1,1-Diphenylalkenes. Part IV.[1] Carbonation and Aldol Addition † Reactions of 1,1-Diphenylpropenyl Anions
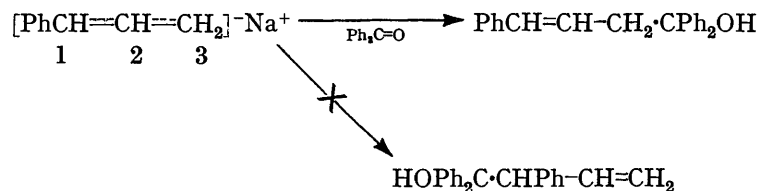
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A series of carbonyl compounds were allowed to react wth carbanions of the type $[Ph_2C{=}CH{=}CHR]^-$ in liquid ammonia. Exclusive attack at C-3 was observed. p-Nitrobenzaldehyde reacted by an alternative pathway; carbanion dimerisation occurred. Carbonation reactions had the same orientation as had the aldol addition reactions. Preliminary results suggest an initial attack at C-1 followed by rearrangement to the C-3 carboxylate product.

IN Part II [2] of this series we noted that the orientation of the reactions of 1,1-diphenylpropenyl anions with alkyl halides can be predicted by the principle of least motion [3] (PLM). The least stable product predominated. The behaviour of 1,1,3-triphenylpropenylsodium, the exception to PLM, was rationalised by a combination of electronic and steric effects. We have now undertaken a survey of the addition reactions of 1,1-diphenylpropenyl anions to aldehydes and ketones in liquid ammonia. Reactions of alkyl substituted allyl Grignard reagents with ketones have been extensively studied [4] and the sensitivity of the reaction to steric factors noted.[4] The reactions of phenylallylmagnesium bromide and phenylallylsodium have also been investigated.[5] For example, it was noted that whereas acetone reacted with

been disproved.[7] Such a transition state for the analogous reactions of phenylallylsodium in liquid ammonia seems improbable.[8]

We therefore anticipated that aldol addition reactions of 1,1-diphenylpropenyl anions [(1a—c), Scheme] would occur exclusively at C-3 and override the effects [9] of the higher negative charge on C-1 in contravention of PLM.[1,2] We find that one isomer only is formed (Table 1), the product of C-3 attack [(2), Scheme]. From our investigations [1,2] of the reactions of these anions (1a—c) with alkyl halides, it appears that C-1 is more nucleophilic than C-3. The possibility therefore arises that the initial kinetically controlled attack by the carbonyl compound at C-1 is followed by a rearrangement to the more stable C-3 isomer (Scheme). We tested this

$$[PhCH{=}CH{=}CH_2]^- Na^+ \xrightarrow{Ph_2C=O} PhCH{=}CH{-}CH_2{\cdot}CPh_2OH$$
$$\underset{1 \quad 2 \quad 3}{}$$

$$HOPh_2C{\cdot}CHPh{-}CH{=}CH_2$$

phenylallylsodium to give a mixture of isomers, benzophenone reacted exclusively at C-3.[5] A six-membered transition state proposed [6] for the reactions of allylic Grignard reagents with carbonyl compounds, has now

hypothesis by maintaining the reaction of benzophenone with 1,1-diphenylbutenylsodium at −78°. The reaction was quenched at −78° after 5 min. No C-1 addition product was observed. Further evidence against the transient involvement of a C-1 adduct is

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† We propose ' aldol addition ' to mean the reaction of a carbanion (or equivalent) or an enolate anion with an aldehyde or ketone without loss of water. This reaction title is preferable to aldol condensation, which implies loss of water, and should remove ambiguity noted by a referee.

[1] Part III, W. S. Murphy, R. Boyce, and E. A. O'Riordan, *Tetrahedron Letters,* 1971, 4157.

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

[3] J. Hine, *J. Org. Chem.,* 1966, **31,** 1236.

[4] M. Cherest, H. Felkin, and C. Frajerman, *Tetrahedron Letters,* 1971, 379, 383; A. J. Kresge and V. Nowlan, *ibid.,* p. 4297.

[5] R. H. DeWolfe, D. E. Johnson, R. I. Wagner, and W. G. Young, *J. Amer. Chem. Soc.,* 1957, **79,** 4798.

[6] W. G. Young and J. D. Roberts, *J. Amer. Chem. Soc.,* 1946, **68,** 649.

[7] H. Felkin and C. Frajerman, *Tetrahedron Letters,* 1970, 1045; H. Felkin, Y. Gault, and G. Roussi, *Tetrahedron,* 1970, **26,** 3761.

[8] D. J. Cram, ' Fundamentals of Carbanion Chemistry,' New York, Academic Press, 1965, p. 32.

[9] R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Amer. Chem. Soc.,* 1973, **95,** 926.

suggested by the results of Kaiser and Hauser[10] who noted that the reverse aldol reaction of sodium 1,1,2,2-tetraphenylethoxide in liquid ammonia is complete only after 4 h.
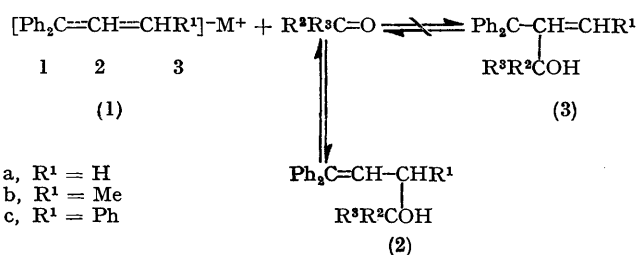
TABLE 1

Aldol addition reactions in liquid ammonia

Carbonyl compound	Carbanion	Metal cation	Yield (%) [a,b]
Benzophenone	(1a)	Na+	97
Fluorenone	(1a)	Na+	71
Acetophenone	(1a)	Na+	35
Benzaldehyde	(1a)	Na+	40
Benzophenone	(1b)	Na+	50
Fluorenone	(1b)	Na+	36
Acetophenone	(1b)	Na+	44
Benzaldehyde	(1b)	Na+	33
Benzophenone	(1c)	K+	0
Benzophenone	(1c)	Na+	0
Benzophenone	(1c)	Li+	48
Fluorenone	(1c)	Li+	25
Acetophenone	(1c)	Li+	15
Benzaldehyde	(1c)	Li+	15
Benzophenone	(4)	Li+	0

[a] Isolated yields. [b] C-3 Product formed exclusively as determined by n.m.r.

No product could be isolated from the reaction of (1c) when the counter-ion was either sodium or potassium.

$$[Ph_2C\!\!=\!\!CH\!\!=\!\!CHR^1]^-M^+ + R^3R^2C\!\!=\!\!O \rightleftharpoons Ph_2C\!\!-\!\!CH\!\!=\!\!CHR^1$$

$$1 \quad\quad 2 \quad\quad 3 \quad\quad\quad\quad\quad R^3R^2COH$$

$$(1) \quad\quad\quad\quad\quad\quad\quad\quad\quad (3)$$

a, R^1 = H
b, R^1 = Me
c, R^1 = Ph

$$Ph_2C\!\!=\!\!CH\!\!-\!\!CHR^1$$
$$R^3R^2COH$$
$$(2)$$

SCHEME

The success achieved with lithium (Table 1) is probably due to its greater ability to co-ordinate to oxygen.[11]

suggest that both equilibria (Scheme) are unfavourable in this case.

In the reactions of benzaldehyde with the anions (1a—c) the product was invariably an oil even in the case of (1a) where formation of diastereoisomers is not possible. p-Nitrobenzaldehyde was used in the hope that crystalline products would be formed. We observed dimerisation of (1a); no aldol addition occurred. The red colour of (1a) was replaced by green [12c] as p-nitrobenzaldehyde was added. The green colour persisted until the reaction was quenched. By analogy with other results [12a,b] we suggest an electron transfer mechanism.

Since the aldol addition reactions of (1a—c) occurred exclusively at C-3, we hoped that this reaction followed by dehydration would provide a simple synthetic route to 1,1-diphenylalka-1,3-dienes. Efficient dehydration

TABLE 2

Dehydration of carbinols

Carbinol	Product	Yield (%) [a]
$Ph_2C\!:\!CH\!\cdot\!CH_2\!\cdot\!C(OH)Ph_2$	$Ph_2C\!:\!CH\!\cdot\!CH\!:\!CPh_2$	96
$Ph_2C\!\cdot\!CH\!\cdot\!C(OH)PhMe$	$Ph_2C\!:\!CH\!\cdot\!CH\!:\!CPhMe$ [b]	70
$Ph_2C\!:\!CH\!\cdot\!CH_2C(OH)\!=\!BP$ [c]	$Ph_2C\!:\!CH\!\cdot\!CH\!:\!C\!=\!PB$ [c]	93
$Ph_2C\!:\!CH\!\cdot\!CH(Me)\!\cdot\!C(OH)Ph_2$	$Ph_2C\!:\!CH\!\cdot\!C(Me)\!:\!CPh_2$	90

[a] Isolated yields. [b] Isomerically pure. [c] BP = Biphenyl-2,2'-diyl.

could be effected in four cases only (Table 2). The remaining carbinols gave complex product mixtures under a wide variety of dehydrating conditions.

Next, the carbonation reactions of the anions (1a—c) were investigated. As we have noted previously,[13] the efficiency of carbonation under these conditions is in part dependent on the metal cation: $K^+ > Na^+ > Li^+$. With one exception, the orientation followed the same course as the aldol addition reactions. However, initial

TABLE 3

Carbonation reactions

Expt. no.	Carbanion	Metal cation	Recovered hydrocarbon	Acid yield (%) [a]	Acidic products (% ratio) [b] C-1	Acidic products (% ratio) [b] C-3
1	(1a)	K+	67	32		100
2	(1a)	Na+	98			
3	(1a)	Li+	94			
4	(1b)	K+	65	33	47	53
5	(1b)	K+	48	49		100
6	(1b)	Na+	93			
7	(1b)	Li+	99			
8	(1c)	K+		76		100
9	(1c)	Na+	27	73		100
10	(1c)	Li+	65	34		100

[a] Isolated yields. [b] Determined by n.m.r.

Aldol additions of the 1,1-(biphenyl-2,2'-diyl)propenyl carbanion (4) were unsuccessful. The colour of the anion was not discharged by the addition of a carbonyl compound, and no product was detected. These results

kinetically controlled attack at C-1 followed by reversal and recombination at C-3 (compare the Scheme) is feasible. Tentative evidence for this mechanism is

[10] E. M. Kaiser and C. R. Hauser, *Chem. and Ind.*, 1965, 1299.
[11] E. M. Kaiser and C. R. Hauser, *J. Amer. Chem. Soc.*, 1967, **89**, 4567.

[12] (a) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, 1966, **88**, 5660, 5662; (b) G. A. Russell and W. C. Danen, *ibid.*, 1966, **88**, 5663; (c) E. M. Kaiser, *ibid.*, 1967, **89**, 3659.
[13] W. S. Murphy and C. R. Hauser, *Chem. and Ind.*, 1969, 832.

provided by entries 4 and 5 (Table 3). When carbonation was quenched after 15 min, a mixture of C-3 and C-1 isomers was isolated (entry 4). When carbonation was allowed to go to completion and the resulting ethereal suspension of the sodium salt left overnight, the C-3 isomer only was detected.

EXPERIMENTAL

General.—Techniques and apparatus were the same as described previously.[1,2]

Aldol Addition Reactions. General Procedure.—Reaction of benzophenone with 1,1-diphenylpropenylsodium (1a). A 500 ml three-necked flask with a cold-finger condenser containing dry ice and acetone and a 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, and a crystal of iron(III) nitrate was then added. The blue colour disappeared, and 1,1-diphenylpropene (4·85 g, 0·025 mol) in dry ether (50 ml) was added. The ensuing red solution was stirred 30 min and a solution of benzophenone (5·0 g, 0·0275 mol) in dry ether (50 ml) was added. The red colour was discharged immediately. The white suspension was stirred 1 min and then poured onto a stirred solution of ammonium chloride (4·7 g, 0·088 mol) in liquid ammonia (200 ml). The ammonia was gradually replaced by ether, and water (100 ml) was added. The ethereal layer was evaporated to a white solid (9·20 g, 97·5%). One isomer only (2; R^1 = H, R^2 = R^3 = Ph) was detected in this crude product (n.m.r.). Recrystallisation from hexane–ethanol yielded 1,1,4,4-tetraphenylbut-3-enol (8·2 g, 87%) m.p. 136·5—138° (lit.,[14] 122·5—123·5°) (Found: C, 89·25; H, 6·65. Calc. for $C_{28}H_{24}O$: C, 89·3; H, 6·4%); $\lambda_{max.}$ 231 and 252 nm (ϵ 11,200 and 11,400); τ 2·55—2·9 (m, 4 × Ph), 3·94 (t, J 7·5 Hz, =CH), 6·85 (d, J 7·5 Hz, CH$_2$), and 7·67 (s, OH).

Dehydration was effected by heating 1,1,4,4-tetraphenyl-but-3-enol (2·0 g, 0·005 mol) with 25% sulphuric acid (100 ml) and acetic acid (5 ml) under reflux 24 h. After cooling, the solution was extracted with ether. The ether was evaporated off to yield 1,1,4,4-tetraphenylbuta-1,3-diene (1·92 g, 96%) m.p. 202—203·5° (lit.,[15] 192—193°) (Found: C, 93·85; H, 6·35. Calc. for $C_{28}H_{22}$: C, 93·85; H, 6·15%); $\lambda_{max.}$ 227, 248, and 339 nm (ϵ 17,600, 18,000, and 27,200); τ 2·53—2·9 (m, 4 × Ph), and 3·2 (s, 2 × =CH).

Reaction of 1,1-diphenylpropenylsodium (1a) with aceto-phenone. The crude product was a yellow oil. It consisted of one isomer (2; R^1 = H, R^2 = Me, R^3 = Ph) and starting materials (n.m.r.). A sample (2 g) was purified by dry column chromatography (95 : 5 hexane–ether) to give the viscous 2,4,4-triphenylpent-4-en-2-ol (0·69 g, 35%) (Found: C, 84·25; H, 7·3. $C_{23}H_{22}O$ requires C, 84·75; H, 7·0%); $\lambda_{max.}$ 253 nm (ϵ 9200); τ 2·6—3·2 (m, 3 × Ph), 4·09 (t, J 8·0 Hz, =CH), 7·5 (d, J 8·0 Hz, CH$_2$), 8·07 (s, OH), and 8·62 (s, Me).

The carbinol (0·4 g, 0·001 mol) was dehydrated as described above. 1,1,4-Triphenylpenta-1,3-diene (0·28 g, 70%) was isolated, m.p. 122—123° (from hexane) (Found: C, 92·15; H, 6·85. $C_{23}H_{20}$ requires C, 93·25; H, 6·75%); $\lambda_{max.}$ 244 and 320 nm (ϵ 3000 and 5000); τ 2·5—2·9 (m, 3 × Ph),

2·95 (d, J 11·5 Hz, =CH), 3·42 (d, J 11·5 Hz, =CH), and 7·71 (s, Me$_3$).

Reaction of 1,1-diphenylpropenylsodium (1a) with fluoren-one. An excess (120%) of fluorenone was used. One isomer only was detected by n.m.r. (2; R^1 = H, R^2 + R^3 = biphenyl-2,2'-diyl). A portion (5 g) of the crude oily product was purified by means of Girard's reagent. 9-(3,3-Diphenylprop-2-enyl)fluoren-9-ol (2·2 g, 71%) was isolated as a white solid, m.p. 114—116° (Found: C, 90·0; H, 6·0. $C_{28}H_{22}O$ requires C, 89·85; H, 5·9%); $\lambda_{max.}$ 238, 259, and 301 nm (ϵ 16,700, 18,600, and 9800); τ 2·2—3·25 (m, 2 × Ph + fluorene), 4·25 (t, J 8·5 Hz, =CH), 7·06 (d, J 8·5 Hz, CH$_2$), and 7·95 (s, OH).

The carbinol (0·76 g, 0·002 mol) was dehydrated as described above. The yellow solid 4,4-(biphenyl-2,2'-diyl)-1,1-diphenylbuta-1,3-diene (0·67 g, 93%) m.p. 188—189° (Found: C, 94·65; H, 5·9. $C_{28}H_{20}$ requires C, 94·4; H, 5·6%); $\lambda_{max.}$ 243, 262, 272, and 390 nm (ϵ 14,200, 10,600, 7600, and 16,000); τ 2·0—2·9 (m, 2 × Ph + fluorene + 2 × =CH).

Reaction of 1,1-diphenylpropenylsodium (1a) with benzalde-hyde. The crude product was a yellow oil. One isomer (2; R^1 = R^2 = H, R^3 = Ph) only was detected (n.m.r.). Of this a portion (2 g) was purified by dry column chromato-graphy. The light yellow gum 1,4,4-triphenylbut-3-enol (0·8 g, 40%) was isolated (Found: C, 88·1; H, 6·95. $C_{22}H_{20}O$ requires C, 88·0; H, 6·65%); $\lambda_{max.}$ 252 nm (ϵ 11,600); τ 2·45—3·15 (m, 3 × Ph), 3·92 (t, J 7·5 Hz, =CH), 5·35 (t, J 7·0 Hz, CH), and 7·48 (t, J 7·0 Hz, CH).

Reaction of 1,1-diphenylbutenylsodium (1b) with benzo-phenone. The crude product was a gum. One isomer only (2; R^1 = Me, R^2 = R^3 = Ph) was present (n.m.r.). A portion (2 g) was purified by dry column chromatography (95 : 5 hexane–ether). 2-Methyl-1,1,4,4-tetraphenylbut-3-enol (0·98 g, 50%), m.p. 109—111° (hexane) was isolated (Found: C, 89·0; H, 7·05. $C_{29}H_{26}O$ requires C, 89·25; H, 6·65%); $\lambda_{max.}$ 254 nm (ϵ 13,600); τ 2·5—3·2 (m, 4 × Ph), 3·91 (d, J 11 Hz, =CH), 6·53 (oct., J 11 and 7·5 Hz, CH), 7·63 (s, OH), and 8·9 (d, J 7·5 Hz, CH$_3$).

Dehydration of this carbinol (0·2 g) was effected as de-scribed above. The white crystalline 2-methyl-1,1,4,4-tetraphenylbuta-1,3-diene, (0·18 g, 90%) m.p. 137—138° (ethanol) was isolated (Found: C, 93·45; H, 6·55. $C_{29}H_{24}$ requires C, 93·5; H, 6·5%); $\lambda_{max.}$ 243 and 317 nm (ϵ 16,800 and 14,000); τ 2·55—3·0 (m, 4 × Ph), 3·36 (s, =CH), and 8·36 (s, Me).

Reaction of 1,1-diphenylbutenylsodium (1b) with acetophen-one. The crude product was a yellow oil. Only one posi-tional isomer (2; R^1 = R^2 = Me, R^3 = Ph) was detected by n.m.r. Of this a sample (2 g) was purified by dry column chromatography (95 : 5 hexane–ether). 3-Methyl-2,5,5-tri-phenylpent-4-en-2-ol (0·87 g, 44%) was isolated as a white solid, m.p. 100—101° (hexane) (Found: C, 86·85; H, 7·9. $C_{24}H_{24}O$ requires C, 87·8; H, 7·3%); $\lambda_{max.}$ 252 nm (ϵ 13,000); τ 2·2—3·1 (m, 3 × Ph), 4·02 (d, J 11·5 Hz, =CH), 7·32 (oct., J 11·5 and 6·0 Hz, CH), 8·29 (s, OH), 8·46 (s, Me), and 8·96 (d, J 6·0 Hz, Me). The ratio of diastereoisomers could not be determined from this spectrum.

Reaction of 1,1-diphenylbutenylsodium (1b) with fluorenone. Excess of fluorenone (100%) was used. This excess was removed from the crude oily product by the Girard reagent. One isomer only (2; R^1 = Me, R^2 + R^3 = biphenyl-2,2'-diyl) was detected (n.m.r.). A portion (1·52 g) of the

[14] W. J. Wasserman and M. J. Kloetzel, *J. Amer. Chem. Soc.*, 1953, **75**, 3036.

[15] Y. Zalkind and A. Kruglov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 803.

product so obtained was purified by dry column chromatography. 9-(1-*Methyl*-3,3-*diphenylprop*-2-*enyl*)*fluoren*-9-*ol* (0·86 g, 33%), m.p. 117·5—118·5°, was isolated (Found: C, 89·4; H, 6·3. $C_{29}H_{24}O$ requires C, 89·6; H, 6·2%); $\lambda_{max.}$ 238, 259, and 307 nm (ε 16,100, 15,000, and 2900); τ 2·25— 3·20 (m, 2 × Ph + fluorene), 4·38 (d, *J* 11·5 Hz, =CH), 6·8 (oct., *J* 11·5 and 7 Hz, CH), 7·88 (s, OH), and 8·92 (d, *J* 7 Hz, Me).

Reaction of 1,1-*diphenylbutenylsodium* (1b) *with benzaldehyde.* The crude product (3·61 g, 92%) was an oil which contained one positional isomer (2; R^1 = Me, R^2 = H, R^3 = Ph) only (n.m.r.). A portion (2 g) was purified by dry column chromatography and then on p.l.c. Pure 2-*methyl*-1,4,4-*triphenylbut*-3-*enol* (0·72 g) was thus isolated as a yellow gum (Found: C, 87·45; H, 7·3. $C_{23}H_{22}O$ requires C, 87·8; H, 7·0%); $\lambda_{max.}$ 252 nm (ε 12,000); τ 2·60— 3·25 (m, 3 × Ph), 4·08 (d, *J* 10 Hz, =CH), 4·25 (d, *J* 10 Hz, =CH, overlapping), 5·65 (dd, *J* 5·5 Hz, CH), 7·12 (s, OH), 7·49 (dec., $AMNX_3$, J_{AX} 10, J_{AM} 11·5, J_{MX} 9 Hz, CH), 9·05 (d, *J* 7 Hz, Me), and 9·22 (d, *J* 7 Hz, Me). This spectrum suggests that the product is a diastereoisomeric mixture in the ratio of 6 : 10. This ratio is based on the relative areas of the two methyl doublets. The assignments are tentative and are derived from a comparison with related systems.[16]

Reaction of 1,1,3-*triphenylpropenyl-lithium* (1c) *with benzophenone.* The crude product (5·85 g) was an oil which contained one isomer (2; $R^1 = R^2 = R^3$ = Ph) only (n.m.r.). A portion (2 g) was purified by dry column chromatography and recrystallised from hexane–ethanol to give pure 1,1,2,4,4-*pentaphenylbut*-3-*enol* (0·95 g, 47·5%), m.p. 140—142° (Found: C, 89·9; H, 6·6. $C_{34}H_{28}O$ requires C, 90·2; H, 6·2%); $\lambda_{max.}$ 245 and 265 nm (ε 9800 and 6900); τ 2·45—3·30 (m, 5 × Ph), 3·46 (d, *J* 11 Hz, =CH), 5·5 (d, *J* 11 Hz, CH), and 7·46 (s, OH).

Reaction of 1,1,3-*triphenylpropenyl-lithium* (1c) *with acetophenone.* The crude product (5·19 g) was an oil which contained one positional isomer (2; $R^1 = R^2$ = Ph, R^3 = Me) only (n.m.r.). A sample (2 g) was purified by dry column chromatography followed by recrystallisation from hexane–ethanol to give pure 2,3,5,5-*tetraphenylpent*-4-*en*-2-*ol* (0·3 g, 15%), m.p. 137·5—140° (Found: C, 88·75; H, 7·0. $C_{29}H_{26}O$ requires C, 89·25; H, 6·65%); $\lambda_{max.}$ 247 and 265 nm (ε 12,300 and 8900); τ 2·4—3·2 (m, 4 × Ph), 3·32 (d, *J* 11 Hz, =CH), 6·25 (d, *J* 11 Hz, CH), 8·05 (s, OH), and 8·41 (s, Me). The ratio of diastereoisomers could not be deduced from this spectrum.

Reaction of 1,1,3-*triphenylpropenyl-lithium* (1c) *with fluorenone.* The crude product (5·79 g) contained one isomer (2; R^1 = Ph, $R^2 + R^3$ = biphenyl-2,2'-diyl) only according to the n.m.r. spectrum. A sample (2 g) was purified by dry column chromatography and recrystallisation from hexane–ethanol. Pure 9-(1,3,3-*triphenylprop*-2-*enyl*)*fluoren*-9-*ol* (0·5 g, 25%) was obtained, m.p. 101—103° (Found: C, 90·3; H, 5·9. $C_{34}H_{26}O$ requires C, 90·65; H, 5·75%); $\lambda_{max.}$ 220, 232, 264, and 312 nm (ε 17,100, 16,200, 11,000, and 1600); τ 2·3—3·4 (m, 3 × Ph + fluorenyl), 3·95 (d, *J* 11·0 Hz, =CH), 5·95 (d, *J* 11·0 Hz, CH), and 7·82 (s, OH).

Reaction of 1,1,3-*triphenylpropenyl-lithium* (1c) *with benzaldehyde.* The crude product (8·96 g) contained one positional isomer only (2; $R^1 = R^2$ = Ph, R^3 = H) according to the n.m.r. spectrum. A sample (2 g) was purified by dry column chromatography and recrystallisation from hexane–ethanol. Pure 1,2,4,4-*tetraphenylbut*-3-*enol* (0·3 g) was

isolated as an oil (Found: C, 89·0; H, 6·2. $C_{28}H_{24}O$ requires C, 89·35; H, 6·4%); $\lambda_{max.}$ 220 and 259 nm (ε 15,800 and 12,200); τ 2·3—3·5 (m, 3 × Ph), 3·8 (d, *J* 11 Hz, =CH), 5·14 (d, deformed, *J* 11 Hz, CH), 6·2 (s, ⁻OH, overlapping), and 6·35 (q, deformed, CH). The ratio of diastereoisomers could not be deduced from this spectrum.

Reaction of 1,1-*diphenylpropenylsodium* (1a) *with* p-*nitrobenzaldehyde.* 1,1-Diphenylpropene (4·85 g) in dry tetrahydrofuran (10 ml) was added to a solution of sodium amide (0·025 mol) in liquid ammonia (250 ml). A red colour appeared. This solution was stirred 30 min. p-Nitrobenzaldehyde (4·56 g, 0·03 mol) in dry tetrahydrofuran (50 ml) was then added. The red colour was replaced by a green colour which persisted. After 30 s the reaction mixture was added to a solution of ammonium chloride (4·7 g) in liquid ammonia (150 ml). The product was then isolated as described above. The crude product (8·67 g) was an oil. A portion (2 g) was purified by dry column chromatography to give 1,1,6,6-tetraphenylhexa-1,5 diene (0·33 g), m.p. 106—107° (lit.,[17] 108°) [Found: C, 93·65; H, 6·95; *M*, 390 (ebullioscopic). Calc. for $C_{30}H_{26}$: C, 93·25; H, 6·75%; *M*, 386]; τ 2·60—3·0 (m, 4 × Ph), 3·95 (t, *J* 7·0 Hz, =CH), 7·72 (s, CH_2), and 7·79 (s, CH_2).

The reaction was repeated using a one-fold excess of p-nitrobenzaldehyde. The reactants were stirred 2 h before the reaction was quenched by addition to ammonium chloride. The yield of dimer was unchanged.

Carbonation of 1,1-*diphenylpropenylpotassium* (1a). To a stirred suspension of potassium amide (0·025 mol) in anhydrous liquid ammonia was added 1,1-diphenylpropene (4·85 g, 0·025 mol) in dry ether (30 ml). The red solution was stirred 30 min and then poured in a nitrogen atmosphere onto a large excess of powdered carbon dioxide. After 2 h, water (50 ml) was added. The aqueous layer was acidified and a white precipitate (2·0 g, 32%) was obtained. The n.m.r. indicated that one isomer only was present. One recrystallisation from acetic acid afforded 4,4-diphenylbut-3-enoic acid (Found: C, 80·65; H, 5·75. Calc. for $C_{16}H_{14}O_2$: C, 80·55; H, 5·85%); m.p. 116—117° (lit.,[18] 112—113°); $\lambda_{max.}$ 252 nm (ε 12,500); τ −0·8 (s, OH), 2·5—2·98 (m, 2 × Ph), 3·69 (t, *J* 7·5 Hz, =CH), and 6·72 (d, *J* 7·5 Hz, CH_2).

Carbonation of 1,1-*diphenylbutenylpotassium* (1b). The reaction was carried out as described above. 2-*Methyl*-4,4-*diphenylbut*-3-*enoic acid* (3·1 g, 49%) was isolated (Found: C, 80·85; H, 6·4. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·3%), m.p. 182—184°; $\lambda_{max.}$ 215 nm (ε 13,600); τ −0·85 (s, OH), 2·5—2·9 (m, 2 × Ph), 3·55 (dd), 4·82 (dd), and 5·10 (dd, ABX_3, J_{AB} 16·0, J_{AX} 6·0, and J_{BX} 2·0 Hz), and 8·22 (dd, *J* 6·0 Hz, Me).

When the carbonation reaction was allowed to stand overnight before work-up a solid (3·12 g, 50%) was isolated (Found: C, 81·2; H, 6·15. Calc. for $C_{17}H_{16}O_2$: C, 80·95; H, 6·3%), m.p. 100—103°; $\lambda_{max.}$ 252 (ε 9000); τ −0·85 (s, OH), 2·4—2·8 (m, 2 × Ph), 3·4 (dd), 4·72 (dd), and 5·0 (dd, ABX_3, J_{AB} 16·0, J_{AX} 6·0, and J_{BX} 2·0 Hz), 3·74 (d, *J* 10·0 Hz, =CH of 3-addition product), 6·5 (dd, *J* 6·5 Hz, Me of 1-addition product), and 8·55 (d, *J* 7·0 Hz, Me). Integration of the n.m.r. indicated that 2-methyl-4,4-diphenylbut-3-enoic acid and 2,2-diphenylpent-3-enoic acid were present in the ratio 53 : 47.

[16] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, p. 163.
[17] A. W. Schmidt and C. Hartmann, *Ber.*, 1941, **74B**, 1325.

Carbonation of 1,1,3-*triphenylpropenylpotassium* (1c). The reaction was carried out as described for (1a). 2,4,4-Triphenylbut-3-enoic acid (3·76 g, 48%) was isolated

(Found: C, 83·8; H, 5·9. Calc. for $C_{22}H_{18}O_2$: C, 83·9; H, 5·7%), m.p. 161—163° (lit.,[18] 166—167°); $\lambda_{max.}$ 255 nm (ε 17,881); τ —1·05 (s, OH), 2·4—3·05 (m, 3 × Ph), 3·37 (d, J 11·0 Hz, =CH), and 5·52 (d, J 11·0 Hz, CH).

[18] K. Zeigler, F. Crossman, H. Kleiner, and O. Schafer. *Annalen*, 1929, **473**, 1.