Reactions of Allene with Amines and Active Methylene Compounds; Adduct Formation in the Presence of Nickel Complexes

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Reactions of morpholine, pyrrolidine, di-n-propylamine, aniline, and n-butylamine with allene in the presence of a nickel salt and di-isopropoxyphenylphosphine have been studied. Mixtures of 1 : 1, two 1 : 2, and two 1 : 3 amine–allene adducts were formed, and with the exception of n-butylamine, the 1 : 3 adducts constituted >50% of the product amines. An essentially analogous reaction occurred with the active methylene compounds, diethyl malonate, ethyl acetoacetate, benzyl cyanide, and benzyl methyl ketone with the preferential formation of 1 : 3 adducts: the inclusion of either sodium phenoxide or sodium borohydride to the catalyst system was found necessary for reaction. The mechanism has been interpreted in terms of a 1 : 1 and 2 : 1 allene–nickel intermediate and a 3 : 1 allene–bisallyl-nickel intermediate. The specificity of reaction has been suggested to be a consequence of the σ, π character of the bis-π-allylnickel complex with preferential reaction of the nucleophilic active hydrogen compound at a π-allylnickel bond

WHILE transition metal catalysed reactions of 1,3-dienes with active methylene compounds and with amines have received considerable attention,[1,2] only one such telomerisation reaction of allene has been reported.[3] In the presence of a rhodium complex the formation of derivatives of 2,3-dimethylbutadiene was effected from reaction of two moles of allene and one of amine or active methylene compound; a similar reaction was observed with amines in the presence of palladium complexes but not with active methylene compounds.

We now report the reactions of amines and active methylene compounds with allene in the presence of catalytic quantities of nickel salts and di-isopropoxyphenylphosphine. The major product is a 3 : 1 allene adduct in almost all cases. Since the adducts incorporate a 1,3-diene unit, they are considered of potential use in the synthesis of alicyclic derivatives.

RESULTS

An amine or active methylene compound (25 mmol) was reacted with allene (75—90 mmol) in the presence of a nickel salt (0.5 mmol) and di-isopropoxyphenylphosphine (0.5 mmol) in a sealed tube.[4] A mixture of (1)—(5) was obtained from the reaction with amines, although the amounts of (1) produced were extremely small, and (3)—(5) were formed from the reaction with active methylene compounds (Tables 1 and 2). Hydrocarbons (6)—(8) were also formed in varying amounts.[5]

The structures were assigned on the basis of their spectral

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[1] R. Baker, A. H. Cook, D. E. Halliday, and T. N. Smith, *J.C.S. Perkin II*, 1974, **1511**, and references therein.

[2] R. Baker, A. H. Cook, and T. N. Smith, *J.C.S. Perkin II*, 1974, **1517**, and references therein.

[3] D. R. Coulson, *J. Org. Chem.*, 1973, **38**, 1483.

[4] Preliminary communication, R. Baker and A. H. Cook, *J.C.S. Chem. Comm.*, 1973, 487

[5] R. J. de Pasquale, *J. Organometallic Chem.*, 1971, **32**, 381.

data, the n.m.r. spectra of the morpholine–allene adducts being typical (Tables 3 and 4). The methyl protons of (4a) and (5a) occur at τ 8.11 and 8.32, characteristic of a methyl group on a 1,3-diene unit and a methyl group on an unconjugated olefinic bond, respectively. Another difference is shown by the methylene protons adjacent to nitrogen of (4a) and (5a) which are at τ 7.23 and 7.07 due to being allylic to one isolated olefinic bond and a conjugated diene, respectively. The spectrum of (3a) with the characteristic methyl group on a conjugated diene at τ 8.11 has been previously reported.

In general, the use of ethanol as solvent increased the conversion in the reactions with amines and reduced hydrocarbon formation. The effect of ethanol on the product ratio was also marked, giving an overall greater specificity (>70%) to (5).

No clear trend is apparent in the competition between 1 : 1, 2 : 1, and 3 : 1 adduct formation with different amines, and

TABLE 1

Reactions of amines with allene catalysed by nickel salts and di-isopropoxyphenylphosphine at 100° [a]

							Products				
Reactant	Ni(salt)$_2$	Ni : P	Allene : amine	Solvent	t/h	Reaction (%)	(1)	(2)	(3)	(4)	(5)
Morpholine	NiBr$_2$	1 : 1	3 : 1	EtOH	1	100		1	22	5	72
	NiBr$_2$	1 : 1	3 : 1	EtOH (×3)	1	48		1	17		82
	NiBr$_2$	1 : 1	3 : 1	HCONMe$_2$	1	47	11	7	34	10	38
	NiBr$_2$	1 : 1	3 : 1	C_6H_6	16	83	4	16	30	8	42
	NiBr$_2$	1 : 1	3 : 1	Et$_2$O	16	69	2	17	31	7	43
	NiBr$_2$	1 : 3	3 : 1	EtOH	1	100	8	2	24		66
	NiBr$_2$	1 : 1	6 : 1	EtOH	1	94		2	22		76
	Ni(acetate)$_2$	1 : 1	3 : 1	EtOH	1	70	4	16	28	5	47
	Ni(acac)$_2$ [b]	1 : 1	3 : 1	EtOH	16	52			20	18	62
Pyrrolidine	NiBr$_2$	1 : 1	3 : 1	EtOH	1	63	9	10	34		47
	NiBr$_2$	1 : 1	6 : 1	EtOH	1	100	7	8	32		53
n-Butylamine	NiBr$_2$	1 : 1	3 : 1	EtOH	1	83		22	34	10	34
	Ni(acetate)$_2$	1 : 1	3 : 1	EtOH	16	40		36	17	15	32
Di-n-propylamine	NiBr$_2$	1 : 1	3 : 1	EtOH	1	12			20	5	75
	NiBr$_2$	1 : 1	6 : 1	EtOH	1	44			32	5	63
Aniline	Ni(acac)$_2$ [b]	1 : 3	3 : 1		16 [c]	16			20	25	55

[a] In all cases Ni(salt)$_2$ (0.5mmol), solvent (2.5 ml), amine (25 mmol), and allene (75—90 mmol). [b] Sodium borohydride (0.2 mmol) added. [c] 75°.

TABLE 2

Reactions of active methylene compounds and allene catalysed by nickel salts and di-isopropoxyphenylphosphine in EtOH for 16 h [a]

						Products		
Reactant	Ni(salt)$_2$	Ni : NaOPh	Ni : NaBH$_4$	T/°C	Reaction (%)	(3)	(4)	(5)
Benzyl cyanide	Ni(acac)$_2$	1 : 1	1 : 0.5	75	21	25	18	57
	Ni(acac)$_2$	1 : 4		75	42	26	20	54
	Ni(acac)$_2$	1 : 4	1 : 0.5	75 [b]	64	37	17	46
	NiBr$_2$		1 : 3	75	12	21	20	59
Benzyl methyl ketone	Ni(acac)$_2$	1 : 1	1 : 0.5	75	22	14	23	63
	Ni(acac)$_2$	1 : 4	1 : 0.5	75	36	21	25	54
Diethyl malonate	Ni(acac)$_2$	1 : 1		100	76	21	12	67
	Ni(acac)$_2$		1 : 3	100	44	35	10	55
Ethyl acetoacetate	Ni(acac)$_2$	1 : 4		100	57	52	14	34

[a] Ni(salt)$_2$ (0.5 mmol), di-isopropoxyphenylphosphine (1.5 mmol), ethanol (2.5 ml), active methylene compound (25 mmol), allene (75—90 mmol). [b] 60 h.

TABLE 3

Spectroscopic properties of products from reaction of allene and morpholine

Product	N.m.r. (τ)	Mass spectrum (m/e)	I.r. (ν/cm^{-1})
(2a)	4.0—4.5 (1 H, m, vinylic) 4.72—5.12 (4 H, m, terminal olefinic) 6.40 (4 H, m, α-O) 7.15 (2 H, s, allylic) 7.20 (2 H, d, J 6 Hz, allylic) 7.66 (4 H, m, α-N)	167 (10%, M), 100 (100) 84 (34), 57 (59), 56 (37) 41 (42), 55 (26), 42 (30)	2 950, 2 800 1 640, 1 600 1 460, 1 290 1 012, 905 875, 815
(5a)	4.62—5.29 (6, H, m, terminal olefinic) 6.41 (4 H, m, α-O) 6.97 (2 H, s, allylic) 7.07 (2 H, s, allylic) 7.69 (4 H, m, α-N) 8.32 (3 H, s, methyl)	207 (7%, M), 105 (9) 100 (100), 56 (18) 42 (13), 41 (18), 39 (14)	2 950, 2,800 1 645, 1 600 1 460, 1 295 1 120, 1 018 903, 878
(4a)	4.8—5.28 (6 H, m, terminal olefinic) 6.41 (4 H, m, α-O) 6.97 (2 H, s, allylic) 7.23 (2 H, s, allylic) 7.69 (4 H, m, α-N) 8.11 (3 H, m, methyl)	100 (100%), 41, 56 39, 57, 105, 207 (M)	2 930, 2 800 1 640, 1 598 1 455, 1 115 902, 880

only n-butylamine does not generally yield more 3 : 1 adduct than 1 : 1 and 2 : 1 combined. Even with the allene : amine mole ratio reduced from the standard conditions of 3 : 1 to 1 : 1, morphine still yields 60% of 3 : 1 adducts in a greatly reduced reaction. Increasing the allene : amine ratio to 6 : 1 does not markedly effect the product ratio, but the reaction rate is substantially increased. Thus, with pyrrolidine, an increase from 63% reaction to total conversion of amine was observed with the change of allene : amine mole ratio from 3 : 1 to 6 : 1, and a similar result was also found with di-n-propylamine.

In contrast to reactions with amines, whilst the use of ethanol was beneficial for the conversions in the reactions of allene with active methylene compounds, no marked effect was observed on the product ratios. A co-catalyst of either sodium borohydride or sodium phenoxide was essential for these reactions,[2] however, and the best reaction conditions were obtained with nickel acetylacetonate, di-isopropoxyphenylphosphine, and sodium phenoxide in the ratio 1 : 3 : 4. A catalyst system consisting of nickel bromide or acetate, di-isopropoxyphenylphosphine, and sodium phenoxide afforded only polymer. This observation is consistent with the formation of phenol from reaction of sodium phenoxide and the active methylene compound. The presence of phenol has been observed to promote the polymerisation of allene.[5] In the presence of nickel acetylacetonate, phenoxide would be regenerated from any phenol produced.

TABLE 4

Spectroscopic properties of (5) formed by reaction of allene and active methylene compounds

Compound	N.m.r. (τ)	Mass spectrum (*m/e*)	I.r. (ν/cm^{-1})
(5f)	2.74 (5 H, s, phenyl) 4.76—5.3 (6 H, m, terminal olefinic) 6.13 (1 H, t, *J* 8 Hz, benzylic) 7.08 (2 H, s, allylic) 7.30 (2 H, d, *J* 8 Hz, allylic) 8.31 (3 H, s, methyl)	235 (30%, *M*), 234 (30) 121 (100), 117 (58) 93 (76), 91 (58) 79 (66)	3 080, 3 030 2 910, 2 245 1 645, 1 600 1 498, 1 455 900, 700 760, 700
(5g)	2.80 (5 H, s, phenyl) 4.85—5.3 (6 H, m, terminal olefinic) 6.21 (1 H, t, *J* 8 Hz, benzylic) 7.12 (2 H, s, allylic) 7.05—7.4 (2 H, m, allylic) 8.07 (3 H, s, acetyl), 8.34 (3 H, s, methyl)	254 (4% *M*), 134 (35) 121 (75), 105 (45) 91 (100), 77 (33) 43 (83)	3 090, 3 030 2 980, 2 910 1 715, 1 600 1 495, 1 460 1 360, 1 160 898, 755, 707
(5h)	4.76—5.28 (6 H, m, terminal olefinic) 5.86 (4 H, q, *J* 7 Hz, methylene) 6.53 (1 H, t, *J* 7.5 Hz, methyne) 7.06 (2 H, s, allylic) 7.17 (2 H, d, *J* 7.5 Hz, allylic) 8.31 (3 H, s), 8.73 (6 H, t, *J* 7 Hz, methyl)	280 (weak, *M*), 91 (100%) 105 (92), 102 (82), 41 (63) 79 (50), 77 (47) 161 (36)	2 950, 1 745—15 1 645, 1 600 1 455, 1 375 1 270, 1 235 1 150, 1 040, 900
(5i)	4.78—5.28 (6 H, m, terminal olefinic) 5.80 (2 H, q, *J* 7 Hz, methylene) 6.32—6.60 (1 H, m, methyne) 7.07 (2 H, s), 7.17—7.30 (2 H, m, allylic) 7.85 (3 H, s), 8.31 (3 H, s), 8.73 (3 H, t, *J* 7 Hz, methyl)	250 (0.5%, *M*), 149 (37) 148 (28), 133 (25), 120 (45) 105 (80), 91 (40) 43 (100)	2 900, 1 735 1 710, 1 645 1 600, 1 450 1 245, 990 900

The reduced reactivity of active methylene compounds with respect to amines necessitates the most reactive conditions being employed, and in all reactions, a 3 : 1 ratio of di-isopropoxyphenylphosphine to nickel salt and ethanol was used. In general, there was a greater proportion of hydrocarbons formed in the methylene reactions than those of amines, which is a probable consequence of their reduced reactivity.

DISCUSSION

Under the conditions of the present reactions, a nickel salt together with di-isopropoxyphenylphosphine has previously been suggested to be a source of a nickel(0) complex.[1,2] Formation of the bis-π-allylnickel species (11) has been suggested to proceed *via* a stepwise mechanism involving a 1 : 1 and 2 : 1 allene–nickel species (Scheme).[5,6] Although no 2 : 1 allene–nickel intermediates have been isolated, the formation of 1 : 1 and 2 : 1, together with 3 : 1 allene–amine adducts in the present reactions with amines is consistent with the interception of a series of such intermediates with the nucleophilic reagent. Further evidence for this is found in the reactions with active methylene compounds where, owing to the reduced reactivity of these reagents, only 3 : 1 adducts are obtained.

The formation of predominantly 3 : 1 adducts in the present reactions with allene and amines and mainly 3 : 1 adducts with active methylene compounds contrasts with formation of analogous 2 : 1 adducts in the presence of rhodium or palladium complexes.[3] Formation of the bis-π-allylnickel intermediate (11) would appear to be particularly favoured compared with the comparable rhodium or palladium complex and might possess some additional inherent stability. The major product (5) in the present reactions results from reaction at the allyl–nickel bond adjacent to the *exo*-methylene group of (11). Such an intermediate has been isolated [6,7] in studies on the oligomerisation reactions of allene and a detailed analysis has been reported.[8] The *X*-ray structure of (11),

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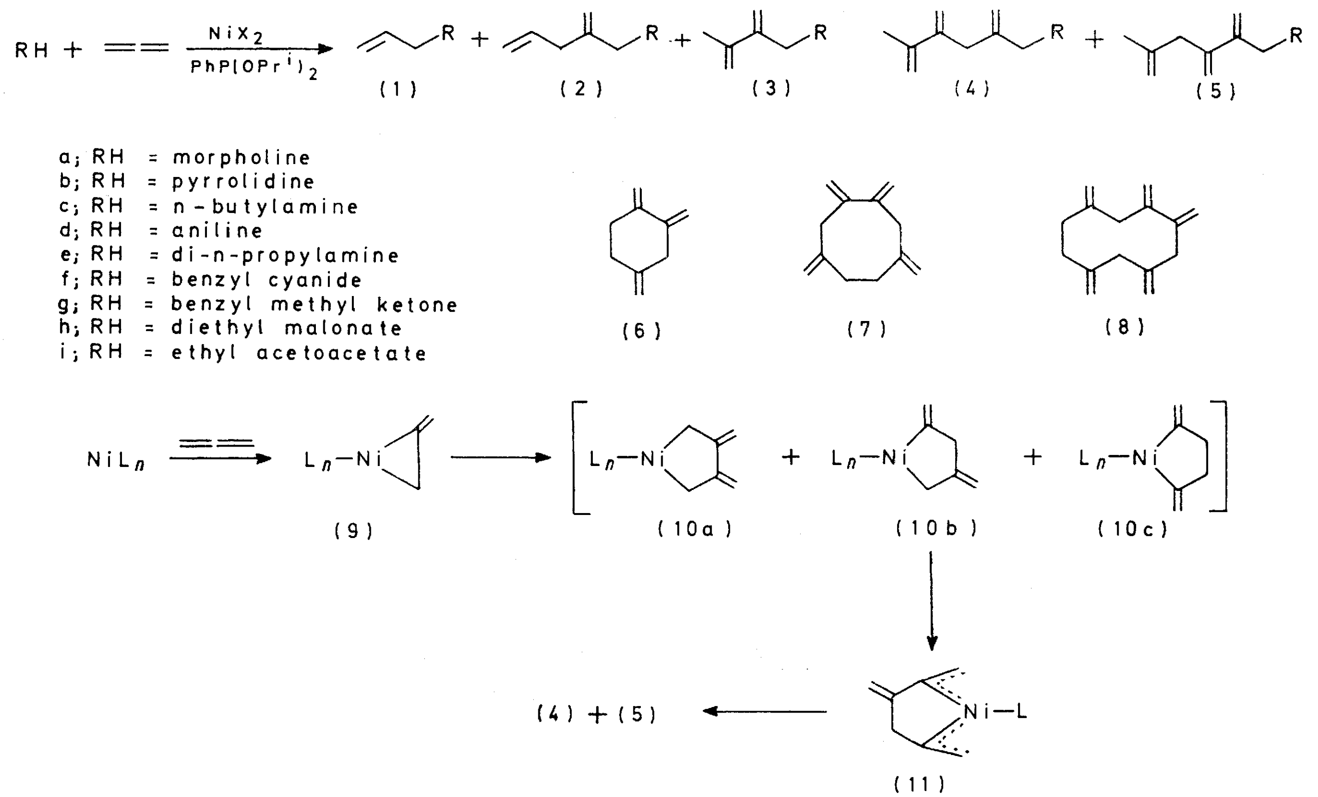
[6] M. Englet, P. W. Jolly, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1972, **11**, 136.

[7] S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Comm.*, 1971, 863.

[8] B. L. Barnet, C. Kruger, and Y.-H. Tsay, *Angew. Chem. Internat. Edn.*, 1972, **11**, 137.

where the ligand is tricyclohexylphosphine, indicated a lack of symmetry of the two allyl groups. The allyl group conjugated with the *exo*-methylene double bond, whilst not completely symmetrical, is more so than the other. This can be considered as evidence that the bis-allyl species has π, σ-character (12). If this is the case under the present reaction conditions, then it can be suggested that a preferential reaction of amine and active methylene compound occurs at the π-allyl- rather than the σ-allyl-nickel portion of the molecule.

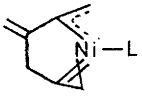


a; RH = morpholine
b; RH = pyrrolidine
c; RH = n-butylamine
d; RH = aniline
e; RH = di-n-propylamine
f; RH = benzyl cyanide
g; RH = benzyl methyl ketone
h; RH = diethyl malonate
i; RH = ethyl acetoacetate

SCHEME

The 'π, σ' nature of bis-allylnickel species is a general phenomenon and detailed studies have indicated that, in the presence of certain ligands, the bisallylnickel complexes (13) and (14) are good representation of these intermediates produced from butadiene and isoprene.[9,10] The postulate that the selectivity produced in the present reaction is due to preferential reaction of nucleophiles at the π-allyl bond is supported by two other observations. Nickel catalysed reaction of isoprene and diethyl malonate yields (15) as the major product derived from the intermediate (14),[11] and in the following paper we describe experiments demonstrating that reaction of electrophilic reagents with (12) take place predominantly at the σ-allyl bond.[12]

Our suggestions are exclusively based on experimental observations and their value might be restricted to that of the ability to predict the course of these and similar reactions. In both series of reactions, formation of (5) is accompanied by appreciable amounts of (4), particularly with the active methylene compound adducts. The selectivity is, therefore, not exclusive and might be a consequence of an equilibrium of (11) and (12). Amines have a greater reactivity in these reactions compared to active methylene compounds and the smaller selectivity



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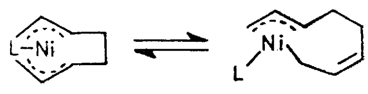

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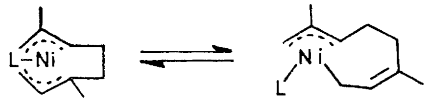

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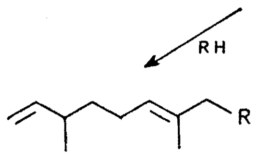

(15)

R = $CH(CO_2Et)_2$

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[9] J. M. Brown, B. T. Golding, and M. J. Smith, *Chem. Comm.*, 1971, 1240.

[10] B. Barnett, B. Bussemeser, P. Heimbach, P. W. Jolly, C. Kruger, L. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, 1972, 1457.

[11] R. Baker, A. Onions, R. J. Popplestone, and T. N. Smith, *J.C.S. Perkin II*, 1975, 1133.

[12] R. Baker and A. H. Cook, *J.C.S. Perkin II*, following paper.

observed with reactions of the latter might be associated with involvement of the corresponding carbanions.

No 1 : 1 adduct is found with active methylene compounds consistent with the smaller reactivity compared to amines and, in both series, formation of (3) is favoured over that of (2) [exclusive formation of (3) is found with active methylene compounds]. It would appear that (10a) is the most important contributor of the bisallene-nickel complexes formed in solution.

EXPERIMENTAL

Reagent amines and active methylene compounds were distilled before reaction. Solvents where applicable, were purged with nitrogen before use. Allene was used as supplied (97%; B.D.H.). Di-isopropoxyphenylphosphine and anhydrous nickel salts were prepared as before.[1,2]

All reactions were performed in sealed Carius tubes (100 ml) and the allene distilled into the reaction vessel on a vacuum line. The sealed tubes were placed in a constant temperature oil-bath and, after the prescribed reaction time, opened and the mixtures filtered and analysed by g.l.c. Yields are expressed in terms of percentage conversion of active hydrogen compound with calibration of the g.l.c. with standard mixtures.

A Pye 104 chromatograph was employed for the quantitative analysis through a 5 ft × 0.25 in 10% E 301 glass column. Fractional distillation gave a crude separation of products followed by preparative g.l.c. on a Pye 105 chromatograph on a 15 ft × 0.375 in, 25% E 301 glass column.

General Reaction Procedure: Reaction of Allene with Morpholine.—A mixture of anhydrous nickel bromide (0.5 mmol), di-isopropoxyphenylphosphine (0.55 mmol), morpholine (25 mmol), ethanol (2.5 ml), and allene (75—90 mmol; 5—6 ml liquid allene) were heated for 1 h at 100°. Morpholine was totally converted to a mixture of (2a) (1%), (3a) (22%), (4a) (5%), and (5a) (72%). A small amount of the cyclic allene trimer (6), tetramer (7), and pentamer (8), were also obtained. Fractional distillation gave a first fraction of ethanol (1.85 g) followed by a fraction containing a mixture of (1a), (2a), (3a), (6), and (7) (0.56 g), b.p. 40—80° at 20 mmHg, a fraction of (7), (3a), (4a), (5a) (0.31 g), b.p. 80—120° at 20 mmHg and a final fraction (2.62 g), 90—105° at 1 mmHg containing (4a), (5a), (8), and phenyldi-isopropoxyphosphine oxide. Complete separation was achieved by preparative g.l.c.

A similar procedure was employed for the other amines and the products were isolated from wide fractions taken on distillation. Spectroscopic properties of the products from allene and morpholine are summarised in Table 3 and similar properties were displayed by the other amine adducts.

Reactions of Allene and Active Methylene Compounds.—*Benzyl cyanide.* Reaction of nickel acetylacetonate (0.5 mmol), di-isopropoxyphenylphosphine (1.5 mmol), sodium borohydride (0.2 mmol), sodium phenoxide (2 mmol), ethanol (2.5 ml), benzyl cyanide (25 mmol), and allene (75—90 mmol) gave a 64% conversion of benzyl cyanide after 60 h at 75° to (3f) (37%), (4f) (17%), and (5f) (46%). Three cyclic hydrocarbons (6)—(8) were also formed in small amounts. Fractional distillation gave a crude separation of products. As with amine–allene reactions, final separation was achieved by preparative g.l.c.

A similar procedure was employed for the other active methylene compounds and the products were isolated from wide fractions taken on distillation. Spectroscopic properties of (5) are summarised in Table 4; those of (3) have been reported.[3] In each case (4) was only obtained as a 30—50% mixture with (5) but the n.m.r. signals for the methyl protons of (4) occurred as follows: (4f), τ 8.11; (4g), 8.14; (4h) 8.10, (4i), 8.09.

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