Reactions of Allene and Aldehydes; Adduct Formation in the Presence of Nickel Complexes

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Reaction of the bis-π-allylnickel complex formed from three moles of allene with acetaldehyde or acrolein and subsequent treatment with aqueous potassium cyanide has been demonstrated to give two isomeric alcohol adducts in a ratio of *ca.* 7 : 1. The specificity of reaction has been suggested to be a consequence of the σ, π-character of the bis-π-allylnickel complex with addition at the σ-allyl system. The reaction was enhanced by the addition of organophosphine ligands and dimethylformamide and depressed by triphenyl phosphite. Hydrocarbons formed by interaction of the solution containing the allene–nickel complexes with aqueous potassium cyanide has yielded information on the structures of these bis-π-allylnickel complexes.

REACTIONS of allene with active methylene compounds and amines have been reported to be catalysed by palladium and rhodium complexes [1] and, in the preceding paper, by nickel complexes.[2] We described the nickel catalysed reactions, which yield predominantly 3 : 1 allene–reagent adducts as involving formation of an allene trimer bis-π-allylnickel complex.[3-9] Reaction of acetaldehyde or acrolein with the complex produced from

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

[2] R. Baker and A. H. Cook, preceding paper; R. Baker and A. H. Cook, *J.C.S. Chem. Comm.*, 1973, 487.

[3] S. Otsuka, A. Nakamura, K. Tani, and S. Ueda, *Tetrahedron Letters*, 1969, 297.

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[5] S. Otsuka, K. Tani, and T. Yamagata, *J.C.S. Dalton*, 1973, 2491.

[6] S. Otsuka, A. Nakamura, T. Yamagata, and K. Tani, *J. Amer. Chem. Soc.*, 1972, **94**, 1037.

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

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

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

allene and bis(cyclo-octadiene)nickel(0) has now been demonstrated to yield 3 : 1 allene–aldehyde adducts with substantial specificity. On the basis of the selectivity obtained in these reactions compared to those with nucleophilic reagents, some general comments have been made regarding the reactivity of the trimeric allene-nickel species.

RESULTS

Typically, a slurry of bis(cyclo-octadiene)nickel(0) in ether was prepared from nickel acetylacetonate (0.02M) [10] and allene (0.07—0.1M) added. Aldehyde (0.025M) was then either added to the resulting red solution at −78° which was then allowed to warm slowly to room temperature or the solution was first treated with an organophosphorus compound (0.02M) at *ca.* −30° followed by the addition of the aldehyde. The reaction was terminated by the addition of aqueous potassium cyanide. Two isomeric alcohols (1) and (2) were obtained (Table) together with the cyclic hydrocarbons (3)—(5) and linear hydrocarbons (6)—(8) in varying yields. Formation of a cyclic allene hexamer oligomer was indicated by g.l.c.–mass spectroscopy and also a linear hexamer (9) assigned on the basis of its n.m.r. spectrum.

Reaction of allene with acetaldehyde and acrolein catalysed by bis(cyclo-octa-1,5-diene)nickel in ether [a]

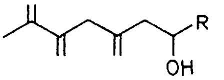
	Additive	Reaction (%) [b]	(1)	(2)
Acetaldehyde		22	7	1
	PPh$_3$	33	6	1
	P(OPh)$_3$	5	7	1
	P(cyclohexyl)$_3$	29	7	1
	DMF [c]	32	6	1
	EtOH [c]	18	7	1
Acrolein		26	5	1

[a] 1.5 Fold excess of aldehyde. [b] Based on nickel acetylacetonate. [c] 1 : 1 Mixture of solvents.

Whilst (1a) was obtained pure, (2a) was obtained as a mixture (2 : 3) with (1a): (1a), τ (CCl$_4$) 4.8—5.18 (6 H, m, terminal olefinic), 6.16 (1 H, sext., J 6 Hz, α-OH), 7.01 (2 H, s, allylic), 7.7 (1 H, s, OH), 7.92 (2 H, 2 × d, J 6 Hz, allylic, β-OH), 8.10 (3 H, s, CH$_3$), 8.88 (3 H, d, J 6 Hz, CH$_3$); (1a) and (2a), τ (CCl$_4$) 4.75—5.30 (6 H, m, terminal olefinic), 5.8—6.5 (1 H, m, α-OH), 7.01 (2 H, s, allylic), 7.4, 7.6 (1 H, 2 × s, OH), 7.88 and 7.92 [2 H, 2 (2 × d), J 6 Hz, allylic, β-OH], 8.32 and 8.10 (3 H, 2 × s, CH$_3$), and 8.83 and 8.88 (3, 2 × d, J 6 Hz, CH$_3$). The signals of the two olefinic methyl group protons of (2a) and (1a) are characteristic of their respective positions, α to an olefin and α to a 1,3-diene, respectively. The allylic methylene protons (which are also β-OH) are shifted downfield by τ 0.13 in (2a) compared with (1a) due to the 1,3-diene unit, and the chirality of the molecules is illustrated by the two, almost superimposed, doublets for these protons.

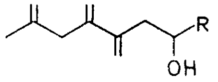
The cyclic oligomers (3)—(5) were assigned on comparison of published spectra [3,4] and the linear allene–trimer oligomer (6) has τ (CCl$_4$) 4.82–5.31 (6 H, m, terminal olefinic), 7.05 (2 H, s, allylic), 8.10 (3 H, s, methyl), and 8.32 (3 H, s, methyl). Only small amounts of the other hydrocarbons were formed in the reactions involving the aldehydes but a mixture of (6) (38%), (3) (6%), (7) and (8) (40%), (4) (6%), (5) (4%), and (9) (1%) and uncharacterised oligomers (5%) was obtained by treatment of the red solution, derived from allene and bis(cyclo-octadiene)nickel(0), with 25% aqueous potassium cyanide solution.

Separation of (7) and (8) could not be achieved but it is clear from the n.m.r. of the mixture, τ (CCl$_4$) 4.8—5.3 (8 H, m, terminal olefinic), 7.09 (3 H, s, allylic), 7.34 (1 H, s, allylic), 8.11 (1.5 H, s, methyl), and 8.32 (4.5 H, s, methyl), that (7) and (8) are present in 1 : 1 ratio. This was further confirmed by the formation of two products, (10) and (11), in the ratio 1 : 1 on reaction of the mixture with tetracyanoethylene. The structure of (9) was assigned on the basis of n.m.r., τ (CCl$_4$) 4.8—5.28 (12 H, m, terminal olefinic), 7.04 (4 H, s, allylic), 7.88 (4 H, s, allylic), and 8.10 (6 H, s, methyl).



(1)

a; R = CH$_3$
b; R = CH=CH$_2$



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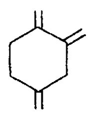
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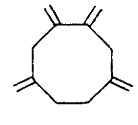
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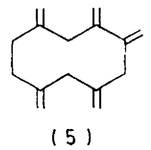
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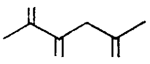
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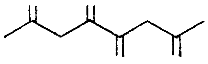
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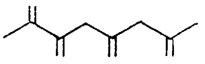
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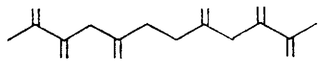
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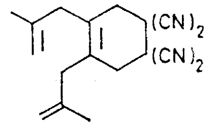
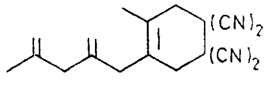


(10)



(11)

DISCUSSION

Reaction of allene with bis(cyclo-octadiene)nickel(0) [Ni(COD)$_2$] has been extensively investigated and shown to yield the hydrocarbons (3)—(5).[5] In the absence of added ligands, (5) was the major product. A multistep reaction pathway was proposed where the nickel(0) species acted as templates for the oligomerisation by forming bis-π-allylnickel intermediates (12)—(14).

In the present reactions, two products (1) and (2) were formed from reaction of allene and aldehyde, both derived from the bis-π-allylnickel species (12). Reaction of aldehydes with bis-π-allylnickel halide and dodecatrienylnickel has previously been reported to give good yields of alcohols.[11,12] *X*-Ray and n.m.r. studies have

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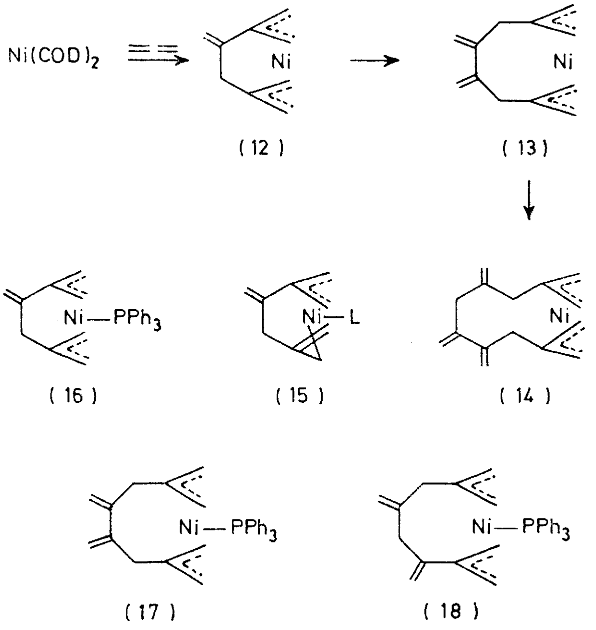
[10] *Inorg. Synth.*, 1974, **15**, 5.

[11] E. J. Corey and M. F. Semmelhack, *J. Amer. Chem. Soc.*, 1967, **89**, 2755.

[12] R. Baker, B. N. Blackett, R. C. Cookson, R. Cross, and D. P. Madden, *Chem. Comm.*, 1971, 343.

already shown that, in the presence of certain ligands, the structure of (12) is more closely represented as a σ,π-allylnickel species (15).[9] From the present results it is apparent that reaction of the aldehyde occurs preferentially at the σ-allylnickel bond. In the experiments with no added organophosphorus ligand, equilibrium formation of the σ,π-allyl form would require an alternative co-ordinating ligand. A degree of σ,π-allyl bonding might be produced as a consequence of the solvent or the presence of cyclo-octadiene from the bis(cyclo-octadiene)-nickel. The effectiveness of dimethylformamide is consistent with the strongly co-ordinating nature of this solvent.



(12) (13)

(16) (15) (14)

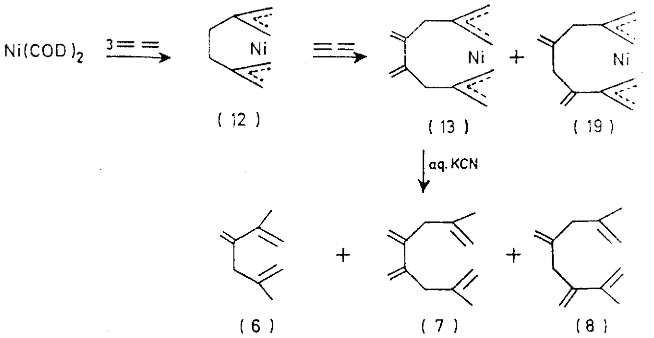
(17) (18)

The present results are in sharp contrast to the reactions of nucleophilic reagents such as amines or active methylene compounds with allene where reaction occurs predominantly at the π-allyl system of (15).[2] Based on these experimental results an important generalisation can, therefore, be suggested that bis-π-allylmetal intermediates which have the ability to exist as σ,π-allyl structures will display predictive regioselectivity towards nucleophilic and electrophilic reagents.

Further evidence on the nature of the bis-π-allylnickel complexes formed from allene in the presence of bis-(cyclo-octadiene)nickel below −30° has been obtained by the addition of triphenylphosphine.[9] Immediate precipitation of the orange complex (17) resulted and the orange-red complex (16) was obtained from the filtrate. The relative amounts obtained indicated that the initial solution contained (12) and (13) in roughly equal amounts. The observation of only one allene-tetramer bis-π-allylnickel species prompted a discussion of the selective addition of allene to (12) at the allylnickel bond adjacent to the *exo*-methylene group.[5]

This assessment has not, however, been confirmed in the present reactions and addition of aqueous potassium cyanide to the mixture obtained from bis(cyclo-octadiene)nickel and allene at −30° yields three major products (6)—(8) in the relative ratio *ca.* 2 : 1 : 1. From this the presence of the intermediate nickel species (12), (13), and (19) are clearly indicated (Scheme). The tetramer complexes (13) and (19) are considered to arise from an unselective reaction of allene at the two allyl groups of (12). The stability of the resulting bisallyl-triphenylphosphinenickel complex could be a determining feature of the observed ' selective ' formation of only one tetramer complex on addition of triphenylphosphine to the reaction mixture. It is of significance that when aqueous cyanide is added to the mixture derived from bis(cyclo-octadiene)nickel (1 equiv.), triphenylphosphine (1 equiv.), and allene at −10°, the ratio of hydrocarbons (7) and (8) found is *ca.* 6 : 1; the presence of triphenylphosphine apparently favours formation of (17) over (18).

In all experiments only one cyclic tetramer (4) and pentamer (5) are formed in any significant concentration, derived from (13). An explanation of this and the earlier results is that (19) might be a precursor to polymer or higher oligomers and the organophosphine adduct is too unstable to be isolated. At no time was an alcohol observed which was derived from the allene-tetramer bis-π-allylnickel complexes present in solution. An analogous result was found from reaction of carbon monoxide with the mixture of the allene–nickel complexes derived from bis(cyclo-octadiene)nickel; a cyclic ketone derived from the trimeric species was the only product other than hydrocarbon observed. There is no apparent reason for the relative inertness of the tetrameric intermediates, and their formation to constitute *ca.* 50% of the solution of intermediates is a limiting feature of the present reactions. No reaction was observed with formalin solution, formaldehyde gas, or with benzaldehyde.



SCHEME

EXPERIMENTAL

Anhydrous nickel acetylacetonate was obtained by vacuum dehydration of the dihydrate by heating at 80° and 1 mmHg for 16 h. Cyclo-octa-1,5-diene was distilled and stored over molecular sieves before use. Triphenylphosphine was recrystallised from benzene-light petroleum and tricyclohexylphosphine was prepared as described by Issleib and Brack [13] and isolated as the carbon disulphide

[13] K. Issleib and A. Brack, *Z. anorg. Chem.*, 1954, **277**, 258.

adduct. This was stored without deterioration, and, when required, the phosphine, m.p. 74—78° was liberated by heating at 100° and 20 mmHg. All other reagents were used as supplied.

A Pye 104 chromatograph was employed for all g.l.c. analysis (5 ft × $\frac{1}{4}$ in; 10% E 301; glass column) and a Pye 105 chromatograph for all preparative g.l.c. (15 ft × $\frac{5}{8}$ in; 25% E 301 glass column).

Preparation of the 'Allene–Nickel' Bisallylic Intermediates.—A solution of $Ni(COD)_2$ in ether was prepared as described.[10] Further diethyl ether (20 ml) was added and the resulting slurry cooled to −78°. Allene (10—12 ml) was condensed into the reaction mixture which was allowed to warm slowly to *ca.* −35°. A red solution of the allene–nickel species gradually formed. After 2—3 h at this temperature $Ni(COD)_2$ dissolved, and the formation of the allene–nickel bisallylic intermediates was regarded as essentially complete. This solution of the complexes subsequently formed the starting point for all reactions.

Reaction of 'Allene–Nickel' Complexes with Acetaldehyde.—The ether solution of the 'allene-nickel' complexes derived from nickel acetylacetonate (6.1 g, 0.023M) was cooled to −78° and acetaldehyde (3 ml, 0.05M) added dropwise. The mixture was allowed to warm slowly to room temperature and stirred for a further 16 h. Aqueous potassium cyanide solution (25%; 0.15M) was added and the solution stirred for 2 h. Extraction with diethyl ether, followed by washing with water and drying ($CaSO_4$) afforded crude material (7.5 g). Distillation (20° and 1 mmHg) of some of the cyclo-octadiene and other low boiling material left product (3.8 g). This was chromatographed on silica gel and light petroleum and light petroleum–diethyl ether (98 : 2) eluted cyclo-octadiene and allene tetramer, pentamer, and higher uncharacterised oligomers. The alcohol products (0.74 g) (22%; based on nickel acetylacetonate) were eluted with light petroleum–diethyl ether (80 : 20) and the ratio of the isomers (1a) and (2a) was determined to be 7 : 1 from g.l.c. and n.m.r. analysis: (1a), $\nu_{max.}$ 3 400, 2 900, 1 600, 1 450, 1 380, 1 120, 1 080, and 900 cm^{-1}, *m/e* 166 (2%, *M*), 107 (100), 91 (90), 83 (60), 79 (67), and 45 (75); (2a), *m/e* 166, 148, 133, 121, 105, 93, 91, 79, 43, and 41.

Very little trimer hydrocarbon (<5% total product) was observed in the g.l.c. analysis of the crude material, but the linear trimer hydrocarbon was isolated by preparative g.l.c. of the distilled fraction.

Reaction of Triphenylphosphine-stabilised 'Allene–Nickel' Bisallylic Intermediates with Acetaldehyde.—A solution of triphenylphosphine (5.0 g, 0.02M) in diethyl ether (15 ml) was added to a diethyl ether solution of the 'allene–nickel' complexes [derived from nickel acetylacetonate (6.3 g, 0.024M)] at *ca.* −40°. The mixture was stirred for 2 h at this temperature and an orange-red precipitate was slowly formed. The mixture was cooled to −78° and acetaldehyde (3 ml) added. After slowly warming to ambient temperature, the mixture was stirred for a further 16 h. Subsequent reaction with 25% aqueous potassium cyanide for 2 h, extraction with ether, washing with water, drying ($CaSO_4$), and removal of solvent gave the crude product (10.7 g). Distillation (20° and 1 mmHg) of some of the cyclo-octadiene and low boiling products afforded precipitation of some triphenylphosphine, and filtration yielded material (6.0 g). This was chromatographed; triphenylphosphine was eluted with light petroleum–diethyl ether (95 : 5) and a 6 : 1 mixture of alcohols (1a) and (2a) (1.21 g; 33% based on nickel acetylacetonate) was obtained.

An analogous procedure was adopted for other similar reactions.

Reaction of 'Allene–Nickel' Complexes with Acrolein.—Acrolein (3 ml) was added to a solution of 'allene–nickel' complexes [derived from nickel acetylacetonate (5.1 g)] in diethyl ether (15 ml) at −78°. The mixture was allowed to warm to ambient temperature and stirred for 16 h. After treatment with aqueous potassium cyanide, extraction with ether, washing with water, drying ($CaSO_4$), evaporation of solvent, and distillation (20° and 1 mmHg) of low boiling components the residue of crude product (3.1 g) was column chromatographed. Elution with light petroleum–diethyl ether (80 : 20) gave a 4 : 1 mixture of isomeric alcohols (1b) and (2b) (0.88 g; 26% based on nickel acetylacetonate), τ (CCl_4) 3,75—4.40 (1 H, m, vinylic), 4.62—5.61 (8 H, m, terminal olefinic), 6.55—7.00 (1 H, m, α-OH), 6.80 (1 H, s, OH), 6.98 (2 H, s, allylic), 7.57 and 7.72 (2 H, d, allylic and β-OH), 8.10, and 8.32 (3 H, s, methyl), $\nu_{max.}$ 3 400, 3 080, 2 920, 1 645, 1 600, 1 445, 1 030, 990, 910, and 895 cm^{-1}, *m/e* 178 (weak, *M*), 107 (70%), 91 (80), 79 (72), 55 (67), 41 (100), and 39 (81).

Reaction of 'Allene–Nickel' Complexes with Aqueous Potassium Cyanide.—Potassium cyanide solution (10 g in 40 ml water) was added to an ether solution of 'allene–nickel' complexes [formed from nickel acetylacetonate (3.4 g)] at −30°. The mixture was stirred vigorously and warmed to room temperature. After a further 4 h stirring, the mixture was ether extracted, washed with water, dried ($CaSO_4$) and, on evaporation of solvent gave crude product (3.1 g). G.l.c. analysis showed formation of linear trimer hydrocarbon (6) (38%), cyclic trimer hydrocarbon (3) (6%), linear tetramer hydrocarbons (7) and (8) (40%) (one peak response on g.l.c.), cyclic tetramer hydrocarbon (4) (6%), pentamer hydrocarbon (5) (4%), linear hexamer hydrocarbon (9) (1%), and uncharacterised oligomers (5%). The products were separated by preparative g.l.c. after a preliminary distillation (20° and 1 mmHg). The linear hydrocarbons (7) and (8) had identical retention times on the standard analytical column and on 5 ft 10% SE 30, 15 ft 15% PPGA, and 5 ft 15% Carbowax 20M columns. However, n.m.r. indicated a mixture, which was confirmed by formation of tetracyanoethylene adducts: (6), *m/e* 122 (41%, *M*), 107 (100), 93 (62), 91 (70), 79 (75), 77 (28), 41 (28), and 39 (30); (7) and (8), *m/e* 162 (*M*), 147, 120, 107, 105, 91, 79, 77, 41, and 39; (9), *m/e* 242 (1%, *M*), 105 (72), 91 (76), 81 (35), 79 (64), 77 (50), 41 (100), and 43 (50).

Reaction of Linear Tetramer Allene Hydrocarbons with Tetracyanoethylene.—The mixture of hydrocarbons in tetrahydrofuran–carbon tetrachloride (75 : 25) was treated with a molar excess of a tetrahydrofuran solution of tetracyanoethylene. The resulting mixture was left at room temperature for 30 min and then analysed by g.l.c. Two products were formed, which were separated by preparative g.l.c. and characterised by n.m.r. as the products of a mixture of hydrocarbons (10) and (11) (1 : 1): (10), oil, τ (CCl_4) 5.10 and 5.25 (4 H, 2 × s, terminal olefinic), 7.00 (2 H, s, allylic), 7.16 (4 H, s, allylic, α-CN), and 8.27 (6 H, s, methyl), *m/e* 290 (27%, *M*), 91 (49), 81 (45), 77 (40), 55 (57), 43 (72), 41 (100), and 39 (63); (11), oil, τ (CCl_4) 5.1—5.35 (4 H, m, terminal olefinic), 7.00 and 7.10 (4 H, 2 × s, allylic), 7.22 and 7.37 (4 H, 2 × s, allylic, α CN), and 8.23 and 8.34 (6 H, 2 × s, methyl), *m/e* 290 (24%, *M*), 81 (38), 79 (42), 55 (67), 43 (95), 41 (100), and 39 (70).

Reaction of Allene with $Ni(COD)_2$ *(1 Equiv.) and Triphenylphosphine (1 Equiv.) and Subsequent Reaction with Aqueous*

Potassium Cyanide.—Allene was reacted with a mixture of $Ni(COD)_2$ [derived from nickel acetylacetonate (3.0 g)] and triphenylphosphine in diethyl ether (30 ml) at −10°. The resulting clear orange-red solution was treated with aqueous potassium cyanide (25%) at −10°, allowed to warm to room temperature, and stirred for 4 h. G.l.c. analysis of the reaction mixture after ether extraction identified the following products: linear trimer hydrocarbon (6) (52%), cyclic trimer hydrocarbon (3) (14%), linear tetramer hydrocarbon (7) and (8) (10%), cyclic tetramer hydrocarbon (4) (20%), and higher oligomers (4%). The linear tetramer hydrocarbons (7) and (8) were analysed by n.m.r. after preparative g.l.c. and shown to be in the ratio *ca.* 6 : 1.

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