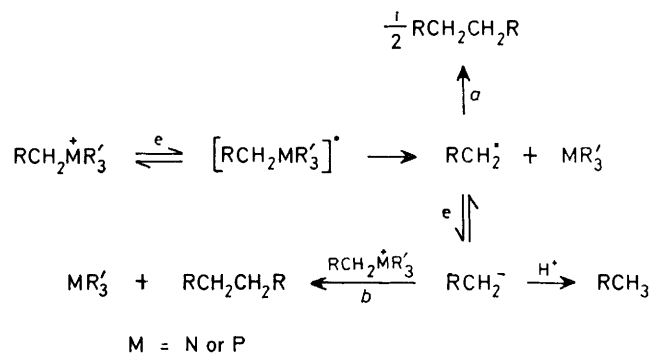# Electro-organic Reactions. Part 16.† The Preparative-scale Cathodic Hydrogenolysis and Coupling of Benzyl-, Allyl-, Cinnamyl-, and Polyenyl-phosphonium Salts

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An investigation of the cathodic reduction of benzyltriphenylphosphonium nitrate confirms that optimum yields of the product of coupling (bibenzyl) are formed at an aluminium cathode using high current densities and in dimethyl-formamide or hexamethylphosphoramide solution. The cathodic reduction of allylphosphonium salts gives mainly cleavage; e.g. α-farnesene (5) is obtained in 32% yield from the corresponding farnesylphosphonium salt. Moderately efficient coupling (ca. 30%) is observed for the electro-reduction of trans-cinnamyltriphenylphosphonium nitrate (6) and a C_{15} polyenylphosphonium salt (7). The products of coupling have been fully characterised; the relative proportions of positional isomers are apparently dictated by steric factors.

THE electro-reduction of 'onium salts has been much studied,[1] particularly from a mechanistic viewpoint. It is usually found that hydrogenolysis competes with coupling; this is consistent with either of the routes depicted in the Scheme. It is generally assumed that the coupling reaction occurs via radical combination (Scheme, route a); experiments [2] using (+)-α-phenyl-ethyltrimethylammonium nitrate gave a coupled product which was racemic. Nucleophilic displacement would have resulted in inversion at one of the chiral centres.

$$\tfrac{1}{2}RCH_2CH_2R$$

$$\uparrow a$$

$$RCH_2\overset{+}{M}R'_3 \underset{\longleftarrow}{\overset{e}{\longrightarrow}} \left[RCH_2MR'_3\right]^{\cdot} \longrightarrow RCH_2^{\cdot} + MR'_3$$

$$e \Big\Updownarrow$$

$$MR'_3 + RCH_2CH_2R \overset{RCH_2\overset{+}{M}R'_3}{\underset{b}{\longleftarrow}} RCH_2^- \overset{H^{\cdot}}{\longrightarrow} RCH_3$$

$$M = N \text{ or } P$$

SCHEME

In addition it was found [3] that for the reduction of benzyltriethylammonium nitrate in NN-dimethylform-amide (DMF) both bibenzyl and toluene were formed; in the presence of carbon dioxide phenylacetic acid was produced entirely at the expense of the toluene, i.e. toluene and phenylacetic acid arose via quenching of the benzyl carbanion whereas bibenzyl arose via combination of benzyl radicals. In the course of several investigations [3b,4,5] it has been found that the relative yields of hydrogenolysis and coupling products are markedly dependent on solvent (protic solvents favour hydrogenolysis) and cathode material (aluminium and magnesium particularly favour coupling).

Finkelstein [6] isolated a 31% yield of bibenzyl as a product of cathodic reduction of benzyltriphenylphos-phonium nitrate in DMF at an aluminium cathode. Savéant and his co-workers [7] found that, in rigorously

† Part 15, C. Adams, N. M. Kamkar, and J. H. P. Utley, *J.C.S. Perkin II,* 1979, 1767.

dried DMF and at a mercury cathode, up to 92% coupling could be observed for reduction of the cumyltri-phenylphosphonium ion. No other cases of even moderately efficient coupling from phosphonium salts have been reported and it is only by analogy with the reactions of the ammonium salts that coupling is believed to involve radicals. There are good reasons for supposing the nucleophilic displacement mechanism to be unimportant for phosphonium salts; a carbanion is more likely to abstract a proton to give ylide formation and there is evidence [8] to suggest that phosphines are poorer leaving groups than the corresponding amines.

Surprisingly, no significant coupling has been observed as a result of electro-reduction of allyl substituted 'onium salts; Ross and his co-workers [3] obtained bicinnamyl in 6% yield from cinnamyldimethylanilinium nitrate by reduction at an aluminium cathode and in DMF solution.

In the above context, and because of the importance of synthetic methods for the extension of polyene chains and the ready accessibility of polyene-substituted phosphonium salts, an investigation of their cathodic reduction was undertaken.

RESULTS AND DISCUSSION

General Conditions for Electrolyses and a Comparison of Ammonium with Phosphonium Salts.—Electrochemical dimerisations, because they are bimolecular, are generally favoured by high current densities and previous work suggests for 'onium salt electrolysis the use of an aluminium cathode and DMF electrolyte. Consequently initial experiments employed such conditions aided by the use of an undivided cell (to allow the achievement of high current densities) and nitrate salts (which allow greater solubility of the phosphonium salts).

The starting point in this study was to compare the likely usefulness of phosphonium vis à vis ammonium salts and to ascertain whether any advantage could be gained from electrolysis at controlled potential. The benzyl 'onium salts reduce at large negative potentials (ca. −2.0 V versus s.c.e.) and consequently the phos-phonium salt (3), activated by methoxycarbonyl substitution, was used for controlled potential electroly-

sis. The results of these experiments are contained in Table 1. Under comparable electrolysis conditions the dimer (bibenzyl) is produced more efficiently from the phosphonium salt (2) then from the ammonium salt (1). For the phosphonium salt (3) it appears that forced electrolysis at high current density favours dimer formation; at controlled potential, and consequently at lower current density, no dimer could be detected in the product mixture. In the light of these results optimum

there is such a marked dependence argues against reduction by the prior generation of solvated electrons.

Although several of the cathodes which promote dimer formation are known to be coated with oxide layers (Al, Mg, Ni, or Ti) it is noteworthy that significant amounts of bibenzyl are formed at the relatively ' clean ' vitreous carbon and smooth platinum cathodes. The role of oxide films in encouraging dimer formation, although long suspected, has never adequately been

TABLE 1

Comparable electrolyses of substrates (1)—(3)

Compound	Conditions [a]	Major products (% yield)
$\overset{+}{PhCH_2NEt_3}Cl^-$ (1)	0.1M; i_0 0.076 A cm^{-2}; 2.8 F mol^{-1}	Bibenzyl [b] (20)
$\overset{+}{PhCH_2PPh_3}NO_3^-$ (2)	0.04M; i_0 0.031 A cm^{-2}; 2.1 F mol^{-1}	Bibenzyl [b] (63) Ph$_3$P (15);[d] Ph$_3$PO (23) [d]
p-MeO$_2$CC$_6$H$_4$CH$_2\overset{+}{PPh_3}$NO$_3^-$ (3) ($ArCH_2\overset{+}{PPh_3}$NO$_3^-$)	0.29M; i_0 0.10 A cm^{-2}; 2.3 F mol^{-1}	(ArCH$_2$)$_2$ [d] (4) (35); Ph$_3$PO [d] (44) ArCH$_3$ [d] (21)
p-MeO$_2$CC$_6$H$_4$CH$_2\overset{+}{PPh_3}$NO$_3^-$ (3) ($ArCH_2\overset{+}{PPh_3}$NO$_3^-$)	0.1M; i_0 0.0025 A cm^{-2} −1.2 V;[c] 8 F mol^{-1}	ArCH$_3$ [e] (81) [no (ArCH$_2$)$_2$ detected]

[a] Aluminium cathode, DMF solution.   [b] G.l.c. analysis with respect to internal standard.   [c] versus Ag–AgI.   [d] Isolated yield.
[e] Analysis by ^{1}H n.m.r.

conditions for the production of bibenzyl from benzyltriphenylphosphonium nitrate were established.

As a consequence of the use of undivided cells the triphenylphosphine produced is substantially converted into triphenylphosphine oxide at the anode. It was found convenient during work-up to treat the product mixture with methyl iodide thus converting the remaining triphenylphosphine into the easily removed methyltriphenylphosphonium iodide.

Product Dependence on Cathode Material, Current Density, and Solvent ; Electrolysis of Benzyltriphenylphosphonium Nitrate.—Benzyltriphenylphosphonium nitrate (2) was electro-reduced under a variety of conditions and the relative yields of bibenzyl and toluene measured. The results are conveniently summarised in Tables 2—4. In DMF solution and at similar current densities the important dependence on cathode material is confirmed and amplified (Table 2). The fact that

TABLE 2

Reduction of $PhCH_2\overset{+}{PPh_3}NO_3^-$ (2) at various cathodes [a]

Cathode [b]	Initial current/ A cm^{-2}	Charge/ F mol^{-1}	Bibenzyl [c] (%)
Al	0.70	2.3	56
Mg	0.69	11.3	43
Ni	0.83	10.1	37
C [d]	0.65	7.3	37
Ti	0.63	7.1	32
Pt	0.78	15.3	28
Cu	0.50	8.4	27
Zn	0.84	6.5	19
Pb	0.73	13.0	17
Ag [e]	0.72	11.3	12
Hg [f]	1.1	4.4	6

[a] Substrate 0.12—0.15M in DMF, undivided cell, cell voltage 80—85.   [b] Usually 1 cm², see Experimental section for details.   [c] G.l.c. analysis with respect to an internal standard (the other major product was invariably toluene but could not be accurately measured due to losses during electrolysis, see Experimental section).   [d] Vitreous carbon.   [e] Porous gauze.   [f] Unstirred pool (0.8 cm²).

established; an early hypothesis that coupling is enhanced by high current densities pertaining at holes in the oxide film would seem to be disproved by Finkelstein's results [3c] with anodised aluminium cathodes

TABLE 3

Effect of current density; reduction [a] of

$$PhCH_2\overset{+}{PPh_3}NO_3^- \text{ (2)}$$

Concentration/ M	Cell voltage	Initial current density/ A cm^{-2}	Charge/ F mol^{-1}	Bibenzyl [b] (%)
0.023	80—85	0.14	3.3	41
0.040	80—85	0.19	3.1	40
0.080	80—85	0.35	2.5	51
0.150	80—85	0.70	2.3	56
0.150	42	0.28	2.5	35
0.150	20 (−3.0) [c]	0.15	3.0	30
0.150	10	0.04	2.4	26
0.150	(−1.5) [c]	0.01	4.0	6

[a] Aluminium cathode, DMF solution.   [b] G.l.c. analysis with respect to an internal standard (see footnote c in Table 2).   [c] versus Ag–AgI.

(electron micrographs of such surfaces shows them to be uniform [9] and amorphous).

The variation of relative yields with current density is, for reaction at an aluminium cathode, as expected (Table 3); the current density may be varied by controlling either the cell voltage or concentration of substrate and in each case dimer formation is favoured by high current densities.

A significant solvent effect was found which, to some extent, may over-ride the current-density effect Table 4). In particular dimer formation in hexamethylphosphoramide (HMPA) is surprisingly efficient in view of the low current density employed, and, although a high current density was sustained in acetonitrile solution, relatively little dimer was formed. An important advantage of

HMPA is that reactions may be run at lower temperatures than with DMF or acetonitrile.

<div style="text-align:center">TABLE 4</div>

Reduction of $PhCH_2\overset{+}{P}Ph_3NO_3^-$ (2) in various solvents [a]

| Solvent	Initial current density/ A cm^{-2}	Charge/ F mol^{-1}	Bibenzyl (%)
Dimethylformamide	0.70	2.3	56
Hexamethylphosphoramide [b]	0.09	3.1	49
Acetonitrile	0.90	2.4	11
Propylene carbonate	0.25	2.0	20

[a] Aluminium cathode, substrate 0.12—0.14M, undivided cell, cell voltage 80—85 V. [b] Substrate dissolved as electrolysis proceeded.

Coupling at Allylic Positions: Reduction of Allyltriphenylphosphonium Bromide and Farnesyltriphenylphosphonium Bromide (4).—The likely products of reduction of the allyltriphenylphosphonium ion include biallyl, propene, and propane, all of which are volatile. Because electrolysis at high current density in DMF, even in a water-jacketted cell, results in relatively high electrolyte temperatures (*ca.* 60—80°), runs in which biallyl (b.p. 59.5°) might be formed were carried out using HMPA. The crude product of electrolysis to 1.6 F mol^{-1} at an aluminium cathode and at an initial current density of 0.140 A cm^{-2}, was carefully examined by g.l.c. and, by peak-matching with an authentic sample, was found to contain only a trace of biallyl. That allyl systems do not readily couple in these circumstances was confirmed by the results of cathodic reduction of farnesyltriphenylphosphonium bromide (4) at aluminium in DMF solution. The dimer (squalene) is involatile and would be readily detected. T.l.c. separation of the products showed that squalene was not formed in detectable amounts and that the major non-phosphorus containing product was that of cleavage, *i.e.* α-farnesene (5) (32% isolated yield, characterised by its ^1H n.m.r. spectrum and mass spectrometry).
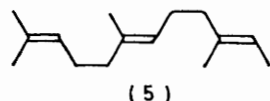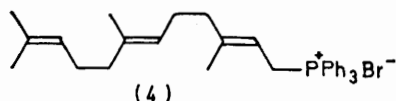

(4)

(5)

Reduction of trans-*Cinnamyltriphenylphosphonium Nitrate* (6) *and* 3-*Methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-dienyltriphenylphosphonium Chloride* (7).—The stability of an intermediate allyl radical should be greatly increased by phenyl substitution and extension of conjugation. Such increased stability and presumably increased lifetime of the radical might be expected to increase the probability of dimerisation. Consequently *trans*-cinnamyltriphenylphosphonium nitrate (6) and 3-methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-

dienyltriphenylphosphonium chloride (7) were reduced in DMF or HMPA solution at aluminium cathodes and the products carefully analysed and characterised.

(6)

(7)
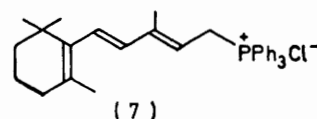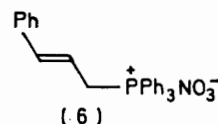
Electrolysis of (6) and separation of the products by t.l.c. gave, in addition to triphenylphosphine and triphenylphosphine oxide, a non-polar oily solid which completely solidified at 0°. This proved to be a mixture of the bicinnamyl isomers (8) and (9) and was formed in a total yield of 28%; electrolysis using HMPA gave the same mixture in 30% yield. The details of analyses and characterisation of the products are given in the Experimental section. The relative proportions of isomers (8) and (9) were, by g.l.c. analysis, 1.1 to 1. They were


(8)   (9)

(10)
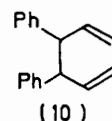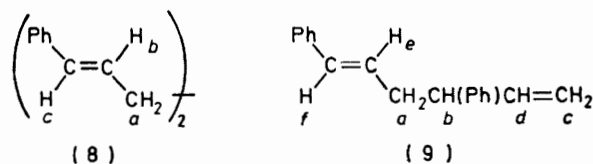
isolated by preparative g.l.c. and separately characterised. It is noteworthy that the third possible isomer, 3,4-diphenylhexa-1,5-diene (10), was not detected. Thermal rearrangement of (10) to (8) has been reported [10] so especial care was taken to check that the product ratios determined by g.l.c. were independent of injector and column temperature. In addition the 90.52-MHz ^{13}C n.m.r. spectrum of the crude product was essentially the sum of the spectra of the separated isomers; specifically, signals were observed for only one terminal methylene (δ 114.7 p.p.m.), two allylic CH$_2$ (δ 33.0 and 39.1 p.p.m.), and one allylic CH (δ 50.1 p.p.m.) functions. Electrolysis in HMPA proceeds at about room temperature and the half-lives [10] of the stereoisomers of (10) are 15 h at 120° (*meso*) and 8 h at 80° ($\pm$). It must be concluded, therefore, that the 3,4-coupled product (10) is not formed.

Furthermore, no evidence for *cis* isomers was found although *cis,cis-*, *cis,trans-*, and *trans,trans*-bicinnamyl have been [10] separated by g.l.c. under similar conditions to those used in this work; the n.m.r. and i.r. spectra would also have indicated any *cis*-isomer, if present. The overall reaction is most probably therefore under

thermodynamic control. This point needs testing rigorously by examining the products of electro-reduction of the cis-cinnamyltriphenylphosphonium ion. However, the synthesis of starting materials is likely to be difficult, e.g. the preparation of cis-cinnamyl halides, from which the phosphonium salt would be prepared, has not been reported.

Cathodic reduction of the trienylphosphonium salt (7) proceeded in HMPA solution to 2.2 F mol^{-1}. The non-polar organic products were separated by preparative scale t.l.c. and identified as the product of hydrogenolysis [(11) isolated in 25% yield], and the previously unreported dimers (12) and (13), isolated in 11 and 6% yields, respectively. A considerable organic residue remained at the baseline of the t.l.c. plates; such losses probably arise from anodic degradation of polyene products. Compounds (11)—(13) were characterised by mass spectrometry and their ^{13}C and ^{1}H n.m.r. spectra (see Experimental section).*

(11)

(12)

(13)
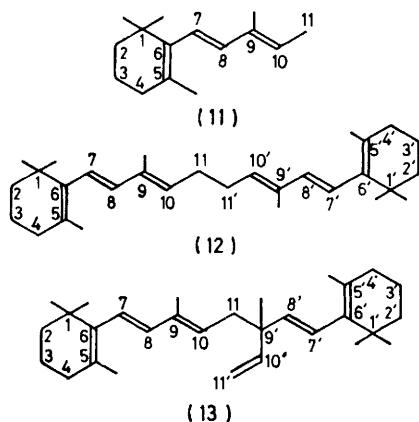
The mode of coupling appears to be analogous to that of the cinnamyl radical; trans-isomers only are formed and the dimer resulting from symmetrical coupling at C-9 is absent. An additional possibility for this system is combination involving bond formation at C-5 and C-7. This is presumably precluded by steric hindrance. There is a good precedent for such hindrance; hydrodimerisation of α- and β-ionone occurs solely [11] at, in those cases, the unhindered carbonyl carbon.

Conclusions.—The results give modest encouragement that the reactions could be developed usefully for polyene synthesis. Reductive coupling is favoured by forcing electrochemical conditions but the reactions may be run under mild chemical conditions. Cells of simple construction may be used and the electrodes (aluminium) are cheap and easily fabricated. Potential control is not necessary, or even desirable, and the electrolyses were performed using a simple direct-current power supply. The yields of dimers, albeit modest, must be judged in the light of the paucity of alternative routes.

The selectivity for dimerisation depends upon steric factors, probably in a predictable fashion. The trans-

* Carotenoid numbering is used for formulae (11)—(13) and in Tables 5 and 6 and associated text.

allylic radicals, at least, are configurationally stable in the conditions used.

EXPERIMENTAL

Solvents and Materials.—NN-Dimethylformamide (DMF) was purified by Thomas and Rochow's method [12] and stored under nitrogen and over freshly activated molecular sieves (4 A). Acetonitrile (Aldrich; 99%) was mixed with dichloromethane (500 cm^3 l^{-1}) and fractionally distilled through an efficient column; the acetonitrile fraction, collected after dichloromethane and the dichloromethane–water azeotrope, was stored over molecular sieves (4 A). Propylene carbonate (B.D.H.; 99%) and hexamethylphosphoramide (HMPA) (B.D.H.; 99%) were both purified by double fractional distillation under reduced pressure and stored as for acetonitrile and DMF.

Electrode materials were as follows: aluminium (0.1 mm sheet; Hopkins and Williams G.P.R.; ⩾99.9%); magnesium (0.4 mm; Magnesium Elektron Ltd.); nickel (0.15 mm; B.D.H., ⩾99.9%); titanium (0.8 mm thick); copper (0.2 mm; Hopkins and Williams; AnalaR; >99.9%); platinum (0.025 mm; B.D.H.; >99.9%); zinc (0.38 mm; Hopkins and Williams); lead (0.45 mm); silver (porous grid; Chloride Technical Ltd.); vitreous carbon (rod; 6 mm diameter; Le Carbone Ltd.).

The ammonium salts were prepared by standard literature methods. Phosphonium salts were prepared by heating triphenylphosphine and the appropriate halide under reflux in xylene, benzene, or acetone. The nitrates were obtained by mixing together aqueous ethanolic solutions of phosphonium halide and silver nitrate. Removal of precipitated silver halide and concentration of the filtrate gave the phosphonium nitrate, generally in 80—90% yield after recrystallisation from ethanol–ether. All salts were dried at 100° under reduced pressure (0.02—0.1 mmHg) over phosphorus pentaoxide for 24 h prior to storage in a vacuum desiccator. Two of the halide starting materials were not obtained by standard methods. 3-Methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-dienyltriphenylphosphonium chloride (7) was donated by Roche Products Ltd. and used as received and farnesyltriphenylphosphonium bromide (4) was kindly supplied by Drs. G. P. Moss and J. Wenger (Q.M.C.).

Electrochemical Apparatus.—A Chemical Electronics TR 70/2A potentiostat was used for controlled potential electrolyses. Experiments at constant cell voltage, or constant current, employed a 'home-built' direct-current power supply capable of delivering 250 V at 1 A. The amount of charge passed was determined using either a Chemical Electronics current integrator or a similar device constructed by Mr. B. Cook of the Q.M.C. electronics workshop. Cells were essentially water-jacketted beakers with provison for parallel plate electrodes, magnetic stirring, and a nitrogen bubbler. When necessary the potential at one of the electrodes could be controlled against a reference electrode contained in a Pyrex tube sealed at one end with a sintered plug positioned adjacent to the electrode concerned. For experiments comparing electrode materials a cathode holder was made which held a 1-cm^2 portion of metal foil clamped in a polytrifluoroethylene frame.

Electrolyses.—Benzyltriphenylphosphonium nitrate (2). Typically the phosphonium salt (0.2—1.2 g depending on the concentration required) was dissolved in dry DMF (15—20 cm^3) in an undivided cell. The electrode (Pt foil anode

and, *e.g.*, aluminium cathode, both 1 cm²) were usually at 15 mm separation. The electrolyte was stirred by magnetic follower and nitrogen was bubbled through the electrolyte during electrolysis. At *ca.* 0.15M concentration of phosphonium salt, in DMF, electrolysis proceeds at initial current densities of 0.7 A cm⁻² at a cell voltage of 85 V. After the consumption of 2—2.5 F mol⁻¹ a small portion of the electrolyte was tested by t.l.c. [silica, EtOAc–HCO₂H (88 : 2 : 10)] to confirm that little or no starting material remained. With some cathode materials this stage was only reached after further electrolysis.

The electrolyte was poured into a saturated salt solution (50 cm³) and shaken with ether (3 × 25 cm³). The combined ethereal extracts were washed with water (2 × 50 cm³) and dried (MgSO₄). The solution was carefully concentrated to *ca.* 10 cm³ and the residue analysed by g.l.c. with methyl *p*-toluate as internal standard [Perkin-Elmer F11, 8% Antarox CO990 column; or Hewlett-Packard 5830A, 5% OV17 (silicone gum rubber)]. Bibenzyl could be isolated by hydrolysis of the internal standard followed by ether extraction. The relatively high temperatures reached during electrolysis (up to 80°) resulted in loss of toluene. In a control experiment, in which known weights of bibenzyl and toluene dissolved in DMF were heated in a cell to 60° for 1.5 h, with nitrogen bubbling, it was shown that the analytical procedure accounted for 96% of the bibenzyl but only 26% of the toluene.

When propylene carbonate was used as solvent it interfered with the g.l.c. analysis; consequently the initially obtained ether extract was stirred with aqueous concentrated sodium hydroxide for *ca.* 6 h. Subsequent washing and drying of the ether layer gave a product mixture free of residual propylene carbonate.

p-Methoxycarbonylbenzyltriphenylphosphonium nitrate (3). Compound (3) (2.715 g, 0.006 mol) was reduced in DMF using an aluminium foil cathode as described for reduction of the benzyl derivatives. The current fell from 950 to 570 mA, whereupon the reaction was stopped; 2.3 F mol⁻¹ has been passed. The mixture was extracted with ether in the usual way, dried (MgSO₄), and the solvent removed by evaporation. The residue (2.043 1 g) was separated on two 40 × 40 cm silica t.l.c. plates by twice running the system in a 15 : 85 mixture of acetone–light petroleum (b.p. 80—100 °C). This gave four bands: (1) (baseline), triphenylphosphine oxide (44%) and traces of the dimer (4,4'-bismethoxycarbonylbibenzyl); (2) the dimer in 35% yield (0.299 7 g), recrystallised from methanol as needles (0.209 3 g, 25%), m.p. 119—120° (lit.,[13] 119°), ν(CHCl₃) 1 715s (aryl ester C=O), 1 610m (aryl C=C), 1 435m (CH₂ scissor), 1 285s and 1 115s cm⁻¹ (aryl ester C–O); δ(CDCl₃) 2.94 (4 H, s, CH₂CH₂), 3.85 (6 H, s, CO₂CH₃), and 7.10, 7.18, 7.87, and 7.95 (8 H, m, ArH), λ$_{max.}$ (95% EtOH) 243 nm, *m/e* 298 (34%, *M*⁺), 267 (21, *M* − CH₃O), 239 (12, *M* − CH₃·CO₂), 149 (100, symmetrical cleavage); (3) methyl *p*-toluate (0.114 2 g, 13%); and (4) methyl *p*-toluate containing a little triphenylphosphine (this additional 8% of methyl *p*-toluate brings the total isolated yield to 21%).

Electrolysis of (3) *at constant potential.* The phosphonium salt (1.956 3 g) was reduced at −1.2 V *versus* Ag–AgI in DMF (*ca.* 40 cm³) at an aluminium cathode (area 9.6 cm²). At various times during the electrolysis, samples were removed (two samples of 15 cm³ leaving a final portion of 11 cm³). Each of the three portions was extracted with ether, washed, and dried in the usual way. After evaporation of the ether, a weighed amount of dibenzyl ether was

added to each sample and the mixture analysed by ¹H n.m.r. Comparison of the areas of the peaks corresponding to the dibenzyl ether and methyl *p*-toluate showed that the samples contained the following amounts of methyl *p*-toluate: 0.134 6 g (at 1.6 F mol⁻¹), 0.179 1 g (2.4), and 0.189 6 g (8.4). The total, 0.503 3 g, corresponds to an overall yield of 81%. In the ¹H n.m.r. spectrum of the crude product there were no signals at δ 2.94 due to the dimer.

Allyltriphenylphosphonium nitrate. This compound (0.755 6 g, 0.002 mol) was reduced at a cell voltage of 85 V using an aluminium cathode in HMPA (*ca.* 40 cm³). The disappearance of the substrate was demonstrated by analytical t.l.c. and the current had fallen from 0.14 to 0.04 A cm⁻² when the reaction was stopped at 1.6 F mol⁻¹. The electrolyte was then poured into water and extracted with ether. The ether extracts were combined, washed with water, dried (MgSO₄), and concentrated by distillation through an efficient fractionating column. Examination by g.l.c. at 30 °C (Perkin-Elmer F11; 15% Apiezon L) and comparison with an authentic sample of biallyl showed that only traces of biallyl were present.

Farnesyltriphenylphosphonium bromide (4). Compound (4) (0.427 1 g, 0.000 8 mol) was reduced in DMF at a cell voltage of 85 V using aluminium foil cathode. When 2.5 F mol⁻¹ had passed, the current had fallen from 0.23 to 0.08 A cm⁻². The electrolyte was poured into saturated salt solution (100 cm³) and extracted with ether (3 × 50 cm³). The combined ethereal extracts were washed with water (50 cm³) and methyl iodide (5 cm³) was added. After a further washing with water, the ether extract was dried (MgSO₄) and evaporation gave a green semi-solid residue (0.363 5 g). T.l.c. on a 40 × 40 cm silica plate using carbon tetrachloride gave two bands (including the baseline). The baseline fraction proved to consist mainly of triphenylphosphine oxide. The other band did not run with an authentic sample of squalene but gave an n.m.r. spectrum that could be due to either α-farnesene or squalene. Mass spectrometry showed the fraction to be α-farnesene (5) (51.9 mg, 32%), δ (CDCl₃) 5.11br (s), 2.05 (s), 1.70 (s), and 1.62 (s) [lit. values for squalene,[14] δ 5.09br (6 H), 2.00 (s, 5 × CH₂CH₂), and 1.60 (s, 8 × CH₃)], *m/e* 206 (13%, *M*⁺), 137 (19, *M* − C₅H₉), and 69 (100, *M* − C₁₀H₁₇).

trans-Cinnamyltriphenylphosphonium nitrate (6). Compound (6) was electrolysed in both HMPA and DMF solution and similar results were obtained. Typically after extraction with ether, washing, and drying, the residue was separated on a silica column using carbon tetrachloride as the eluant. This gave a yellow semi-solid product (31% yield based on C₁₈H₁₈). Examination of this by g.l.c. showed two major peaks (Perkin-Elmer F11; 5% silicone gum rubber). G.l.c.–m.s. (F11 interfaced with an A.E.I. MS 12) indicated that both peaks were due to isomers of bicinnamyl (each gave peaks at *m/e* 234 and 117).

A sample of the mixture was separated on preparative scale g.l.c. (Varian Aerograph 90-P; 5% silicone gum rubber; 210°) and three fractions were collected. The third fraction was a solid at room temperature (41.3 mg). The second (22.1 mg) and first (38.5 mg) peaks were oils. Each sample was examined by analytical g.l.c. The first and third fractions each gave only one peak, whereas the second was a mixture of all three peaks, the relative areas being 0.41 : 1.00 : 0.32 in order of increasing retention times. Note that the ratio of the weights of the isolated first and third fractions is 1.00 : 1.07.

Fractions 1 and 3 were then examined by 270-MHz ¹H

n.m.r. with spin-decoupling, and ^{13}C n.m.r. Detailed assignments are discussed below but are taken to characterise fraction 1 as *trans*-1,4-diphenylhexa-1,5-diene (9) and fraction 3 as *trans,trans*-bicinnamyl (8), m.p. 74—78 °C (lit. [10] 81—82 °C).

Solution i.r. and u.v. spectra of fractions 1 and 3 were obtained: fraction 1 ν(CHCl$_3$) 2 920s and 1 445m (CH$_2$), 1 600m and 1 490m (aryl C=C), 960s (*trans*-RCH=CHR), and 910s cm^{-1} (RCH=CH$_2$), $\lambda_{max.}$ 252 (ε 18 100), 284, and 293 nm; [lit.,[10] 252 (ε 18 600), 283, and 294 nm]; fraction 3, ν(CHCl$_3$) 2 920s and 1 445m (CH$_2$), 1 600m and 1 495m (aryl C=C), 960s (*trans*-RCH=CHR), and 690s cm^{-1} (Ph–C), $\lambda_{max.}$ 256 (ε 34 700), 284, and 293 nm [lit.,[10,15] ν(CCl$_4$) 965s and 690s cm^{-1}, $\lambda_{max.}$ 258 (ε 32 700), 293, and 294 nm].

High-resolution m.s. of each sample gave a molecular ion consistent with the formula C$_{18}$H$_{18}$ (Found: for fraction 1, M, 234.140 4. Found: for fraction 3, 234.141 1. Calc. for C$_{18}$H$_{18}$: M, 234.140 85). Mass spectrometric fragmentation was similar for both isomers with prominent peaks at m/e 117 (100%) and 91 (*ca.* 20).

N.m.r. spectra were recorded on a 100-MHz Varian HA-100 spectrometer or, for ^{1}H decoupling experiments, on a 270-MHz Bruker W-H-270 instrument. ^{13}C N.m.r. spectra were recorded on a 90.5-MHz Bruker W-H-360 spectrometer. The identification of the products of electrolysis of *trans*-cinnamyltriphenylphosphonium nitrate (6) is confirmed by the n.m.r. spectroscopic data given below. The ^{13}C n.m.r. spectrum of the fraction identified as *trans*-1,4-diphenylhexa-1,5-diene (9) showed two aliphatic signals, one due to a CH$_2$ group (δ 49.9 p.p.m.), the other to a terminal =CH$_2$ group (δ 114.5 p.p.m.).

Chemical shifts from the 100-MHz ^{1}H n.m.r. spectra are as follows: *trans*-1,4-diphenylhexa-1,5-diene (9), δ (CDCl$_3$) 2.66 (2 H, t, CH$_2$), 3.45 (1 H, m, C*H*Ph), 4.95—5.2 (2 H, m, =CH$_2$), 5.85—6.5 (3 H, m, CH=CH and C*H*=CH$_2$), and 7.26 (10 H, s, Ar-H); *trans,trans*-bicinnamyl (8), δ (CDCl$_3$) 2.39 (4 H, t, CH$_2$CH$_2$), 6.2—6.55 (4 H, m, 2 × CH=CH), and 7.0—7.4 (10 H, m, Ar-H).

Spin-decoupling experiments at 270 MHz allowed unambiguous assignment of the signals and affirmed the distinction between the isomers made by the ^{13}C n.m.r. measurements. Irradiation at the allylic proton resonances gave for *trans,trans*-bicinnamyl (8) a simple doublet for each of the vinylic proton signals with J 15.8 Hz. The value of the coupling constant confirms the *trans,trans*-stereochemistry. For *trans*-1,4-diphenylhexa-1,5-diene (9) irradiation at the allylic CH$_2$ [labelled a in formula (9)] simplified the signal for proton e into a doublet (J_{ef} 15.7 Hz) which confirmed the *trans*-stereochemistry. The signal for b was also simplified whereas those for c, d, and f were unchanged. Irradiation at the frequency corresponding to the signal for proton b resulted in simplification of the signals at a and d with no effect on those at c, e, or f. Decoupling at c had no effect on signals for a, b, e, or f, but substantially simplified the signal at d. Coupling constants may be measured from the simplified spectra and are J_{ae} 7.1, J_{ab} 7.1, J_{bd} 7.3, J_{ef} 15.7, J_{cd} (*cis*) 10.0, and J_{cd} (*trans*) 17.3 Hz. These observations confirm both the structure and stereochemistry of the products (8) and (9).

3-Methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-dienyltriphenylphosphonium chloride (7). Compound (7) (0.936 5 g, 0.001 4 mol) was reduced in HMPA solution as described previously. The electrolysis was halted when 2.2 F mol^{-1} had been passed, by which time the current had fallen from 0.053 to 0.012 A cm^{-2}. The mixture was

extracted, washed, and dried as before. The yellow residue (0.509 0 g) was separated by t.l.c. on two 40 × 40 cm HF plates using n-pentane at −4 °C. This gave (11) (74.2 mg, 25%), (13) (18.0 mg, 6.0%), and (12) (32.2 mg, 11%). Similar reduction in DMF gave a 19% yield of the dimers. The structural assignments were based on the ^{13}C and ^{1}H n.m.r. data which is given, together with literature values and detailed analyses of the spectra, in Tables 5 and 6. High-

TABLE 5

Products of electrolysis of (7); ^{1}H n.m.r. spectroscopic data

Product	Chemical shift δ (lit. chemical shift) [multiplicity, integration, assignment]
(11)	1.01 (1.03) [a] [s, 6 H, 1-CH$_3$], 1.69br (1.71) [a] [s,[b] 5-CH$_3$], 1.77br (1.81, 1.76) [a] [s,[b] 9- and 11-CH$_3$], 1.50 (1.46) [a] [m, 2 H, 2-CH$_2$], 2.00 (2.01) [a] [m, 2 H, 4-CH$_2$], 5.0—6.2 [m, 3 H, 7-, 8-, and 10-vinyl H]
(12)	1.02 (1.03) [a] [s, 12 H, 1-CH$_3$], 1.70br (1.71) [a] [s, 5- and 5′-CH$_3$], 1.79br (1.81) [a] [s, 9- and 9′-CH$_3$], 1.51 (1.46) [a] [m, 4 H, 2- and 2′-CH$_2$], 2.01 (2.01) [a] [t, J ca. 6 Hz, 4 H, 4- and 4′-CH$_2$], 5.98br (ca. 6.1) [a] [s, 4 H, 7-,7′-,8-, and 8′-vinyl H], 5.42br (5.5) [c] [m, 2 H, 10- and 10′-vinyl H], 2.26 (2.36) [d] [t, 4 H, 11- and 11′-CH$_2$]
(13)	1.02, 0.98 (1.03) [a] [2 s, 12 H, 1- and 1′-CH$_3$], 1.67br, 1.70br (1.71) [a] [2 s, 5- and 5′-CH$_3$], 1.79br (1.81) [a] [s, 9-CH$_3$], 1.17br [s, 9′-CH$_3$], 2.33 [d, J 7 Hz, 2 H, 11-CH$_2$], 4.8—6.0 [m, vinyl H]

[a] Measured for 1,3,3-trimethyl-2-(3,7-dimethylnona-1,3,5,7-tetraenyl)cyclohexene (axerophtene).[16] [b] Part of 11-CH$_3$ doublet included. [c] Estimated by calculation.[17] Value for *trans,trans*-bicinnamyl.

TABLE 6

Products (11)—(13) of electrolysis of (7); ^{13}C n.m.r. spectroscopic data

Carbon atom	Chemical shift [a] (11)	(12)	(13)	Lit. value [b]
1,1′	34.2	34.1	34.2, 34.0	34.3
2,2′	39.6	39.5	39.7, 39.5	39.8
3,3′	19.4	19.4	19.3, 19.3	19.5
4,4′	32.9	32.9	32.9, 32.6	33.0
5,5′	128.1		128.2, 127.4	128.2
6,6′			137.9, 137.9	138.2
7,7′	125.2		125.6, 127.6	125.0
8,8′	137.9	137.9	138.1, 140.7	137.9
9,9′	135.0		135.2, 43.5 [d]	135.0 (49.9) [d]
10,10′	123.9	124.4	124.2, 146.3 [d,e]	124.0 (141.5),[d] (145.1) [e]
11,11′	13.8	35.6 [c]	29.6 [d,e] 111.6 [d,e]	13.8 (32.8),[c] (39.0) [d] (114.5) [d] (111.5) [e]
1,1′-Me	28.9	28.9	28.8, 28.7	29.0
5,5′-Me	21.6	21.6	21.5, 21.2	21.6
9,9′-Me	11.9	12.3	12.5, 24.1	12.0

[a] Measured in CDCl$_3$ using Bruker W-H-360 (90.52 MHz) or, for (11) and (12), a Bruker HFX-90 (22.63 MHz); values in p.p.m. from Me$_4$Si. [b] Measured [18] for (11). [c] Value for *trans,trans*-bicinnamyl. [d] Value for *trans*-1,4-diphenylhexa-1,5-diene. [e] Measured [19] for 3,7-dimethylocta-1,6-dien-3-ol (linalool).

resolution m.s. measurement gave for the dimers a molecular weight of 406.359 3 (Calc. for $C_{30}H_{46}$: M, 406.359 9).

From the low-resolution mass spectra the following fragmentations were observed: (11), m/e 204 (44%), 189 (20), 146 (48), 133 (55), 119 (100), 74 (45), and 41 (41); (12), m/e 406 (9%), 203 (100), 119 (35), 105 (22), 69 (33), 55 (22), and 41 (21); (13), m/e 406 (8%), 203 (100), 117 (53), 119 (42), 105 (31), 69 (41), 43 (53), and 41 (37). The symmetrical cleavage of the dimers (to m/e 203) is quite characteristic giving, as for the bicinnamyl isomers, the base peak.

The n.m.r. data in Tables 5 and 6 are in good agreement with published data. The ^{13}C n.m.r. spectra also confirm that the C(9)–C(10) bond is *trans*; for *cis*-isomers the C(9)-methyl carbon gives [10] a signal at δ 20.4 p.p.m. whereas for (11) and (13) values of δ 12.5 p.p.m. are observed.

The ^1H n.m.r. spectra give good agreement with published values for the chemical shifts of 1-, 5-, 9-, and 11-methyl and the vinylic 7- and 8-H. For (11) and (12) the 10-H signals (lit.,[16] δ 5.59) appear as a very broad multiplet at δ 5.0—5.5. (Integration of this and the vinylic 7- and 8-H signals gives a ratio of 1 : 1.9 as expected.)

The ^{13}C n.m.r. spectrum of (13) serves to confirm its structure. The number of hydrogens attached to each carbon atom was determined by ^1H continuous-wave off-resonance decoupling. The spectrum of (13) shows four main characteristics: (a) two signals are observed for all but C(9)–C(11) and 9-Me, (b) a signal at δ 111.6 p.p.m. which is characteristic of a terminal olefinic group, (c) a peak at very low field (δ 146.3 p.p.m.) which may be ascribed to C(10'), and (d) signals at δ 29.6 and 43.5 p.p.m., due respectively to C(11) and C(9').

The presence of the terminal olefinic group and the fact that the signals of C(1)—C(8) were pairs indicated that the structure was as shown. The observed shifts for the carbons are all in good agreement with those expected, from measurements on previously reported or analogous compounds.

The ^1H n.m.r. data are in agreement with the above assignments. The 1- and 5-methyl groups appear as doublets whereas the 9-methyl group gives a singlet. Also, another sharp peak, presumably due to the 9'-methyl group, appears at δ 1.17 p.p.m. The 11-CH_2 group may just be discerned as a doublet, being coupled to the vinylic 10-H; the olefinic region is, however, too complex for detailed analysis (there are eight different olefinic protons present).

The ^{13}C spectrum of (12) may be satisfactorily accounted for. The C(11) signal appears downfield at δ 35.6 p.p.m. and corresponds well with the value obtained for *trans,trans*-bicinnamyl. Again, the position of the 9-methyl signal indicates that the C(9)–C(12) double bond is *trans*.

The ^1H n.m.r. spectrum of (12) shows singlets in the expected positions due to the 1-, 5-, and 9-Me and the vinylic 7- and 8-H protons. The 11-CH_2 group gives the same unusual triplet as previously seen in the spectrum of *trans,trans*-bicinnamyl. Specifically, the group appears as a triplet, whose peaks are all of approximately equal intensity. The coupling with the allylic 10-H (typically J 7 Hz) should give a doublet. The spacing between the outermost, slightly stronger peaks, is ca. 7 Hz. This failure of simple, first-order analysis may be caused by virtual coupling of the 11- and 11'-CH_2 groups. The vinylic 10-H signal appears as a very broad peak. The 4-CH_2 group appears as a triplet at δ 2.01 and the 2-CH_2 group appears at δ 1.51. This is in good agreement with literature values.

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