

[6] H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, 1964, **29**, 3327.

The mixture was stirred for 18 hr., poured into water, extracted with ether, and worked up in the usual way.

The following αβ-unsaturated aldehydes and ketones gave the trienes indicated.

(*a*) Acraldehyde, with the Shemyakin modification, yielded 1-*phenylhexa*-trans-1,cis-3,trans-5-*triene* (15%), b. p. 145°/15 mm., $\nu_{max.}$ 1000, 965, 900, 745, 735, 690br cm.$^{-1}$ (Found: C, 92·0; H, 8·2. $C_{12}H_{12}$ requires C, 92·3; H, 7·7%).

(*b*) Crotonaldehyde gave 1-phenylhepta-1,3,5-triene (30%) which was separated by chromatography on alumina into: (i) 1-*phenylhepta*-trans-1,cis-3,trans-5-*triene*, $\lambda_{max.}$ 307 mμ (log ε 3·9), $\nu_{max.}$ 955, 732, 689 cm.$^{-1}$ (Found: C, 92·0; H, 8·2. $C_{13}H_{14}$ requires C, 91·7; H, 8·3%). On distillation this afforded 5-*methyl*-6-*phenylcyclohexa*-1,3-*diene*, b. p. 120°/15 mm. (air-bath), $\lambda_{max.}$ 257, 264, 269 mμ (log ε 3·47, 3·5, 3·48), $\nu_{max.}$ 740, 700, 690 cm.$^{-1}$ (Found: C, 91·5; H, 8·7%); (ii) 1-*phenylhepta*-trans-1,trans-3,trans-5-*triene*, m. p. 81—83° (from ethanol), $\lambda_{max.}$ 310, 324, 340 mμ (log ε 4·58, 4·60, 4·45), $\nu_{max.}$ 995, 744, 690 cm.$^{-1}$ (Found: C, 91·4; H, 8·5%).

(*c*) Tiglic aldehyde, with the Shemyakin modification, yielded 5-*methyl*-1-*phenylhepta*-trans-1,cis-3,trans-5-*triene* (17%), $\lambda_{max.}$ 312 mμ (log ε 3·87), $\nu_{max.}$ 958, 731, 689 cm.$^{-1}$ (Found: C, 91·2; H, 8·8. $C_{14}H_{16}$ requires C, 91·2; H, 8·8%).

Tiglic aldehyde without the Shemyakin modification gave a mixture of isomers (66%) from which, by crystallisation from ethanol, was obtained 5-*methyl*-1-*phenylhepta*-trans-1,trans-3,trans-5-*triene*, m. p. 81—83° (from ethanol), $\lambda_{max.}$ 320, 325, 342 mμ (log ε 4·42, 4·45, 4·29), $\nu_{max.}$ 995, 745, 690 cm.$^{-1}$ (Found: C, 91·1; H, 8·7%).

5-Methyl-1-phenylhepta-1,3,5-triene (1 g.) was heated under nitrogen at 210° for 2 hr. Distillation gave a colourless oil (270 mg.), b. p. 200°/15 mm. (air-bath), which was placed on a column of neutral alumina (Brockmann grade I; 100 × 1 cm.) and eluted with light petroleum (b. p. 40—60°), to give: (i) 1,6-*dimethyl*-5-*phenylcyclohexa*-1,3-*diene*, $\lambda_{max.}$ (265), 270, (275) mμ (log ε 3·45, 3·46, 3·45), $\nu_{max.}$ 740, 700, 688 cm.$^{-1}$ (Found: C, 90·8; H, 8·9%); (ii) 5,6-*dimethyl*-1-*phenylcyclohexa*-1,3-*diene*, $\lambda_{max.}$ 309 mμ (log ε 4·1), $\nu_{max.}$ 760, 730, 700, 690 cm.$^{-1}$ (Found: C, 90·9; H, 8·8%). On gas chromatography on a 4 ft. × $\frac{1}{4}$ in. column of Celite (100—120 mesh) coated with 15% of polyethylene glycol adipate, and a nitrogen flow rate of 20 ml./min., these cyclic dienes and 2,3-dimethylbiphenyl were readily separated at 164°; relative retention volumes, respectively, 1·91 : 2·67 : 3·75 (2-methylhexadecane = 1·00).

(*d*) *p*-Methoxycinnamaldehyde afforded 6-p-*methoxyphenyl*-1-*phenylhexa*-1,3,5-*triene* (59%). The all-*trans*-isomer crystallised from ethanol, m. p. 176—178°, $\lambda_{max.}$ 357, 370, 389 mμ (log ε 4·70, 4·75, 4·58), $\nu_{max.}$ 1240, 1165, 1030, 955, 820, 740, 688 cm.$^{-1}$ (Found: C, 87·2; H, 6·5. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%).

(*e*) β-Ionone yielded 4-methyl-1-phenyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-triene.[4]

Pyrolysis of Phenyl-trienes.—A sample of the triene was mixed with 10 (w/w) of 10% palladium–charcoal and heated in a sealed, evacuated tube to 180° for 15 min. for the *trans,cis,trans*-trienes, and to 250° for 1 hr. for the all-*trans*-isomers. The contents of the tube were distilled to yield the biphenyl which was identified by comparison of its infrared and ultraviolet spectra, and gas-chromatographic retention times with those of an authentic sample (except *p*-methoxyphenylbiphenyl). Biphenyl was further identified by mixed melting point with an authentic specimen.

Pyrolysis of 6-*p*-methoxyphenyl-1-phenylhexa-1,3,5-triene yielded 2-p-*methoxyphenylbiphenyl* as a colourless oil, b. p. 153° (air-bath)/0·2 mm., $\lambda_{max.}$ 245, 262, 270 mμ (log ε 4·39, 4·08, 3·95), $\nu_{max.}$ 1221, 1175, 1035, 832, 764, 744, 700 cm.$^{-1}$ (Found: C, 87·6; H, 6·5; OMe, 11·1. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2; OMe, 11·9%).

The authors thank Sir James Cook, F.R.S., for his interest in this work.

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