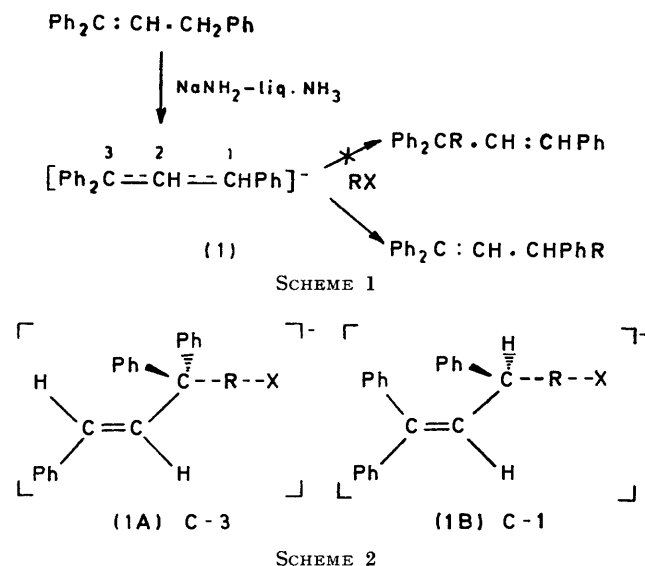


1,1-Diphenylalkenes. Part V.¹ C-1 vs. C-3 Alkylation of Allylic Carbanions; Applicability of the Principle of Least Motion

By Richard Boyce, Brendan A. Hayes, William S. Murphy,* and Edward A. O'Riordan, Department of Chemistry, University College, Cork, Ireland

The product of C-1 alkylation is the only one observed when 1,3,3-triphenylprop-2-enylsodium (1) is alkylated in liquid ammonia. However, exclusive C-3 alkylation results when the 3-phenyl groups are linked by an *ortho-ortho'*-bond, as in 2-(fluoren-9-ylidene)-1-phenylethylsodium (2), 2-(fluoren-9-ylidene)ethylsodium (3), or 2-(fluoren-9-ylidene)-1-methylethylsodium (4), or when the 1-phenyl group is reduced, as in 1-cyclohexyl-3,3-diphenylprop-2-enylsodium (5). It is concluded that the principle of least motion is generally applicable to these alkylation reactions and that the reactions of compound (1) are exceptions to the principle.

THE principle of least motion (PLM) is that 'those elementary reactions will be favoured that involve the least change in atomic position and electronic configuration.'² The principle has been successfully applied to the orientation of protonation reactions of mesomeric carbanions,^{3a} collapse of allylic carbocations,^{3a} elimination,⁴ chlorination,⁵ enolisation,^{6a} and molecular rearrangements.^{6a,b} Qualitatively at least, the energy required to effect internal geometric changes has been shown to be approximately proportional to the sum of the squares of the changes in bond number.³ We have been interested in the applicability of PLM to the alkylation of allylic carbanions, choosing 3,3-diphenylprop-2-enide ions for study, since the changes in bond number during alkylation distinctly favour one isomer.⁷



We observed⁷ exclusive C-1 alkylation of 1,3,3-triphenylprop-2-enylsodium (1) (Scheme 1), contrary to that predicted by PLM. Our efforts to understand the behaviour of compound (1) by varying its steric and electronic properties, are the subject of this report.

Consideration of the transition states leading to C-1 and C-3 alkylation of (1) (Scheme 2) suggests a balance

¹ Part IV, R. Boyce, W. S. Murphy, and E. A. O'Riordan, *J.C.S. Perkin I*, 1974, 792.

² F. O. Rice and E. Teller, *J. Chem. Phys.*, 1938, **6**, 489; 1939, **7**, 199.

³ (a) J. Hine, *J. Org. Chem.*, 1966, **31**, 1236; (b) S. I. Miller, *Adv. Phys. Org. Chem.*, 1968, **6**, 185.

⁴ J. Hine, *J. Amer. Chem. Soc.*, 1966, **88**, 5525.

between steric and electronic factors. C-3 Attack is favoured by stabilisation of the negative charge by one extra phenyl group (1A); this orientation is predicted by PLM. To explain the observed C-1 alkylation of (1), we considered the hypothesis that the energy difference between the two transition states due to resonance stabilisation is relatively small and less than the energy difference due to the different steric requirements of C-1 and C-3. It should follow that in all other cases where a phenyl group does not reside on C-1, the stabilising effect of the two phenyl groups on C-3 should override steric factors and conform to PLM.

This hypothesis was tested by studying modifications of the structure (1). The diphenylmethylene group was replaced by a fluorenylidene group as in (2) so as to reduce the steric requirements of C-3, while maintaining the electronic factors constant (see later). Exclusive C-3

Alkylations in liquid ammonia

Alkyl halide	Carbanion	% Yield ^a	Products (% ratio)	
			C-3	C-1
MeI	(1)	87 ⁷		100
PhCH ₂ Cl	(1)	97 ⁷		100
CH ₂ :CH·CH ₂ Br	(1)	98 ⁷		100
Br[CH ₂] ₃ Br	(1)	92 ⁷		100
MeI	(2)	98	100	
PhCH ₂ Cl	(2)	87	100	
CH ₂ :CH·CH ₂ Br	(2)	68	100	
Br[CH ₂] ₃ Br	(2)	26 ^b	100	
MeI	(3)	95 ^b	100	
PhCH ₂ Cl	(3)	89 ^b	100	
MeI	(4)	91 ^c	100	
PhCH ₂ Cl	(4)	79 ^b	100	
MeI	(5)	91 ^d	100	
PhCH ₂ Cl	(5)	56 ^d	100	
CH ₂ :CH·CH ₂ Br	(5)	68 ^d	100	

^a Isolated yield of crude product. ^b Traces of unidentified side-products formed. ^c Structural assignment tentative; see Experimental section. ^d Crude product recycled three times to complete reaction of starting material.

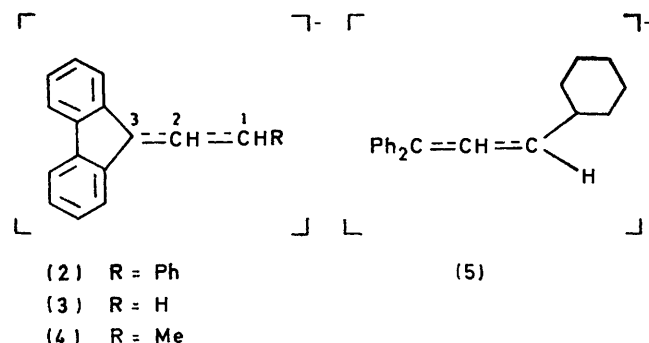
alkylation of (2) is observed (Table). The sum of the squares of the changes in bond number of (2) leading to C-3 alkylation totals 0.58 and for C-1 alkylation totals 0.95 (see Appendix). On the basis of PLM, C-3 attack is favoured by a factor of *ca.* 2. C-3 Alkylation of (1) is, however, favoured by the same factor (1.01 : 0.55)⁷ but C-1 alkylation only is observed (Table). It appears,

⁵ L. A. Paquette and W. C. Farley, *J. Org. Chem.*, 1967, **32**, 2725.

⁶ (a) O. S. Tee, *J. Amer. Chem. Soc.*, 1969, **91**, 7144; (b) O. S. Tee and K. Yates, *ibid.*, 1972, **94**, 3074.

⁷ R. Boyce, W. S. Murphy, and K. P. Klein, *J.C.S. Perkin I*, 1972, 1292.

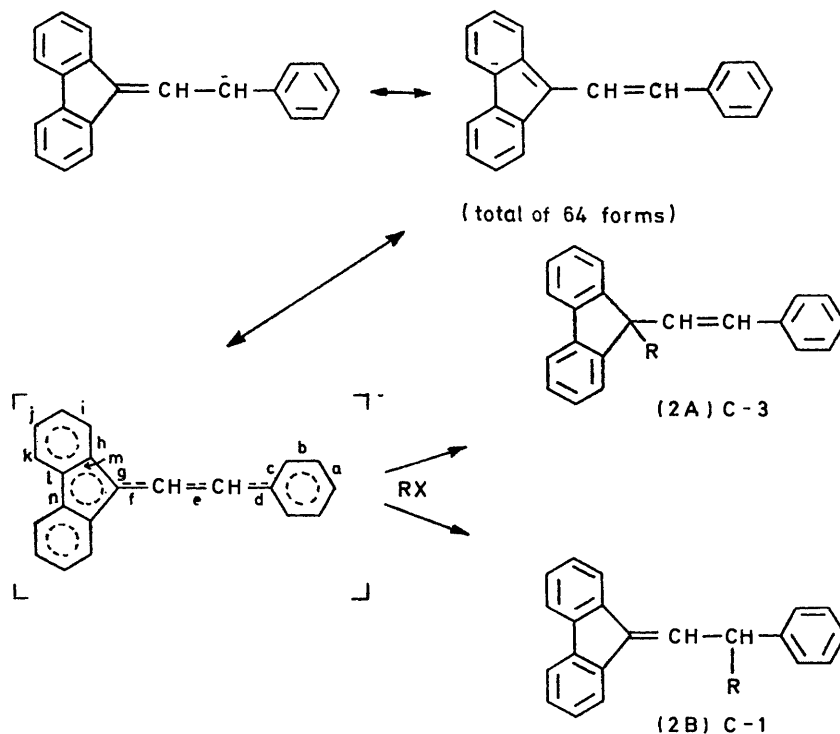
therefore, that steric factors are directing the course of the reaction of (1). As expected, the anions (3) and (4) undergo alkylation at least predominantly at C-3 (Table) in accord with PLM.



Next, the carbanion (5) was investigated. We reasoned that by replacing the phenyl group on C-1 of (1)

alkylations of other mesomeric carbanions⁹ suggest that the principle is generally applicable. However, exceptions are to be expected due in certain cases to steric effects as we have noted, or perhaps, as suggested by Hine,¹⁰ to a large energy difference between the two possible products.

Appendix.—PLM calculations for the reaction of (2) are as follows. The method of calculation is general. The bond numbers of the resonance hybrid (2) [(2A) and (2B); Scheme 3], which were determined from the contributing canonical forms, are summarised in Table I.* The bond numbers were determined from the contributing canonical forms.¹¹ As had others,^{2a,b} we assumed that all canonical forms made an equal contribution.¹² The sum of the squares of the changes in bond numbers leading to species (2A) and (2B) are summarised in Tables II and III, respectively.*† It follows that, on the basis of PLM, C-3 alkylation of (2) is favoured by a factor of *ca.* 2.



SCHEME 3

by a cyclohexyl group, the steric requirements of C-1 would remain almost constant⁸ but bond number changes would favour C-3 alkylation. Exclusive C-3 alkylation is observed (Table) as predicted: the sum of the squares of the changes in bond number leading to C-3 alkylation of (5) is 0.4 and for C-1 alkylation is 1.5.

In conclusion, PLM is applicable to the alkylation of 3,3-diphenylprop-2-enide ions. The results of the

* Tables I—III are available as Supplementary Publication No. SUP 21246 (4 pp.). For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index Issue.

† In ref. 7, Σ (change in bond number) in Tables 2 and 3 should read Σ (change in bond number).³

EXPERIMENTAL

The same techniques and apparatus were used as described previously.⁷

9-(2-Phenylethylidene)fluorene.—This alkene was prepared from fluorenone (90 g, 0.5 mol) and 2-phenylethylmagnesium-

⁸ E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Wiley, New York, 1967, p. 44.

⁹ (a) R. Y. Mixer and W. G. Young, *J. Amer. Chem. Soc.*, 1956, **78**, 3379; (b) G. Brieger and D. W. Anderson, *Chem. Comm.*, 1970, 1325.

¹⁰ J. Hine, *Chem. Eng. News*, 1966, 57.

¹¹ L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

¹² See however, W. C. Herndon, *J. Chem. Educ.*, 1974, **51**, 10.

ium bromide (1.0 mol) in dry ether (200 ml) as described earlier.⁷ The intermediate carbinol was dried and without purification was refluxed with 20% H₂SO₄ (250 ml) for 3 h. The product (104.5 g, 78%) had m.p. 94–95° (lit.,¹³ 94–96°) (Found: C, 94.05; H, 6.0. Calc. for C₂₁H₁₆: C, 94.05; H, 5.85%); λ_{max}, 246, 265, and 265 nm (ε 19,000, 23,000, and 29,800); τ 1.9–2.9 (m, Ph + fluorene), 3.18 (t, J 8.0 Hz, =CH), and 5.8 (d, J 8.0 Hz, CH₂).

9-Ethylidene fluorene.—This alkene was prepared similarly [fluorenone (90 g, 0.5 mol); ethylmagnesium bromide (0.62 mol); ether (200 ml); 20% H₂SO₄ (200 ml)]. The product (58.0 g, 61%) had m.p. 103–104° (from propan-1-ol) (lit.,¹⁴ 102–103°); τ 2.1–2.9 (m, fluorene), 3.2 (q, J 8.0 Hz, =CH), and 7.7 (d, J 8.0 Hz, CH₂).

9-Propylidene fluorene.—This alkene was prepared similarly [fluorenone (90 g, 0.5 mol); n-propylmagnesium bromide (0.62 mol); ether (200 ml); 20% H₂SO₄ (200 ml)]. The product (55.0 g, 53%) had m.p. 41–42° (from ethanol) (lit.,¹⁵ 44.5–46°) (Found: C, 93.1; H, 6.75. Calc. for C₁₆H₁₄: C, 93.2; H, 6.8%); τ 2.1–2.8 (m, fluorene), 3.3 (t, J 8.0 Hz, =CH), 7.12 (quint, J 8.0 Hz, CH₂), and 8.7 (t, J 8.0 Hz, CH₂).

9-(2-Cyclohexylethylidene) fluorene.—An ethereal solution of 2-cyclohexylethylmagnesium bromide (0.25 mol) in dry ether (100 ml) was poured onto an excess of crushed solid carbon dioxide. After 12 h the ether layer was extracted with aqueous sodium carbonate. Acidification was followed by extraction with ether. The ethereal extract was dried (Na₂SO₄) and evaporated to yield the liquid 3-cyclohexylpropionic acid (28.7 g, 73.6%) (Found: C, 69.45; H, 10.2. Calc. for C₉H₁₆O₂: C, 69.3; H, 10.35%); τ –1.73 (s, CO₂H), 7.64 (t, J 7.5 Hz, CH₂), and 8.0–9.3 (m, CH₂ and C₆H₁₁). This acid (28.0 g, 0.175 mol) was dissolved in absolute ethanol (150 ml) which was saturated with dry HCl gas. This solution was refluxed for 16 h and evaporated. A solution of the resulting oil in ether was washed successively with aqueous sodium hydroxide and water, dried (Na₂SO₄), and evaporated to yield, as a light yellow oil, ethyl 3-cyclohexylpropionate (30.0 g, 90.0%) (Found: C, 72.1; H, 10.55. Calc. for C₁₁H₂₀O₂: C, 71.7; H, 10.9%); τ 5.91 (q, J 8.0 Hz, CH₂), 7.72 (t, J 8.0 Hz, CH₂), 7.9–9.4 (m, CH₂ and C₆H₁₁), and 8.77 (t, J 8.0 Hz, CH₃). A solution of this ester (30.0 g, 0.16 mol) in dry ether (100 ml) was added slowly to ethereal phenylmagnesium bromide (0.40 mol). The reaction was completed by heating under reflux for 1 h. Acidic work-up was followed by extraction with ether. A red oil was isolated which was dissolved in hexane and cooled to –14°. A cream coloured solid separated which afforded 3-cyclohexyl-1,1-diphenylpropan-1-ol (30.0 g, 62.7%), m.p. 62.5–64° (from hexane) (Found: C, 85.55; H, 8.6. C₂₁H₂₆O requires C, 85.8; H, 8.9%); τ 2.4–2.9 (m, 2 × Ph), 7.5–7.9 (t, poorly resolved, CH₂), 7.9 (s, OH), and 8.1–9.4 (m, CH₂ and C₆H₁₁). This carbinol (28.8 g, 0.98 mol) was heated under reflux for 3 days with 25% H₂SO₄ (300 ml) and acetic acid (15 ml). Ether was added. The ethereal layer was washed with water and aqueous Na₂SO₃, dried (Na₂SO₄), and evaporated to yield, as a pure (t.l.c. and g.l.c.) oil, 3-cyclohexyl-1,1-diphenylpropene (27.60 g, 100%) (Found: C, 90.85; H, 8.7. C₂₁H₂₄ requires C, 91.4; H, 8.75%); λ_{max}, 255 nm (ε 12,200); τ 2.6–3.1 (m, 2 × Ph), 3.9 (t, J 7.5 Hz, =CH), 8.0 (t, J 7.5 Hz, CH₂), and 8.1–9.4 (m, C₆H₁₁).

Alkylation Reactions.—The same procedures for alkyl-

ation reactions and work-up were used as described in Part II.⁷

Alkylation of the carbanion (2). (a) *With methyl iodide.* The oily product (2.42 g, 98%), pure as isolated (g.l.c., t.l.c., and n.m.r.), was trans-9-methyl-9-styrylfluorene (Found: C, 93.5; H, 6.7. C₂₂H₁₈ requires C, 93.6; H, 6.4%); λ_{max}, 265 nm (ε 29,400); τ 2.15–3.0 (m, fluorene), 3.4 (d, AB, J 15 Hz, =CH), 3.85 (d, J 15 Hz, =CH), and 8.38 (s, CH₃).

(b) *With benzyl chloride.* The crude oily product (4.12 g, 87%) consisted exclusively of the C-3 alkylation product (g.l.c., t.l.c., and n.m.r.). This was treated with cold hexane. Recrystallisation from methanol afforded 9-benzyl-9-styrylfluorene (2.4 g, 50%), m.p. 148–149° (Found: C, 93.55; H, 6.3. C₂₈H₂₂ requires C, 93.9; H, 6.2%); λ_{max}, 236 and 267 nm (ε 27,500 and 30,400); τ 2.25–3.8 (m, Ph, fluorene, and 2 × =CH overlapping), and 6.63 (s, CH₂). Owing to signal overlap, the stereochemistry could be not assigned.

(c) *With allyl bromide.* The crude oily product (2.49 g, 97%) consisted exclusively of the C-3 alkylation product and 9-(2-phenylethylidene)fluorene (t.l.c. and n.m.r.). A portion (1.7 g) was purified by dry-column chromatography [hexane–ether (95 : 5) as eluant]. A liquid fraction (1.2 g, 68%), pure by t.l.c. and g.l.c., proved to be 9-allyl-9-styrylfluorene (Found: C, 93.2; H, 6.8. C₂₄H₂₀ requires C, 93.55; H, 6.55%); λ_{max}, 236 and 265 nm (ε 27,600 and 27,600); τ 2.2–3.1 (m, Ph and fluorene), 3.59 (s, CH=CH), 4.2–5.5 (m, CH=CH₂), and 7.15 (d, J 6.0 Hz, CH₂). Stereochemistry could not be assigned.

(d) *With 1,3-dibromopropane.* The crude product consisted of the C-3 alkylation product and 9-(2-phenylpropylidene)fluorene contaminated with traces of unidentified side-products (g.l.c.). No product resulting from C-1 attack was present (n.m.r.). The crude product was dissolved in hexane and cooled to –14°. A white solid (0.81 g, 26%) separated, which afforded 9-(3-bromopropyl)-9-styrylfluorene, m.p. 106.5–108° (from hexane) (Found: C, 74.65; H, 5.65; Br, 20.5. C₂₄H₂₁Br requires C, 74.05; H, 5.45; Br, 20.5%); λ_{max}, 230 and 266 nm (ε 29,400 and 23,000); τ 2.0–3.0 (m, Ph and fluorene), 3.56 (s, =CH), 3.60 (s, =CH), 6.85 (t, J 7.0 Hz, CH₂), 7.60 (t, J 8.0 Hz, CH₂Br, deformed), and 8.77 (quint, J 7.0 Hz, CH₂, deformed). Stereochemistry could not be assigned. No 9,9'-distyryl-9,9'-trimethylene-difluorene was detected.⁷

Alkylation of the carbanion (3). (a) *With methyl iodide.* The crude product (4.5 g, 95%) consisted of the C-3 alkylation product contaminated with traces of unidentified side-products (t.l.c. and n.m.r.). A portion (0.5 g) was subjected to preparative t.l.c. to yield 9-methyl-9-vinylfluorene (0.38 g, 75%) (Found: C, 92.8; H, 6.85. C₁₆H₁₄ requires C, 93.3; H, 6.85%); τ 2.6–3.1 (m, fluorene), 4.4 (dd, AMX, J_{XM} 9, J_{AX} 16 Hz, =CH), 5.11 (dd, J_{AX} 16, J_{AM} 2 Hz, =CH), 5.26 (dd, J_{XM} 9, J_{AM} 2 Hz, =CH), and 8.58 (s, CH₃). Although uncharacterised, the minor products had n.m.r. spectra which were not consistent with the spectrum expected for the C-1 alkylation product.

(b) *With benzyl chloride.* The crude product (7.1 g, 89%) consisted of the C-3 alkylation product contaminated with traces of unidentified side products (t.l.c. and n.m.r.). A portion (0.5 g) was subjected to preparative t.l.c. to yield 9-benzyl-9-vinylfluorene (0.24 g, 47.5%) as a white solid, m.p. 81–82° (from methanol) (Found: C, 93.95; H, 6.3. C₂₂H₁₈ requires C, 93.6; H, 6.4%); τ 2.3–3.4 (m, fluorene and Ph),

¹³ R. Kuhn and U. Breyer, *Annalen*, 1963, **661**, 173.

¹⁴ E. J. Greenlow, D. McNeill, and E. N. White, *J. Chem. Soc.*, 1952, 986.

¹⁵ S. Wawzonek, E. Dufek, and N. M. Sial, *J. Org. Chem.*, 1956, **21**, 276.

3.71 (dd, AMX, J_{XM} 9, J_{AX} 16 Hz, =CH), 4.81br (d, J_{AX} 16, J_{AM} < 1 Hz, =CH, overlapping), 4.90 (d, J_{XM} 9, J_{AM} < 1 Hz, =CH, overlapping), and 6.64 (s, CH₂). The n.m.r. spectra of the side products were not consistent with that expected for the C-1 alkylation product.

Alkylation of the carbanion (4). (a) *With methyl iodide.* The crude product (5.0 g, 91%) consisted of the C-3 alkylation product contaminated with traces of unidentified side products (t.l.c. and n.m.r.). No C-1 alkylation product was evident. A portion (0.5 g) was subjected to preparative t.l.c. to yield 9-methyl-9-(prop-1-enyl)fluorene (0.32 g, 63.5%) (Found: C, 92.35; H, 6.95. C₁₇H₁₆ requires C, 92.75; H, 7.25%); τ 2.2–3.1 (m, fluorene), 4.3–4.5 (m, 2 × =CH, finely split), and 8.45 (m, 2 × CH₃, overlapping). This n.m.r. spectrum is unexpected, although the structural assignment appears correct.

(b) *With benzyl chloride.* The crude product consisted of the C-3 alkylation product contaminated with traces of unidentified side products (t.l.c. and n.m.r.). No C-4 alkylation product was evident. The crude solid was recrystallised from ethanol to yield trans-9-benzyl-9-(prop-1-enyl)fluorene (6.51 g, 88%), m.p. 89–90° (Found: C, 93.4; H, 6.6. C₂₃H₂₀ requires C, 93.25; H, 6.75%); τ 2.2–3.4 (m, Ph and fluorene), 4.05 (d, ABX₃, J_{AB} 15 Hz, =CH), 4.51 (s, =CH), 6.72 (s, CH₃), and 8.35 (d, J_{AX} + J_{BX} 6 Hz, CH₃). None of the minor products, although unidentified, showed properties consistent with the C-1 alkylation product.

Alkylation of the carbanion (5). (a) *With methyl iodide.* The product was obtained free from starting material by recycling three times. This crude product was found to be isomerically pure (n.m.r.). Thus, trans-1-cyclohexyl-3,3-

diphenylbut-1-ene was obtained as an oil (3.28 g, 90.6%), b.p. 185° at 0.5 mmHg (Found: C, 90.85; H, 8.7. C₂₂H₂₆ requires C, 91.0; H, 8.9%); λ_{max} 230 and 255 nm (ϵ 1600 and 1400); τ 2.95 (s, 2 × Ph), 4.15 (d, ABX, J_{AB} 16.5 Hz, =CH), 4.9 (dd, J_{AB} 16.5, J_{AX} 6 Hz, =CH), 7.8–9.4 (m, C₆H₁₁), and 8.4 (s, CH₃, overlapping).

(b) *With benzyl chloride.* The product was obtained free from starting material by recycling three times. It consisted exclusively of stilbene and the C-3 alkylation product (g.l.c. and n.m.r.). The product (2.55 g, 56.0%) was freed from stilbene by distillation. trans-1-Cyclohexyl-3,3,4-triphenylbut-1-ene was obtained (Found: C, 90.2; H, 8.15. C₂₈H₃₀ requires C, 91.8; H, 8.2%); λ_{max} 230 and 260 nm (ϵ 3100 and 1400); τ 2.93 (s, 3 × Ph), 4.13 (d, ABX, J_{AB} 16.5 Hz, =CH), 5.18 (dd, J_{AB} 16.5, J_{AX} 6 Hz, =CH), 6.59 (s, CH₂Ph), and 7.60–9.50 (m, C₆H₁₁).

(c) *With allyl bromide.* Again, it was necessary to recycle the crude product three times to complete the alkylation (g.l.c.). The crude oily product (2.90 g, 68%) was isomerically pure (t.l.c. and n.m.r.). A sample (0.2 g) was purified by preparative t.l.c. trans-1-Cyclohexyl-3,3-diphenylhexa-1,5-diene (0.12 g, 60%) was obtained (Found: C, 91.35; H, 8.35. C₂₄H₂₈ requires C, 91.1; H, 8.8%); λ_{max} 230 and 260 nm (ϵ 3100 and 1400); τ 2.75 (s, 2 × Ph), 3.95 (d, ABX, J_{AB} 16.5 Hz, =CH), 4.2–5.2 (m, 2 × =CH and =CH₂), 6.95 (d, J 6.0 Hz, CH₂), and 7.6–9.3 (m, C₆H₁₁).

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