

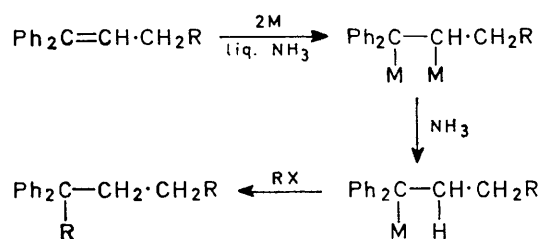
1,1-Diphenylalkenes. Part II.¹ Alkylation of 1,1-Diphenylpropene Carbanions. The Principle of Least Motion

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Carbanions of the type $[\text{Ph}_2\text{C}=\text{CH}=\text{CHR}]^-$ were alkylated in liquid ammonia. A preponderance of α -alkylation occurred when R was H or Me, in accord with the principle of least motion. Contrary to predictions, exclusive α -alkylation occurred when R was Ph. The mechanism and synthetic utility of these reactions are discussed.

THE principle of least motion detailed by Hine² has been applied to protonation reactions of mesomeric carbanions,² anion capture by allyl carbonium ions,² and elimination³ and chlorination reactions.⁴ The principle has been particularly useful in explaining some apparent anomalies in the way structure affects the reactivity of resonance-stabilised species. We intended to investigate the applicability of the principle to alkylation reactions of allyl carbanions and at the same time hoped to extend the synthetic value of these intermediates. We chose the 1,1-diphenylpropene system since (i) we have shown¹ that 1,1-diphenylalkenes are useful intermediates for the synthesis of saturated alkanes (Scheme 1) and wished to investigate the scope of their reactions,

and (ii) 1,1-diphenylpropene appeared to be a suitable model system for investigating the principle of least



SCHEME 1

motion. The principle states² that 'those elementary reactions will be favoured that involve the least change

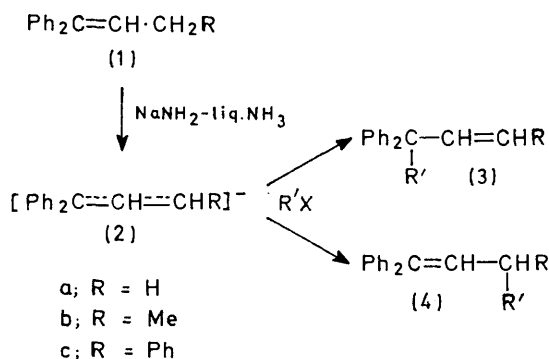
¹ Part I, W. S. Murphy and C. R. Hauser, *J. Org. Chem.*, 1966, **31**, 1781.

² J. Hine, *J. Org. Chem.*, 1966, **31**, 1236.

³ J. Hine, *J. Amer. Chem. Soc.*, 1966, **88**, 5525.

⁴ L. A. Paquette and W. C. Farley, *J. Org. Chem.*, 1967, **32**, 2725.

in atomic position and electronic configuration.' Qualitatively, at least, the energy required to effect internal geometric changes has been shown² to be approximately proportional to the sum of the squares of the changes in bond number. The appropriateness of 1,1-diphenylpropenyl anions for study was indicated by the observation that bond number changes during alkylation distinctly favoured one isomer (Scheme 2).



SCHEME 2

We found that carbanions of type (2) were readily formed and smoothly alkylated in liquid ammonia. Table 1 summarises the reactions of compound (2a) with

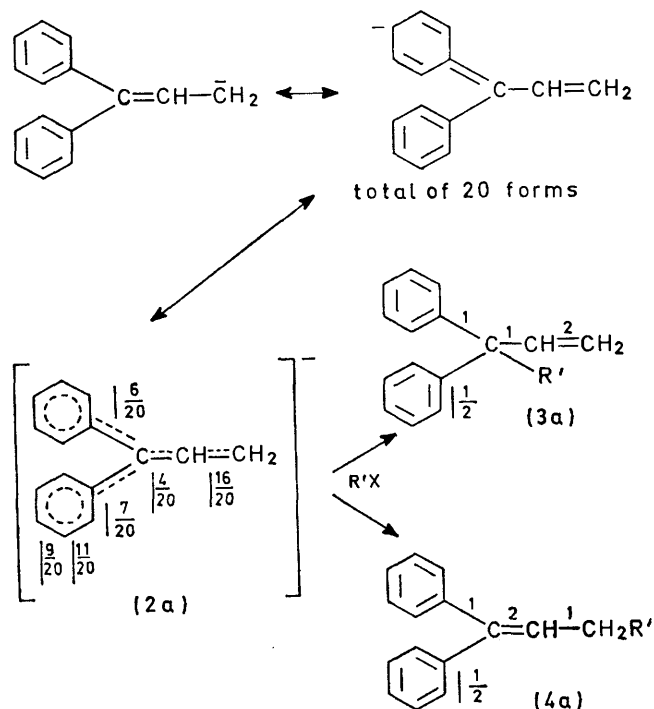
TABLE 1

Alkylation of 1,1-diphenylpropenylsodium in liquid ammonia

Alkyl halide	% Yield	Products (% ratio)	
		(3a)	(4a)
PhCH ₂ Cl	97	77.5	22.5
MeI	98	64.5	35.5
CH ₂ =CH·CH ₂ Br	97	58.6	41.4
Br[CH ₂] ₃ Br	73	58.1	41.9

a variety of alkylating agents. These results were in accord with the predictions of the principle of least motion calculated in the following way. The bond numbers of the resonance hybrid (2a) (Scheme 3) were determined from the contributing canonical forms. As had others,² we assumed that all canonical forms made an equal contribution. The sum of the squares of the changes in bond numbers leading to species (3a) and (4a) are summarised in Tables 2 and 3, respectively. Comparison of the calculations suggests that isomer (3a) should predominate. Our results (Table 1) are in accord with these predictions. We next investigated the 1,1-diphenylbut-1-enyl system (2b) (Scheme 2). Table 4 summarises the reactions with a variety of alkylating agents. The principle of least motion was again applied as above. The sum of the squares of the changes in bond number of the reactions (2b) → (3b) totalled 37/100 and that leading to (4b) totalled 157/100. A preponderance of (3b) was predicted, and the results (Table 4) conform. Finally we studied the 1,1,3-triphenylpropenyl system. Table 5 summarises the results of the reaction of 1,1,3-triphenylpropenylsodium (2c) with some alkyl halides. Application of the principle

of least motion predicted a preponderance of (3c), since the reaction (2c) → (3c) involved a total change of



SCHEME 3

187/338 and that leading to (4c) of 343/338. The results (Table 5) are contrary to expectations.

Pending further results we are unable to conclude that the principle of least motion can be generally applied to the alkylation reactions of mesomeric carbanions. Alternatively, however, analysis of the transition states suggests that a balance between resonance and steric effects can explain the difference

TABLE 2

Sum of the squares of the changes in bond numbers in the reaction (2a) → (3a)

Net change	Number of equivalent changes	Σ (change in bond number)
26/20 - 1	2	18/100
24/20 - 1	1	4/100
36/20 - 2	1	4/100
27/20 - 1½	4	9/100
31/20 - 1½	4	1/100
29/20 - 1½	4	1/100

Total 37/100

TABLE 3

Sum of the squares of the changes in bond numbers in the reaction (2a) → (4a)

Net change	Number of equivalent changes	Σ (change in bond number)
26/20 - 1	2	18/100
24/20 - 2	1	64/100
36/20 - 1	1	64/100
27/20 - 1½	4	9/100
31/20 - 1½	4	1/100
29/20 - 1½	4	1/100

Total 157/100

TABLE 4

Alkylation of 1,1-diphenylbut-1-enylsodium in liquid ammonia

Alkyl halide	% Yield	Products (% ratio)	
		(3b)	(4b)
PhCH ₂ Cl	81	100	
MeI	88	100	
CH ₂ =CH·CH ₂ Br	64	70	30 *
Br[CH ₂] ₃ Br	33	100	

* A referee pointed out that this exceptional result might be due to a Cope rearrangement during distillation. This is not so. The reaction was repeated. The ratio of isomers (n.m.r.) was essentially unchanged when the products were isolated by preparative t.l.c.

TABLE 5

Alkylation of 1,1,3-triphenylpropenylsodium in liquid ammonia

Alkyl halide	% Yield	Products (% ratio)	
		(3c)	(4c)
PhCH ₂ Cl	97	100	
MeI	88	100	
CH ₂ =CH·CH ₂ Br	98	100	
Br[CH ₂] ₃ Br	38	100	

between the results of alkylation of compounds (2a) and (2b). The anomalous alkylation reactions of (2c) could result from the dominance of steric effects.

These alkylation reactions extend the synthetic utility of 1,1-diphenylalkenes. Although the synthetic value of 1,1-diphenylpropene is limited by concomitant formation of two isomers which are difficult to separate, this restriction does not generally apply to either 1,1-diphenylbut-1-ene (and probably higher homologues) or 1,1,3-triphenylpropene. The α -alkylation products derived from 1,1-diphenylbut-1-ene are pure *trans*-alkenes.

EXPERIMENTAL

M.p.s were determined with an Electrothermal apparatus. U.v. spectra were measured with a Unicam SP 800 spectrophotometer (95% ethanol as solvent) and i.r. spectra with a Perkin-Elmer Infracord model 137. N.m.r. spectra were recorded for solutions in [2H]chloroform with either a Varian A100 (100 MHz) or a Perkin-Elmer R10 (60 MHz) instrument (tetramethylsilane as internal standard). T.l.c. was carried out on plates with Merck silica gel HF₂₅₄. Column chromatography involved the use of Woelm alumina of appropriate activity. For g.l.c. we employed copper columns (5 ft \times 0.25 in) packed with 5% SE-30 on 60–80 mesh Chromosorb W in an Aerograph A 350-B thermal conductivity gas chromatograph. Hydrogen was used as carrier gas at a flow rate of 50–55 ml min⁻¹.

1,1-Diphenylpropene (1a).—A solution of propiophenone (67.0 g, 0.5 mol) in dry ether (100 ml) was added slowly to an ethereal solution of phenylmagnesium bromide (0.6 mol). The reaction was completed by heating under reflux for 1 h. The mixture was poured on to 10% sulphuric acid (200 ml) at 0°. The ether layer was separated, dried (Na₂SO₄), and evaporated to afford crude 1,1-diphenylpropan-1-ol (91.7 g, 0.43 mol), m.p. 90–94°, which without further purification was heated under reflux for 3 h as a suspension in 20% sulphuric acid (200 ml). Extraction with ether followed by evaporation of the extract gave 1,1-diphenylpropene (1a) (72.2 g, 0.36 mol), m.p. 48–49°

⁵ K. T. Sengen and P. H. Wise, *J. Amer. Chem. Soc.*, 1951, **73**, 4766.

⁶ A. W. Schmidt and C. Hartmann, *Ber.*, 1942, **74B**, 1325.

(lit.,⁵ 48.5–49°) (Found: C, 92.65; H, 7.3. Calc. for C₁₅H₁₄: C, 92.8; H, 7.2%); λ_{\max} 217, 231, and 250 nm (ϵ 12,050, 10,900, and 12,100); τ 2.4–3.0 (m, 2 \times Ph), 3.82 (q, *J* 6.5 Hz, =CH), and 8.25 (d, *J* 6.5 Hz, Me).

1,1-Diphenylbut-1-ene (1b) and 1,1,3-Triphenylpropene (1c).—Compounds (1b) and (1c) were prepared in the same manner by replacing propiophenone with butyrophenone or methyl dihydrocinnamate, respectively. 1,1-Diphenylbut-1-ene (1b) (78% yield) had b.p. 160–161° at 10 mmHg (lit.,⁶ 108–110° at 0.4 mmHg) (Found: C, 92.5; H, 7.45. Calc. for C₁₆H₁₆: C, 92.3; H, 7.7%); λ_{\max} 214 and 251 nm (ϵ 13,000 and 9400); τ 3.0–3.5 (m, 2 \times Ph), 4.3 (t, *J* 8.0 Hz, =CH), and 8.23 (quint, *J* 6.5 Hz, CH₂), and 9.33 (t, *J* 7.0 Hz, Me). 1,1,3-Triphenylpropene (1c) (58% yield) had b.p. 168–170° at 0.25 mmHg (lit.,⁷ 214° at 7 mmHg) (Found: C, 93.55; H, 6.55. Calc. for C₂₁H₁₈: C, 93.35; H, 6.65%); λ_{\max} 213 and 252 nm (ϵ 18,600 and 19,600); τ 2.6–3.2 (m, 3 \times Ph), 3.78 (t, *J* 7.0 Hz, =CH), and 6.58 (d, *J* 7.0 Hz, CH₂).

Alkylation Reactions. General Procedure.—Alkylation of the carbanion (2a) with benzyl chloride. A 500 ml three-necked flask with a cold finger condenser and pressure equalising dropping funnel was maintained under a positive pressure of dry oxygen-free nitrogen. The reaction solution was stirred magnetically throughout. Anhydrous commercial liquid ammonia (300 ml) was further dried by the addition of small pieces of sodium until the blue colour persisted. A trace of anhydrous iron(III) nitrate was then added. Sodium (0.63 g, 0.0275 g-atom) was added in small pieces. Complete conversion of sodium into sodium amide was indicated by the disappearance of the blue colour. 1,1-Diphenylpropene (1a) (4.85 g, 0.025 mol) in dry ether (50 ml) was added. Formation of the carbanion (2a) was indicated by the immediate formation of a deep red colour. The mixture was then stirred for 30 min. Benzyl chloride (3.5 g, 0.0275 mol) in dry ether (20 ml) was added dropwise. The red colour had disappeared when addition was complete. The ammonia was evaporated off. Ether and water (100 ml) were added and the two layers were separated. The ether layer (with which were combined ethereal extracts of the aqueous layer) was dried (MgSO₄) and evaporated to leave a pale yellow viscous oil (5.1 g, 98%), which was shown by g.l.c. to consist of the olefins (3a; R' = CH₂Ph) (75.6%), (4a; R' = CH₂Ph) (21.8%), and (1a) (2.6%). Recrystallisation from methanol afforded 3,3,4-triphenylbut-1-ene (3a; R' = CH₂Ph) (2.97 g, 42%), m.p. 51.5–53° (Found: C, 92.65; H, 7.3. C₂₂H₂₀ requires C, 92.95; H, 7.05%); λ_{\max} 216 nm (ϵ 14,000); τ 2.8–3.3 (m, 3 \times Ph), 3.55 (dd), 4.80 (dd), and 5.40 (dd) (3H, ABX, *J*_{AB} 1.5, *J*_{AX} 17.2, *J*_{BX} 11.0 Hz), and 6.4 (s, CH₂). Evaporation of the mother liquor afforded an oil (3.5 g) which consisted (g.l.c.) of olefin (3a; R' = CH₂Ph) (54%) and 1,1,4-triphenylbut-1-ene (4a; R' = CH₂Ph) (46%) (Found: C, 92.55; H, 6.8%); λ_{\max} 216 and 262 nm (ϵ 14,500 and 4000); the n.m.r. spectrum of (3a; R² = CH₂Ph) (above) was superimposed on τ 3.89 (t, *J* 6.0 Hz, =CH), 7.4 (q, *J* 6.5 Hz, CH₂), and 8.8 (t, *J* 7.0 Hz, CH₂). The spectral and integration data were consistent with the g.l.c. results.

Alkylation of the carbanion (2a) with methyl iodide. The product (5.1 g, 98%), a viscous oil (Found: C, 92.0; H, 7.7. Calc. for C₁₆H₁₆: C, 92.3; H, 7.70%) consisted of the olefins (3a; R' = Me) (64.5%) and (4a; R' = Me) (35.5%) (g.l.c.). Preparative g.l.c. gave two fractions, A and B.

⁷ C. F. Koelsch and P. R. Johnson, *J. Org. Chem.*, 1941, **6**, 534.

Fraction A was 3,3-diphenylbut-1-ene (3a; R' = Me) (88% pure), *m/e* 208 (M^+); τ 2.5—3.0 (m, 2 \times Ph), 3.64 (dd), 4.85 (dd), and 5.12 (dd) (3H, ABX, J_{AB} 1.5, J_{AX} 18.0, and J_{BX} 10.5 Hz), and 8.24 (s, Me). Traces of (4a; R' = Me) were present. Fraction B was 1,1-diphenylbut-1-ene (4a; R' = Me) (91% pure); *m/e* 208 (M^+); τ 2.5—3.0 (m, 2 \times Ph), 3.94 (t, J 8.0 Hz, =CH), 7.9 (quint, J 8.0 Hz, CH_2), and 9.00 (t, J 7.0 Hz, Me).

Alkylation of the carbanion (2a) with allyl bromide. The product (5.63 g, 97%), purified by preparative t.l.c., was a viscous oil (Found: C, 92.45; H, 7.6. Calc. for $C_{18}H_{18}$: C, 92.3; H, 7.7%) which consisted of olefins (3a; R' = $CH_2\cdot CH\cdot CH_2$) (58.6%) and (4a; R' = $CH_2\cdot CH\cdot CH_2$) (41.4%) (g.l.c.); λ_{max} 216 and 257 nm (ϵ 14,600 and 4700); τ 2.4—2.9 (m, 2 \times Ph), 3.5 (dd), 4.7 (dd), and 5.2 (dd) (3H, ABX, J_{AB} 1.5, J_{AX} 18.0, J_{BX} 12.0 Hz), 4.05—4.55 (3H, m, ca. 12 peaks), and 6.85 (d, J 6.5 Hz, CH_2). This spectrum corresponded to (3a; R' = $CH_2\cdot CH\cdot CH_2$). The presence of (4a; R' = $CH_2\cdot CH\cdot CH_2$) was indicated by signals at τ 3.85 (t, J 6.5 Hz, =CH) and 7.75 (t, poorly resolved, J 3.0 Hz, 2 \times CH_2).

Alkylation of the carbanion (2a) with 1,3-dibromopropane. The crude product (5.19 g, 97%) was a yellow viscous oil which g.l.c. showed to consist of olefin (1a) (20.1%), uncharacterised product (7.1%), 3,3,7,7-tetraphenylnona-1,8-diene (43.4%) and 1,1,9,9-tetraphenylnona-1,8-diene (29.4%). The mixture of the last two products was eluted by hexane from the chromatography column (Found: C, 92.45; H, 7.55. Calc. for $C_{33}H_{32}$: C, 92.2; H, 7.35%); λ_{max} 216 and 256 nm (ϵ 10,800 and 4700); τ 2.2—3.1 (m, 4 \times Ph), 3.75 (dd), 4.95 (dd), and 5.38 (dd) (6H, ABX, J_{AB} 3.0, J_{AX} 17.6, J_{BX} 10.0 Hz), 7.9 (quint, poorly resolved, CH_2), and 8.73 (d, poorly resolved, CH_2). The presence of the latter isomer and its ratio to the former were determined by integration of the signal at τ 4.08 (t, =CH).

Alkylation of the carbanion (2b) with benzyl chloride. The product (7.1 g, 95%) was a white solid which consisted of olefins (3b; R' = CH_2Ph) (81%) and (1b) (15%) and benzyl chloride (4%) (g.l.c.). Recrystallisation from methanol gave *trans*-4,4-diphenylpent-2-ene (3b; R' = CH_2Ph) (5.7 g, 77%), m.p. 110—112° (Found: C, 92.4; H, 7.6. $C_{22}H_{22}$ requires C, 92.55; H, 7.45%); λ_{max} 218 nm (ϵ 10,600); τ 2.5—3.5 (m, 3 \times Ph), 4.00 (dq), 5.11 (dq, overlapping), and 8.33 (dd) (5H, ABX₃, J_{AB} 15, J_{AX} 6.5, J_{BX} 1.5 Hz), and 6.53 (s, CH_2).

Alkylation of the carbanion (2b) with methyl iodide. The product (5.2 g, 94%) was a light yellow oil which consisted of olefins (3b; R' = Me) (95%) and (1b) (5%). Distillation afforded *trans*-4,4-diphenylpent-2-ene (3b; R' = Me) (4.0 g, 73%), b.p. 100—101° at 0.2 mmHg (Found: C, 91.85; H, 8.4. $C_{17}H_{18}$ requires C, 91.9; H, 8.1%); λ_{max} 215 nm (ϵ 11,500); τ 2.6—3.0 (m, 2 \times Ph), 3.96 (dq), 4.70 (dq, overlapping), and 8.25 (d) (5H, ABX₃, J_{AB} 15, J_{AX} 6.5, J_{BX} 1.5 Hz), and 8.25 (s, overlapping).

Alkylation of the carbanion (2b) with allyl bromide. The product (6.0 g, 97%) was a yellow oil which consisted of 1,1-diphenylbut-1-ene (1b) (33.6%) and an inseparable mixture of *trans*-4,4-diphenylhepta-1,5-diene (3b; R' = $CH_2\cdot CH_2\cdot CH_2$) and 1,1-diphenyl-3-methylhexa-1,5-diene (4b; R' = $CH_2\cdot CH_2\cdot CH_2$) (66.4%) (g.l.c.). Careful distillation afforded the mixture of the last two (3.0 g, 43.5%), b.p. 92—94° at 0.05 mmHg (Found: C, 92.15; H, 8.45. Calc. for $C_{19}H_{20}$: C, 91.95; H, 8.06%); λ_{max} 215 and 256 nm (ϵ 13,400 and 3500); τ 2.6—3.1 (m, 2 \times Ph), 3.96 (dq), 4.98 (dq, overlapping), and 8.32 (dd) (5H, ABX₃, J_{AB} 16.0,

J_{AX} 6.5, J_{BX} 1.5 Hz), 4.2—4.66 (m, ca. 12 peaks, vinyl protons), and 6.98 (2H, dt, J 6.5 and 1.4 Hz, allyl protons). This spectrum, corresponding to (3b; R' = $CH_2\cdot CH_2\cdot CH_2$) was superimposed on that of (4b; R' = $CH_2\cdot CH_2\cdot CH_2$): τ 4.13 (d, J 10.0 Hz, =CH), 7.6 (1H, m, probably sept), 7.92 (2H, t, J 6.5 Hz, allyl), and 9.0 (d, J 6.5, Me). Integration indicated the ratio of (3b) to (4b) to be 70 : 30.

Alkylation of the carbanion (2b) with 1,3-dibromopropane. The product (5.2 g, 91%) consisted of 1,1-diphenylbut-1-ene (1b) and *trans*,*trans*-4,4,8,8-tetraphenylnonca-2,9-diene (t.l.c.). Trituration with hexane-ethanol at -78° afforded after recrystallisation from hexane, the *diene hydrate* (1.7 g, 33%), m.p. 108—109° (Found: C, 88.5; H, 8.2. $C_{35}H_{36}\cdot H_2O$ requires C, 88.6; H, 8.05%); ν_{max} 3450 cm^{-1} ; λ_{max} 215 nm (ϵ 14,000); τ 2.87 (s, 4 \times Ph), 4.08 (dq), 5.0 (dq, overlapping), and 8.33 (dd) (10H, ABX₃, J_{AB} 15, J_{AX} 6.5, J_{BX} 1.5 Hz), 7.8 (t, J 6.5 Hz, poorly resolved, 2 \times CH_2), and 8.9 (p, poorly resolved, CH_2).

Alkylation of the carbanion (2c) with benzyl chloride. The crude product (8.71 g, 97%) could not be analysed by g.l.c. However, t.l.c. indicated the formation of one product only. Trituration with hexane-ethanol at -78° yielded 1,1,3,4-tetraphenylbut-1-ene (4c; R' = CH_2Ph) (5.5 g, 60%), m.p. 55—57° (from methanol) (Found: C, 93.05; H, 6.75. $C_{28}H_{24}$ requires C, 93.3; H, 6.7%); λ_{max} 219 and 257 nm (ϵ 15,600 and 11,600); τ 2.6—3.4 (m, 4 \times Ph), 3.75 (d, J 10.5 Hz, =CH), 6.40 (quint, J 6.5, CH), and 7.00 (d, J 6.5 Hz, CH_2).

Alkylation of the carbanion (2c) with methyl iodide. The crude product (6.82 g, 95%) was an oil which consisted of 1,1,3-triphenylpropene (1c) (7.2%) and 1,1,3-triphenylbut-1-ene (4c; R' = Me) (92.8%) (t.l.c. and g.l.c.). Fractional distillation afforded pure (4c; R' = Me) (2.5 g, 35.2%), b.p. 110—112° at 0.1 mmHg (Found: C, 92.65; H, 7.1. $C_{22}H_{20}$ requires C, 92.95; H, 7.05%); λ_{max} 219 and 257 nm (ϵ 15,300 and 13,200); τ 2.3—3.2 (m, 3 \times Ph), 3.79 (d, J 10.5 Hz, =CH), 6.37 (quint, J 6.5 Hz, CH), and 8.64 (d, J 6.5 Hz, Me).

Alkylation of the carbanion (2c) with allyl bromide. T.l.c. of the crude product (7.6 g, 98%) indicated that one product only was formed. It crystallised when stored for 3 days. Recrystallisation from methanol afforded 1,1,3-triphenylhexa-1,5-diene (4c; R' = $CH_2\cdot CH\cdot CH_2$) (6.3 g, 81%), m.p. 53—55° (Found: C, 92.65; H, 7.25. $C_{24}H_{22}$ requires C, 93.0; H, 7.1%); λ_{max} 219 and 256 nm (ϵ 15,400 and 14,200); τ 2.5—3.1 (m, 3 \times Ph), 3.78 (d, J 10.5 Hz, =CH), 4—4.8 (m, 12 peaks) and 5.08 (dd) ($CH=CH_2$), 6.5 (sext, J 10.5 and 6.5 Hz, CH), and 7.55 (t, J 6.5 Hz, CH_2).

Alkylation of the carbanion (2c) with 1,3-dibromopropane. T.l.c. of the crude oily product (6.7 g, 92%) indicated that one product only was formed. A sample (1.5 g) applied to a chromatography column was eluted with light petroleum-hexane. A gum (0.56 g, 38%) which slowly crystallised *in vacuo* proved to be 1,1,3,7,9,9-hexaphenylnona-1,8-diene, m.p. 38—41° (Found: C, 93.3; H, 6.8. $C_{45}H_{40}$ requires C, 93.1; H, 6.9%); λ_{max} 217 and 256 nm (ϵ 13,000 and 10,400); τ 2.5—3.2 (m, 6 \times Ph), 3.9 (d, J 10 Hz, 2 \times =CH), 6.7 (sext, poorly resolved, 2 \times CH_2), and 8.50 (quint, poorly resolved, CH_2).

We acknowledge a State Maintenance Grant (to R. B.) and the support of the National Science Foundation (to K. P. K.). We thank Prof. T. B. H. McMurry for n.m.r. spectra.