# Photocyclisation of Some 1,6-Diarylhexa-1,3,5-trienes

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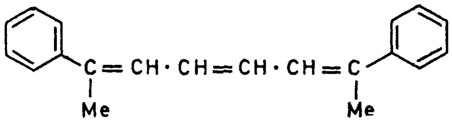
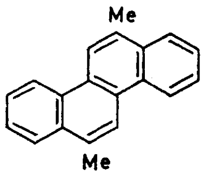
On irradiation in benzene solution in the presence of air or iodine, 1,6-dimethyl-1,6-diphenylhexa-1,3,5-triene is converted into 6,12-dimethylchrysene. Under the same conditions 3-methyl-1,6-diphenylhexatriene gives chrysene, by ejection of the methyl group, but 1,3,6-triphenylhexatriene unexpectedly cyclises to 1,2,4-triphenylbenzene.

Wittig condensation of cinnamylidenetriphenylphosphorane with benzylideneacetone takes an unusual course, affording 2-methyl-1,4-diphenylbenzene as one product. An example of double-bond isomerisation during a Wittig reaction is reported.

OXIDATIVE photocyclisation of 1,6-diarylhexa-1,3,5-trienes has been used to prepare a variety of chrysene derivatives with substituents on the terminal rings.[1] It seemed of interest to determine if the same procedure applied to 1,6-diarylhexatrienes substituted on the polyene chain would lead to chrysenes with substituents on the two middle rings, and to this end we have examined the oxidative photocyclisation of 1,6-dimethyl-1,6-diphenylhexa-1,3,5-triene (I). In the event both the all-*trans*- and the *trans,cis,trans*-isomers of the hexatriene were readily converted into 6,12-dimethylchrysene (II) by irradiation in benzene solution in the presence of air or iodine.

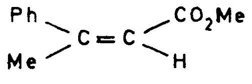


(I)

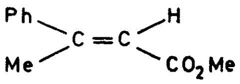


(II)

We hoped to prepare four geometrical isomers of the dimethyldiphenylhexatriene from *cis*- and *trans*-β-methylcinnamyltriphenylphosphonium periodates by the modified Wittig procedure of Bestmann, Armsen, and Wagner.[2] The starting materials were *cis*- and *trans*-methyl β-methylcinnamates, which were themselves obtained stereoselectively by conjugate addition of a lithium diorgano-cuprate reagent to the appropriate αβ-acetylenic ester.[3] Thus, reaction of lithium dimethylcuprate with methyl phenylpropiolate gave methyl *cis*-β-methylcinnamate (III) in 85% yield and with almost complete stereoselectivity. The identification of the product (III) was supported by the n.m.r. spectrum, which showed singlets at τ 7·9 (3H) and 4·1 (1H), and by hydrolysis to the acid.[4] In the same way lithium diphenylcuprate and methyl tetrolate gave methyl *trans*-β-methylcinnamate (IV) (80%), again with high stereoselectivity. Hydrolysis gave the known acid,[4] confirming the structure, and the n.m.r. spectrum showed singlets at τ 7·45 (3H) and 3·8 (1H). The downfield shifts of these signals relative to those of the corresponding protons in the *cis*-isomer are in accord with the assigned structures.[5] Reduction of the two esters with lithium aluminium hydride and aluminium chloride afforded the corresponding allylic alcohols, whence the bromides and the triphenylphosphonium salts were obtained by standard methods.



(III)



(IV)

Reaction of *trans*-β-methylcinnamyltriphenylphosphonium periodate with ethanolic lithium ethoxide proceeded smoothly, affording 1,6-dimethyl-1,6-diphenylhexa-1,3,5-triene as a mixture of two isomers. The main, crystalline, product is regarded as the all-*trans*-isomer on the basis of a strong i.r. peak at 960 cm$^{-1}$ and the absence of a '*cis*' u.v. peak at 250—270 nm.[6] The other product was an oil, possibly not completely pure. It showed only very weak i.r. absorption in the 960—970 cm$^{-1}$ region and had a '*cis*' u.v. peak at 260 nm; it is presumably largely the *trans,cis,trans*-isomer. Surprisingly, the same two isomers were obtained from reaction of the *cis*-β-methylcinnamyltriphenylphosphonium periodate with lithium ethoxide; isomerisation of the 'cinnamyl' double bonds must have occurred at some stage in one or other of the series. We have no reason to suspect that conversion of the two cinnamate esters into the allylic bromides and thence into the phosphonium salts was accompanied by loss of stereochemical integrity (see Experimental section), and it seems likely that isomerisation took place in the ylide derived from one of the periodates.

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[1] (*a*) C. C. Leznoff and R. J. Hayward, *Canad. J. Chem.*, 1972, **50**, 528; (*b*) W. Carruthers, N. Evans, and R. Pooranamoorthy, *J.C.S. Perkin I*, 1973, 44.

[2] H-J. Bestmann, R. Armsen, and H. Wagner, *Chem. Ber.*, 1969, **102**, 2259.

[3] E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, 1969, **91**, 1851; J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, p. 1853.

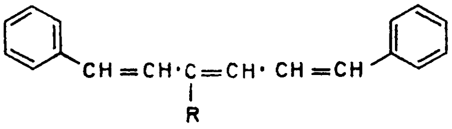
[4] R. Stoermer, F. Grimm, and E. Laage, *Ber.*, 1917, **50**, 959.

[5] See J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1966, vol. 2, pp. 710ff.

[6] *Cf.* K. Lunde and L. Zechmeister, *J. Amer. Chem. Soc.*, 1954, **76**, 2308.

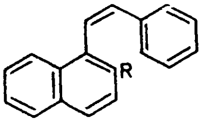
Resonance interaction involving the double bond and the negative charge in cinnamylphosphoranes has been demonstrated[7] and at least one other example of *cis–trans* isomerisation in an allylic phosphorane has been recorded.[8] We have no evidence on the direction of the isomerisation in the present case, but it seems reasonable to suppose that the *cis*-ylide isomerises to the *trans*- and that the crystalline hexatriene isolated is the all-*trans*-isomer and the oil the *trans,cis,trans*-.

In related experiments we have studied the photocyclisation of 1,3,6-triphenylhexa-1,3,5-triene (V; R = Ph). Nothing is known of the mechanism of the oxidative cyclisation of diphenylhexatrienes to chrysenes, but it has been supposed that the reaction may take place in steps by way of the 1-α-styrylnaphthalene [as (VI)]. It seemed of interest to determine if the reaction could be interrupted at this intermediate stage by means of a blocking phenyl group [*cf.* (VI; R = Ph)] or whether it would proceed further to give 6-phenylchrysene. In the event neither process occurred.



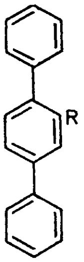
$\mathrm{CH{=}CH{\cdot}\underset{R}{C}{=}CH{\cdot}CH{=}CH}$

(V)

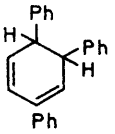


(VI)

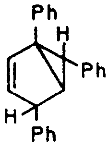
Irradiation of 1,3,6-triphenylhexatriene, obtained by reaction of cinnamylidenetriphenylphosphorane with benzylideneacetophenone,[9] in benzene or cyclohexane solution in the presence of iodine led rapidly to a single crystalline product, $C_{24}H_{18}$, formed in high yield. However, the u.v., i.r., and n.m.r. spectra and the chemical properties of this product are inconsistent with either the styrylnaphthalene or phenylchrysene structure and, together with the m.p., strongly suggest that it is 1,2,4-triphenylbenzene (VII; R = Ph).[10] In agreement, the same compound was obtained in 90% yield on heating (50 °C) a solution of 1,3,6-triphenylhexatriene in benzene solution in the presence of iodine.[11] Nevertheless, there seems little doubt that the product from the irradiation experiment is formed mainly in a photoreaction, for a solution of the hexatriene in benzene irradiated at 20 °C in the presence of iodine gave 1,2,4-triphenylbenzene in 90% yield within 1 h, whereas in the absence of light only a 10% yield of 1,2,4-triphenylbenzene was obtained (g.l.c.). The formation of triphenylbenzene in the photoreaction may be envisaged as taking place by way of the cyclohexadiene (VIII) or the bicyclohexene (IX), each of which could arise from the hexatriene by a well known path,[12] although it is not immediately obvious why such a course should be followed with 1,3,6-triphenylhexatriene and not with the 1,6-diphenyl compound. Re-examination of the photocyclisation of the latter and analysis of the crude product by g.l.c. revealed that, as already reported,[13] the main volatile product was chrysene, and no more than a trace of a product which might have been *o*-terphenyl was present. For comparison the irradiation of 3-methyl-1,6-diphenylhexatriene was also examined. After 1 h the triene appeared to be largely unchanged; on more prolonged exposure much polymeric material was produced and a small amount of chrysene was isolated, formed, presumably, from the styrylnaphthalene (VI; R = Me) with ejection of the methyl substituent.



(VII)



(VIII)



(IX)

For the preparation of 3-methyl-1,6-diphenylhexa-1,3,5-triene the Wittig reaction between cinnamylidenetriphenylphosphorane and benzylideneacetone was used. In contrast to the reaction with benzylideneacetophenone described above, this reaction was unexpectedly troublesome. When n-butyl-lithium in ether was used to generate the phosphorane, although some of the desired hexatriene was obtained, the main product was a viscous oil which we have been unable to identify. With ethanolic lithium ethoxide as base, the main product was again the viscous oil, accompanied in this case by a crystalline product, $C_{19}H_{16}$, which was clearly not a hexatriene. It was identified as 2-methyl-1,4-diphenylbenzene (VII; R = Me) by comparison with a specimen synthesised from *trans,trans*-1,4-diphenylbutadiene and acrylic acid (see Experimental section). The mode of formation of this product is uncertain. One possibility is that it arises by way of a methyldiphenylcyclohexadiene formed, perhaps, by cyclisation of the hexatriene (XI), itself derived from the six-membered complex (X),[14] or by a novel rearrangement of an initial

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[7] H-J. Bestmann, O. Kratzer, and H. Simon, *Chem. Ber.*, 1962, **95**, 2750.

[8] I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 1958, 843.

[9] H-J. Bestmann and O. Kratzer, *Chem. Ber.*, 1962, **95**, 1894; F. Bohlmann, *ibid.*, 1956, **89**, 2191.

[10] Preliminary account, W. Carruthers, N. Evans, and D. Whitmarsh, *J.C.S. Chem. Comm.*, 1974, 526.

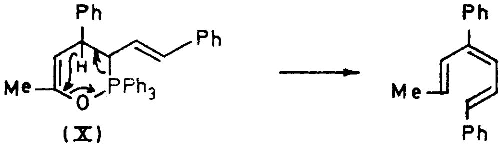
[11] *Cf.* F. S. Edmunds and R. A. W. Johnstone, *J. Chem. Soc.*, 1965, 2898.

[12] See, for example, A. Padwa, L. Brodsky, and S. Clough, *J. Amer. Chem. Soc.*, 1972, **94**, 6767; W. G. Dauben, R. G. Williams, and R. D. McKelvey, *ibid.*, 1973, **95**, 3932; W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, *ibid.*, 1972, **94**, 4285.

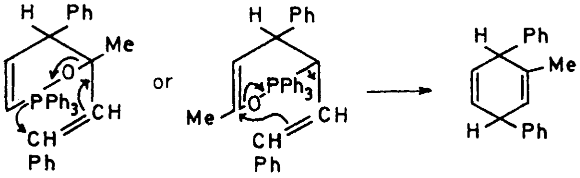
[13] W. Carruthers, N. Evans, and R. Pooranamoorthy, *J.C.S. Perkin I*, 1973, 44.

[14] *Cf.* H. H. Inhoffen, K. Bruckner, G. F. Domagk, and H. M. Erdmann, *Chem. Ber.*, 1955, **88**, 1415.

six-membered adduct [*e.g.* (XII) ⟶ (XIII)]; the latter variation on a known theme[15] is necessitated by



(X) (XI)



(XII) (XIII)

the unusual orientation of the product obtained in the present experiment.

## EXPERIMENTAL

General experimental conditions were as described in *J.C.S. Perkin I*, 1974, 421.

*Methyl* cis-β-*Methylcinnamate* (III).—A solution of lithium dimethylcuprate was prepared by addition of copper(I) iodide (14·8 g) to a cooled (0 °C) solution of methyl-lithium [from lithium (4·6 g) and methyl iodide (50 g) in ether (200 cm³), evaporation, and addition of tetrahydrofuran (250 cm³)]. The green solution was cooled to −76 °C under nitrogen (more tetrahydrofuran was added if the cuprate began to crystallise out) and a cold (−76 °C) solution of methyl phenylpropiolate (10 g) in tetrahydrofuran (50 cm³) was added. The mixture was stirred for 16 h, then methanol (20 cm³) was added to quench the reaction and the solution was allowed to warm to room temperature. Most of the solvent was evaporated off and the mixture was acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the washed and dried solution gave the *ester* as an oil, b.p. 56—57° at 0·05 mmHg (9·3 g). G.l.c. (3% SE30 at 119 °C) showed that the product was almost completely free of the *trans*-isomer (Found: C, 74·9; H, 6·95. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%). Hydrolysis afforded *cis*-β-methylcinnamic acid, m.p. 131° (lit.,[4] 131·5°).

*Methyl* trans-β-*Methylcinnamate* (IV).—This was prepared in the same way as the *cis*-isomer from methyl tetrolate (5·2 g) and lithium diphenylcuprate [from lithium (2·0 g), bromobenzene (22·4 g), and copper(I) iodide (11·1 g)] in tetrahydrofuran (250 cm³) at −76 °C. It distilled at 70—72° and 0·05 mmHg (yield 4·8 g). G.l.c. as before showed that it was almost free of the *cis*-isomer (Found: C, 75·3; H, 6·8. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%). Hydrolysis gave the *trans*-cinnamic acid, m.p. 98—99° (lit.,[4] 98·5°).

cis-β-*Methylcinnamyl Alcohol*.—A solution of methyl *cis*-β-methylcinnamate (5 g) in ether (150 cm³) was added dropwise to a cooled and stirred mixture of lithium aluminium hydride (3·3 g) and aluminium chloride (3·7 g) in ether (50 cm³). After 0·5 h the cis-*alcohol* was recovered and distilled at 66—68° and 0·05 mmHg (Found: C, 81·15; H, 8·25%; $M^+$, 148. $C_{10}H_{12}O_2$ requires C, 81·0; H, 8·2%; *M*, 148); $\tau$ 8·0br (s, =C–$CH_3$), 6·05 (d, *J* 7·0 Hz, $CH_2$), and 4·32br (t, *J* 7·0 Hz, =C–H). The p-*nitrobenzoate* formed prisms in light petroleum, m.p. 78° (Found: C, 68·65; H, 5·3; N, 4·5. $C_{17}H_{15}NO_4$ requires C, 68·7; H, 5·1; N, 4·7%).

trans-β-*Methylcinnamyl Alcohol*.—This was obtained in the same way as the *cis*-isomer from methyl *trans*-β-methylcinnamate. It had b.p. 78—80° at 0·05 mmHg (Found: C, 80·95; H, 8·0%; $M^+$, 148. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%; *M*, 148); $\tau$ 8·05br (s, =C–$CH_3$), 5·7 (d, *J* 8 Hz, $CH_2$), and 4·05br (t, *J* 8 Hz, =C–H). The *p*-nitrobenzoate could not be crystallised.

G.l.c. of the crude products of the reductions (3% SE30 at 137 °C) showed that each isomer had been produced virtually free from the other.

cis- *and* trans-β-*Methylcinnamyl Bromides*.—These were prepared from the corresponding alcohols (6 g) and phosphorus tribromide (4·5 g) in ether (50 cm³) and pyridine (1 cm³) at reflux for 1 h. The cis-*isomer* had b.p. 105—107° at 13 mmHg (yield 4·6 g) (Found: C, 56·7; H, 5·1%; $M^+$, 211. $C_{10}H_{11}Br$ requires C, 56·9; H, 5·2%; *M*, 211); $\tau$ 8·05 (s, =C–$CH_3$), 6·22 (d, *J* 8 Hz, $CH_2$), and 4·28 (t, *J* 8 Hz, =C–H). In this case g.l.c. analysis (3% SE30 at 120 °C) indicated about 7% conversion into the *trans*-bromide.

The trans-*bromide* had b.p. 115—118° at 13 mmHg (yield 4·8 g) (Found: C, 57·8; H, 5·3%; $M^+$, 211); $\tau$ 8·0 (s, =C–$CH_3$), 6·05 (d, *J* 9 Hz, $CH_2$), and 4·05 (t, *J* 9 Hz, =C–H). G.l.c. of the crude product (SE30; 120 °C) showed almost complete absence of the *cis*-isomer.

cis- *and* trans-β-*Methylcinnamyltriphenylphosphonium Salts*.—The bromides described above (5 g) were converted into the triphenylphosphonium salts with triphenylphosphine (9 g) in refluxing benzene. The salt from the *cis*-bromide had m.p. 225—228°, and that from the *trans*-bromide, m.p. 232—233°; a mixture had m.p. 216—225°. The phosphonium bromides were converted into the periodates as described previously.[2]

1,6-*Dimethyl*-1,6-*diphenylhexa*-1,3,5-*triene*.—An ethanolic solution of lithium ethoxide (0·5M; 47 cm³) was added slowly to a refluxing solution of *trans*-β-methylcinnamyltriphenylphosphonium periodate (10·8 g) in ethanol (150 cm³) under nitrogen. The red solution was boiled for 3 h, cooled, filtered, and evaporated to dryness, and the crude product was chromatographed on silica gel. Elution with light petroleum containing increasing proportions of benzene afforded first 2-phenylbut-2-ene and then the hexatriene fraction (1·64 g). Crystallisation from light petroleum–benzene (4 : 1) gave the *all*-trans-*isomer* (0·6 g) as pale yellow flakes, m.p. 170—171° (Found: C, 92·4; H, 7·7%; $M^+$, 260. $C_{20}H_{20}$ requires C, 92·3; H, 7·7%; *M*, 260); $\lambda_{max}$ (cyclohexane) 222, 235, 241, and 347—351 nm (log ε 4·01, 3·91, 3·90, and 4·76). More of this crystalline isomer was obtained from the mother liquors by further chromatography and crystallisation. The remaining material then afforded the trans,cis,trans-*hexatriene*, obtained by preparative layer chromatography as a yellow gum (108 mg), purified by short-path distillation at 240 °C and 0·1 mmHg (Found: C, 92·4; H, 7·8%; $M^+$,

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[15] See, for example, A. Padwa and L. Brodsky, *J. Org. Chem.*, 1974, **39**, 1318; G. Büchi, and H. Wüest, *Helv. Chim. Acta*, 1971, **54**, 1767; F. Bohlmann and Ch. Zdero, *Chem. Ber.*, 1973, **106**, 3799; W. G. Dauben, D. J. Hart, J. Ipaktschi, and A. P. Kozikowski, *Tetrahedron Letters*, 1973, 4425.

260); $\lambda_{max.}$ (cyclohexane) 224, 227sh, 242, 263, and 331 nm (log ε 4·34, 4·30, 4·08, 4·03, and 4·55).

*Wittig Reaction of Cinnamylidenetriphenylphosphorane and Benzylideneacetone*.—(*a*) n-Butyl-lithium in ether (5 cm$^3$; 2·40 mol dm$^{-3}$) was added carefully to a suspension of cinnamyltriphenylphosphonium bromide (5·60 g) in ether (100 cm$^3$) under nitrogen, and the mixture was stirred for 1 h. Benzylideneacetone (1·84 g) in ether (50 cm$^3$) was added dropwise and the mixture was stirred overnight at room temperature and at reflux for a further 2 h. Solvent was evaporated off and the residual oil chromatographed on alumina. Elution with toluene–light petroleum (1 : 5) gave a yellow oil (965 mg) and then 3-methyl-1,6-diphenylhexa-1,3,5-triene as yellow needles, m.p. 130° (from methanol) (lit.,[16] 130—131°) (Found: $M^+$, 246. Calc. for $C_{19}H_{18}$: $M$, 246); $\lambda_{max.}$ 241, 248·5infl, 260·5, 269, 323infl, 340, 355, and 372 nm (log ε 4·06, 4·04, 4·04, 4·02, 4·38, 4·57, 4·63, and 4·46). Rechromatography of the first eluate on alumina gave a colourless oil, b.p. 180—200° at 0·01 mmHg (Found: C, 93·2; H, 7·0%; $M^+$, 246. Calc. for $C_{19}H_{18}$: C, 92·6; H, 7·4%; $M$, 246); $\lambda_{max.}$ 230, 309·5, and 334 nm (log ε 4·00, 3·81, and 3·54). It was difficult to decide whether this product was pure. G.l.c. (3% SE30 at various temperatures) showed only one peak, but the n.m.r. spectrum was complex and could not be interpreted beyond showing that the product contained aromatic, aliphatic, and olefinic protons: $\tau$ 2·82 (15H, m), 3·38 (1H, d), 4·10 (1H, m), 6·06 (1H, dd), 7·12 (1H, m), 7·60 (2H, s), 7·73 (1H, dd), and 8·28 (3H, s). However, the olefinic double bond(s) could not be reduced catalytically (10% palladium–charcoal and hydrogen for 16 h) and the substance could not be dehydrogenated with dichlorodicyanobenzoquinone in boiling toluene or with 10% palladium–charcoal in boiling ψ-cumene.

(*b*) A solution prepared from lithium (135 mg) and ethanol (60 cm$^3$) was added dropwise to a stirred solution of cinnamyltriphenylphosphonium bromide (8·8 g) and benzylideneacetone (2·8 g) in ethanol (110 cm$^3$). The solution was stirred at 45—50 °C for 4 h, then evaporated, and the residue was chromatographed on alumina. Elution with benzene–light petroleum (1 : 4) gave an oil (616 mg) identical with that obtained in experiment (*a*) and then 3-methyl-1,4-diphenylbenzene (260 mg) as needles, m.p. 90 or 97—98° (*cf.* ref. 17), not depressed when mixed with a specimen synthesised as described below.

3-*Methyl*-1,4-*diphenylbenzene*.—A mixture of 2,5-diphenylcyclohex-3-enecarboxylic acid[18] (1·4 g) and sulphur (160 mg) was heated at 180—200 °C for 3 h. Crystallisation of the recovered acidic material from chloroform gave 2,5-diphenylbenzoic acid (0·59 g), m.p. 178° (lit.,[19] 177—179°). Reduction of the methyl ester with lithium aluminium hydride (160 mg) in boiling tetrahydrofuran gave 2,5-*diphenylbenzyl alcohol* (120 mg) as fine needles, m.p. 100—101° (Found: C, 87·9; H, 6·3%; $M^+$, 260. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%; $M$, 260). Reduction of this alcohol (105 mg) with hydrogen and 10% palladium–charcoal (100 mg) in ethanol (20 cm$^3$) containing hydrochloric acid (1 cm$^3$) gave 3-methyl-1,4-diphenylbenzene as prismatic needles from methanol, m.p. 89—90 or 97—98° (lit.,[17] 90 or 98°) (Found: C, 93·2; H, 6·6%; $M^+$, 244. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%; $M$, 244); $\lambda_{max.}$ 264 nm (log ε 4·36).

*Irradiation Experiments*.—The general conditions were as described in ref. 1*b*.

Irradiation of 1,6-dimethyl-1,6-diphenylhexa-1,3,5-triene for 12 h in benzene gave 6,12-dimethylchrysene in 20% yield after purification by chromatography and crystallisation; m.p. 239° (lit.,[20] 237°). The *sym*-trinitrobenzene complex formed orange-red needles in benzene, m.p. 223—224° (lit.,[20] 222°). A cleaner product was obtained if this cyclisation was effected in air, without iodine.

With 1,3,6-triphenylhexa-1,3,5-triene reaction was complete within 1 h (u.v.). G.l.c. of the crude material showed only one significant product. Chromatography and crystallisation from methanol gave fine needles (1,2,4-triphenylbenzene), m.p. 99—100° (60%) (lit.,[21] 100°) (Found: $M^+$, 306·1407. Calc. for $C_{24}H_{18}$: $M$, 306·1409); $\lambda_{max.}$ (cyclohexane) 248 and 270infl nm (log ε 4·52 and 4·38); $\tau$ 2·3—2·8 (complex m). The product was inert to ozone and diborane and was unaffected by permanganate–periodate reagent.[22] Repetition of the experiment under non-oxidative conditions (absence of iodine, degassed solution, nitrogen atmosphere) for 1 or 24 h in benzene or cyclohexane gave an oil from which no pure product could be isolated. The n.m.r. spectrum was complex and g.l.c. showed that the material contained at least four main products.

Irradiation of 3-methyl-1,6-diphenylhexatriene in benzene was discontinued after 3 h. Much polymeric material was produced, and preparative layer chromatography gave chrysene (4·2%) as the only isolable product

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[16] B. M. Michailov and L. S. Povarov, *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.*, 1959, 1859.

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