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REACTION OF AMINOALCOHOLS WITH BUTADIENE CATALYSED BY PALLADIUM COMPLEXES

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Abstract—Reactions of amino alcohols $RNHCH_2CH_2OH$ (R = methyl, ethyl, n-Bu, T-Bu, Ph. $PhCH_2$-, $-CH_2CH_2OH$) and diisopropanolamine with buta-1, 3-diene in the presence of catalytic quantities of palladium acetylacetonate and triphenylphosphine have been studied. With two molar equivalents of butadiene, exclusive formation of the N-(octadienyl) amino alcohols occurs (except where R = Ph) the N-2, 7 octadienyl aminoalcohol being formed in ≥ 96% selectivity. Butenyl adducts were not formed, and in only one case (R = Ph) was any preferential ether formation observed (1.5% yield) compared to 93% yield of the N-octadienyl-aminoalcohol. In the presence of excess butadiene, alkyl aminoalcohols form exclusively the N-octadienyl-aminoalcohols and octa-1, 3, 7 triene, excepting for diethanolamine which undergoes both N-octadienylation and octadienyl mono etherification. Etherification of alkyl-aminoalcohols can be induced by the presence of molar quantities of phosphine 5. The effect of added ligand on the course of reaction is discussed in terms of intra- and inter molecular H bonding.

The Pd or Ni catalysed reaction of active hydrogen compounds with 1,3-butadiene has been reported for alcohols, amines, carboxylic acids, phenols, active methylene and methyne compounds, oximes, hydrazones and Schiff bases.[1] Generally, for the Pd catalyzed reaction, the major products are octadienyl, derivatives of the active hydrogen compounds, with smaller amounts of the corresponding butenyl compounds.

Our results on the Pd-catalyzed reaction of butadiene with a number of multifunctional active-hydrogen compounds, viz alkanolamines provide a highly selective synthetic route to a number of long chain tertiary aminoalcohols which are interesting intermediates for a variety of polymer applications.

RESULTS

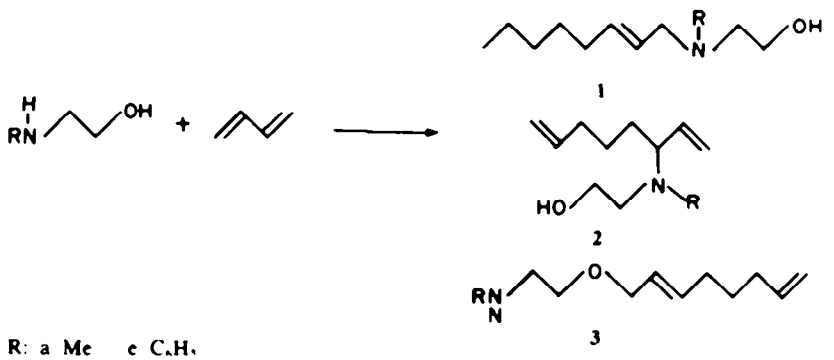
In a prelinary communication,[2] in the reaction of a series of alkanolamines with butadiene catalyzed by palladium acetylacetonate and triphenylphosphine we noted the exclusive formation of N-(octadienyl) aminoalcohols.

Now in accordance with Table 1 and supported in the Experimental, the reaction in an autoclave for up to 16 hr at 80° is shown to yield a mixture of compounds **1–3**. Traces (< 1%) of octa-1,3,7-triene were also formed. The stereochemistry of the internal double bond of adducts **1** were assigned as *trans* on the basis of strong absorption in the 970 cm^{-1} region of the IR spectrum.

The unambiguous assignment of the octadienyl group being attached to N, as opposed to O, was made on the basis of NMR doublet at δ 3.0 ppm due to ($N-CH_2-CH=$) and absence of doublet at δ 3.9 ppm ($O-CH_2-CH=$), mass spectrometry of the TMS-derivatives (base peaks M103* ($M-CH_2OTMS$) and presence of peak 29 + R, corresponding to $RNH=CH_2$) and the subsequent synthesis and characterisation of acetyl derivatives.

Acetylation of the N-octadienyl-aminoalcohols (Experimental) yielded in each case a 5–10% mixture of 2,7-octadienyl acetate and 1,7-octadien-3-yl acetate, presumably via nucleophilic substitution of the amino group by acetate ion.

In the presence of 5 mole equivalents of butadiene, diethanolamine afforded the mono-octa-2,7-dienyl ether **4g** in good yield.



R: a Me e C_6H_5
b Et f $C_6H_5CH_2$
c nBu g CH_2-CH_2-OH
d tBu h $CH_2-CH(CH_3)-OH$

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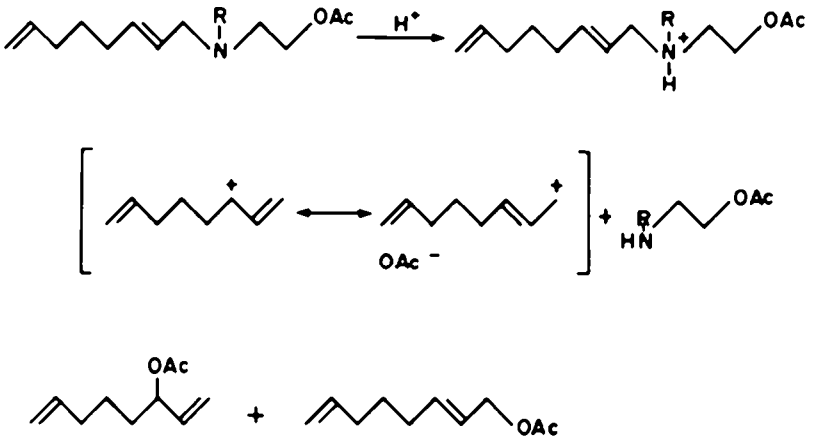
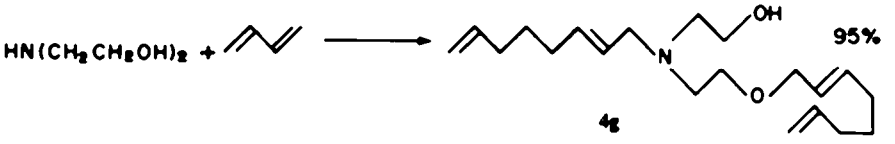


*Except for 1h, which had a base peak M-117 (M-CHOTMS)

CH,



Prolonged reaction (5 days) of **4g** with butadiene afforded no further telomerisation, however, and octa-1,3,7-triene was formed, **4g** being recovered, unchanged.

N-methylaminoethanol, in the presence of 5 mole equivalents of butadiene afforded solely N-methyl-N-octa-2,7-dienylamino-ethanol **1a** (with trace amounts of branched chain isomer) and octa-1,3,7 triene. Octatriene formation was observed to occur only after total conversion of the aminoalcohol. Compound **1a** was similarly treated with butadiene and catalyzed by palladium acetylacetonate and triphenylphosphine, at 90° for 3 days. Again, no ether formation was observed and (80% conversion) octa-1,3,7-triene and **1a** were isolated.

It appears therefore that the catalytic system does not permit the etherification of one single OH group by leading to octadienylated ether from aminoalcohol.

We have considered the factors which could favour etherification and studied the influence of different

Table 1. Reaction of butadiene with alkanolamines, catalysed by $Pd(Acac)_2 + 2\,PPh_3$*

Alkanolamine (0.25 mole)	Time (hours)	Alkanolamine Conversion %	% moles 1	2	3	other
$CH_3NHCH_2CH_2OH$ (a)	16	100	98	2	-	
$C_2H_5NHCH_2CH_2OH$ (b)	16	100	98.5	1.5	-	
$n.C_4H_9NHCH_2CH_2OH$ (c)	16	95	98	2	-	
$t.C_4H_9NHCH_2CH_2OH$ (d)	16	100	99	-	-	1**
$C_6H_5NHCH_2CH_2OH$ (e)	2	99	93	-	1.5	5.5**
$C_6H_5CH_2NHCH_2CH_2OH$ (f)	4	100	97	3	-	
$NH(CH_2CH_2OH)_2$ (g)	16	95	96	4	-	
$HN(CH_2CHOHCH_3)_2$ (h)	2	100	97	3	-	

* Reaction conditions : 0.25 mmole Pd $(acac)_2$; Pd : PPh_3, 1 : 2 ; 0.25 mole alkanolamine, 0.5 mole butadiene, 80°C, glass autoclave.

** Not identified

parameters on the catalytic system by maintaining constant the other experimental conditions as far as possible: (a) nature of the anion bound to the Pd; (b) nature of the phosphine; (c) influence of an added OH; (d) influence of a cocatalyst.

DISCUSSION

The striking selectivity of telomerisation of butadiene with aminoalcohols to afford almost exclusively linear octadienylamino alcohols is worthy of note.

Previous work[3] has shown the marked selectivity for 2,7-octadienyl adduct formation, by Pd/phosphine complexes, due to direct attack of the nucleophile at the most accessible C of the Π-allyl unit.

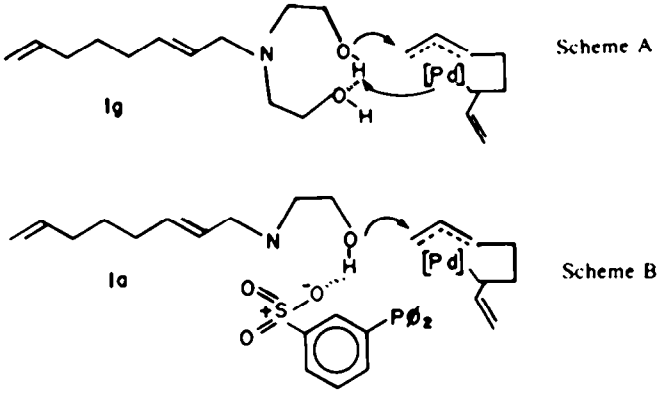
In only one case, that of the weak base, N-phenylaminoethanol, was any secondary amino ether product **3e** observed in 1.5% yield, compared to 93% yield for the isomeric aminoalcohol **1e**.

In a recent Japanese patent[4], 2-aminoethanol, 2-amino-1-propanol and 3-amino-1-propanol were telomerised with butadiene in the presence of $(PPh_3)_2$ Pd-maleic anhydride to form isomeric mixtures of N-octadienyl and N,N-di(octadienyl) aminoalcohols. Again no ether formation was observed.

Direct trans-allylation of aliphatic octadienyl ethers with amines does not to occur in the presence of Pd-complexes[5], but preferential N-octadienylation of the aminoalcohols does occur with the system studied here, rather than by primary etherification and subsequent intra-or inter-molecular *trans* (O→N) allylation.

From the results of the reaction involving N-methylamino-ethanol with excess butadiene, it would appear that the active catalyst for N-octadienylation is not active for subsequent butadiene telomerisation with the alcohol group of the N-octadienyl aminoalcohols (except for **1g**—see below). However, the catalyst precursors palladium acetylacetonate and triphenylphosphine have been shown to form an active catalyst for telomerisation with primary alcohols.[6] We do not know whether N-octadienylation, O-octadienylation, and linear dimerisation involve distinct catalytic species, or whether the catalyst is firmly coordinated by the allylamino compounds, thus prohibiting further reaction or dissocation by alcohol groups.

From the results of the Table 2 it appears that the nature of the anion bound to the Pd (runs 11–14), as well as the sterical and electronical nature of the phosphine (runs 1–9) have little influence on the distribution of the different products of the reaction apart from the percentage of octatriene-1,3,7. The result we obtained with diethanolamine (95% of monoetherification) leads us to supposed that an added OH has a great influence on the etherification. As it appears from experiments 15–20, the nature of the added alcohol has a great influence on the distribution of the different products. The 2,2,2-trifluoroethanol which is very reactive towards the telomerisation[7] reacts before having an action on the aminoalcohol. The t-butanol which is bulky cannot approach the coordination sphere and does not have an efficient action. However the results observed in the case of the added linear alcohols confirm the important role of the OH. This role could be to dissociate the octadienyl-aminoalcohol from the Pd; however this reaction is probably not so important, as experiment 23 with DMF shows. An alternative role can be to activate the OH group by mean of H-bonding, thus rendering the O more nucleophilic for attack on the Π allyl Pd-complex. This can be represented by Scheme A. The influence of the hydrophilic phosphine **5** supports this mechanism; the possibility of an intramolecular H-bonding between the catalyst and the aminoalcohol leads to O-octadienylation according to Scheme B. The efficiency of this intramolecular activation leads to a quantitative formation of the dioctadienylated product (Exp. n°10).



EXPERIMENTAL

Reactions with butadiene were performed in heavy-walled, screw-top tubes or in a 250 ml glass autoclave. The aminoalcohols and butadiene were used as supplied without further purification.

Bis-acetylacetonato-palladium was prepared by the literature method.[8] (Found C, 39.3; H, 4.52; $C_{10}H_{14}O_4Pd$ requires: C, 39.43; H, 4.63).

A Pye 104 chromatograph coupled to a AEI MS 30 mass spectrometer was employed for GLC analysis, (usually of silylated products, helium carrier gas, 30 ml min^{-1} through a 1.5 m × 4 mm glass column, 3% SP 2250 on Supelcoport 100–120). Quantitative analyses were carried out using an internal standard, peak areas being measured by means of an integrator.

NMR spectra were obtained with a Hitachi Perkin–Elmer R 24 instrument using TMS as internal standard and CCl_4 as solvent. IR spectra were recorded between KBr discs using a Perkin–Elmer 457 Grating Infra Red Spectrometer.

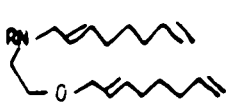
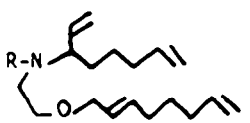
The analysis were carried out by GLC on a Carlo Erba Fractovap G1 chromatograph, after silylation of 10 mg of the product with 1 ml of Trisil BSA, helium as carrier gas,

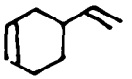
Table 2.

RUN	Catalytic System (constitution in mmole) (reaction with N Methylaminoethanol at 80°C/20 h)	(a) MOB %	(a) MOL %	(a) DIL %	(a) DIB %	(a)(b) OCT %	(a)(b) VCH %
1	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2)	2	92	3	3	11	
2	$Pd(acac)_2$(0,1) + P(o tolyl)$_3$(0,2)	7	93			27	
3	$Pd(acac)_2$(0,1) + $P(pClC_6H_4)_3$(0,2)	5	94		1	3	
4	$Pd(acac)_2$(0,1) + P(cyclohexyl)$_3$(0,2)	4,5	95,5			6	
5	$Pd(acac)_2$(0,1 + diphos (0,2)	3	86	8	3	5	
6	$Pd(acac)_2$(0,1) + P(OMe)$_3$	2	93	2,5	2	4	
7	$Pd(acac)_2$(0,1) + PBu_3	4	64	24	8	9	
8	$Pd(P\emptyset_3)_4$ (0,1)	3,5	95	1,5		0	
9	$Pd(acac)_2$(0,1)		96	2	2		10
10	$Pd(acac)_2$(0,1) + $\emptyset_2P\emptyset mSO_3Na$ (0,2)[d]			100		16	
11	$PdCl_2$(0,1) + $P\emptyset_3$(0,2)	7	93			0,2	
12	$PdBr_2$(0,1) + $P\emptyset_3$(0,2)	6	94			0,4	
13	PdI_2(0,1) + $P\emptyset_3$(0,2)	4	96			0,2	
14	$Pd(OAc)_2$(0,1) + $P\emptyset_3$(0,2)	1	79	17	3	46	
15	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + EtOH (25)[c]	1	72	22	5	7	
16	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + EtOH (100)		74	25	1	0	
17	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + nBuOH(25) [c]		74	22	4	2	

18	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + n octanol(25) [c]		72	22	5	29	
19	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + CF_3CH_2OH (25) [c]	3	92	5		19	
20	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2 + tBuOH (25)	3	93	4		5	28
21	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + CO_2	1	71	14	14	34	
22	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + $\emptyset ONa$	5	95			13	
23	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + DMF (25)	2,5	95	2,5		14	
24	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + Net$_3$F (25)	4	95	1	0	0	
25	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + KF(10) + DMF		90	10		38	
26	$Pd(acac)_2$(0,1) + $P\emptyset_3$(0,2) + CF_3CO_2H (25)		30	63	7	0	
27	$Pd(acac)_2$(0,1 + $P\emptyset_3$(0,2) + CF_3CO_2H (4)			89	11	18	

a) MOL <u>1a</u> MOB <u>2a</u>

a) DIL  DIB 

a) OCT  VCH 

b) with regard to the butadien added

c) the telomerisation product of alcohol is also isolated.

d) ref. (10)

30 ml min^{-1} through a 1.5 m × 4 mm steel column, 3% SP 2250 on Supelcoport 100–120. Programmed temp. 150°–250° at 10°/min.

General procedure

A mixture of bis-acetylacetonato-palladium (0.25 mmole), triphenylphosphine (0.5 mmole) N-ethylaminoethanol (0.25 mole) and butadiene (0.5 mole) was heated, with stirring, for 16 hr at 80° in a 250 ml glass autoclave. The developed pressure rose to a maximum of 5 kg cm^{-2} after 30 min. After 16 hr the pressure was 0.5 kg cm^{-2}. The yellow-brown soln ((after silylation with Me_3) SiCl, was analysed by GLC-MS and shown to contain N-ethyl-aminoethanol (trace), **1b** (98.5%), **2b** (1.5%) and octa-1,3,7-triene (trace).

Fractional distillation gave a first fraction containing mainly octa-1,3,7-triene and starting material (0.3 g) b.p. 125–130°/13 mm. Further distillation afforded a second fraction containing **1b** and **2b** (47.9 g) b.p. 125–130°/13 mm.

N-*Ethyl*-N(2,7 *octadienyl*)-2 *amino ethanol* **1h**. NMR δ (CCl_4) 6.2–5.3 (3H, M), 5.27-4.73 (2H, m), 3.88 (1H, s), 3.5 (2H, t, J 6Hz), 3.0 (2H, d, J 4 Hz), 2.48 (4H, m), 2.05 (4H, m), 1.52 (2H, m), 1.0 (3H, t, J 7 Hz). GC/MS (as TMS ether), retention time 19.6 min; *m/e* 269 (M^+, 2%), 254 (5%), 200 (4%), 166 (100%), 109 (20%), 73 (15%), 67 (70%), 58 (90%), 55 (25%). IR (neat) cm^{-1} ν max 3400, 3080, 2975, 2930, 2850, 1665, 1640, 1458, 1440, 1050, 990, 975, 913, n_D^{21} = 1.4722.

N-*Ethyl*-N(1,7 *octadien*-3-*yl*)-2 *amino ethanol* **2b**. GC/MS (as TMS ether), retention time 17 min; *m/e* 269 (M^+, 2%), 200 (27%), 166 (100%), 109 (12%), 58 (80%).

Reaction of butadiene with other alkanolamines

The general procedure described above was used for the other alkanolamines except that **1e** and **1f** were isolated as their HCl salts. The results are presented in Table 1. The physical properties and elemental analyses of **1a–1h** are presented in Table 3.

Spectral properties of N-(2,7-*octadienyl*)-*aminoalcohols*

N-*Methyl*-N(2,7-*octadienyl*)-2 *amino ethanol* **1a**. NMR δ (CCl_4). 6.15–5.3 (3H, m, CH=), 5.25–4.7 (2H, m, CH_2=) 3.67 (1H, s, –OH), 3.5 (2H, t, J 6 Hz, $-CH_2O$), 2.98 (2H, d, J 4 Hz, =CH-CH_2N), 2.43 (2H, t, J 6 Hz, N-CH_2), 2.17 (3H, s, N-CH_3), 2.07 (4H, m, =C-CH_2C-CH_2-C=), 1.52 (2H, m, C-CH_2-C). IR (neat) ν cm^{-1}: 3400, 3080, 2980, 2800, 1665, 1640, 1455, 975, 910, 980. GC/MS as TMS ether (RT 18.4 min), *m/e* 255 (M^+ 4%), 240 (8%), 186 (2%), 152 (100%), 109 (30%), 73 (40%), 67 (90%), 55 (40%), 44 (95%).

N-*n Butyl*-N(2,7-*octadienyl*)-2 *amino ethanol* **1c**. NMR δ (CCl_4) 6.33–5.3 (3H, m, =CH-), 5.3–4.7 (2H, m, $=CH_2$) 3.47 (2H, t, J 6 Hz, $-CH_2O$), 3.30 (1H, s, OH), 3.00 (2H, d, J 4 Hz, N-CH_2-C=), 2.53 (4H, m, $-CH_2$-N-CH_2-), 2.05 (4H, m, =C-CH_2-C-CH_2), 1.43 (6H, m, C-CH_2-C), 0.9 (3H, m, C-CH_3). IR (neat) ν cm^{-1}: 3420, 3080, 2960, 2930, 2860, 1660, 1640, 1460, 1050, 990, 975, 910, 880. GC/MS as TMS ether (RT 24.1 min), *m/e* 297 (M^+ 1%), 282 (4%), 254 (6%), 228 (3%), 194 (100%), 172 (3%), 109 (15%), 86 (30%), 73 (15%), 67 (55%), 55 (20%).

N-*t Butyl*-N(2,7-*octadienyl*)-2 *amino ethanol* **1d**. NMR δ (CCl_4) 6.33–5.33 (3H, m, =CH-), 5.3–4.73 (2H, m, $=CH_2$), 3.38 (2H, t, J 6 Hz, $-CH_2$-O), 3.13 (2H, d, J 4 Hz N-CH_2-C=), 3.0 (1H, s, OH), 2.63 (2H, t, J 6 Hz, N-CH_2), 2.05 (4H, m, =C-CH_2-C=), 1.5 (2H, m, C-CH_2-C), 1.1 (9H, s, -C-CH_3)$_3$. IR (neat) ν cm^{-1} 3420, 3080, 2980, 2930, 2860, 1660, 1640, 1480, 1460, 1440, 1395, 1365, 1270, 1220, 1205, 1135, 1060, 1025, 995, 975, 915, 875. GC/MS as TMS ether (RT 22.5 min), *m/e* 297 (M^+ 1%), 282 (5%), 240 (4%), 195 (10%), 194 (100%), 138 (60%), 109 (20%), 73 (8%), 67 (40%), 57 (35%), 55 (8%).

N-*Phenyl*-N-(2,7 *octadienyl*)-2 *amino ethanol* **1e**. NMR δ (CCl_4) 7.4–6.37 (5H, m, C_6H_5), 6.3–5.3 (3H, m, CH=), 5.3–4.73 (2H, m, $=CH_2$), 3.78 (3H, m, CH_2OH), 3.63–2.9 (4H, m, CH_2N CH_2C=), 1.99 (4H, m, =C-CH_2-C-CH_2-C=), 1.43 (2H, m, C-CH_2-C). IR (neat) ν cm^{-1} 3400, 3080, 3070, 3030, 2970, 2930, 2860, 1665, 1640, 1600, 1575, 1505, 1460, 1440, 1395, 1360, 1220, 1115, 1040, 995, 975, 915, 865, 750, 695, 515. GC/MS as TMS ether (RT 34 min), *m/e* 317 (M^+ 17%), 302 (1%), 248 (1%), 214 (100), 109 (25%), 106 (100%), 73 (20%), 67 (85%), 55 (30%).

N-*Benzyl*-N (-2,7 *octadienyl*)-2 *amino ethanol* **1b**. NMR δ (CCl_4) 7.2 (5H, s, C_6H_5), 6.17–5.3 (3H, m, =CH), 5.23–4.77 (2H, m, $=CH_2$), 3.52 (5H, m, $PhCH_2$, $-CH_2OH$), 3.03 (2H, d, J 4 Hz=C-CH_2N), 2.55 (2H, t, J 6 Hz NCH_2C-), 2.03 (4H, m, =C-CH_2-C-CH_2-C=), 1.47 (2H, m, C-CH_2-C). IR (neat) ν cm^{-1} 3420, 3080, 3070, 3030, 2980, 2930, 2860, 2840, 2720, 1665, 1640, 1600, 1495, 1455, 1445, 1370, 1055, 1030, 990, 975, 915, 875, 740, 700, 475. GC/MS as TMS ether (RT 38.2 min), *m/e* 331 (M^+ 1%), 316 (5%), 262 (2%), 240 (8%), 228 (100%), 120 (50%), 109 (15%), 91 (100%), 73 (20%), 67 (70%), 55 (30%).

N-2,7 *octadienyl*)N,N'-*diethanol amine* **1g**. NMR δ (CCl_4) 6.2–5.33 (3H, m, =CH), 5.3–4.73 (2H, m =CH_2), 4.43 (2H, s –OH), 3.6 (4H, t, J 6 Hz, $-CH_2O$), 3.17 (2H, d, J 4 Hz, N-CH_2-C=), 2.65 (4H, m, NCH_2-C), 2.07 (4H, m, =C-CH_2-C-CH_2-C=), 1.52 (2H, m, C-CH_2-C). IR (neat) ν cm^{-1} 3400, 3080, 2930, 2860, 1825, 1665, 1640, 1450, 1050, 975, 910, 880. GC/MS as bis TMS ether (RT 19.8 min), 357 (M^+ 1%), 342 (8%), 228 (1%), 255 (45%), 254 (100%), 146 (15%), 130 (25%), 109 (25%), 73 (20%), 67 (40%), 55 (12%).

N-(2,7 *octadienyl*)-N(-2 *methyl ethanol*)-2 *amino ethanol* **1h**. NMR δ (CCl_4) 6.15–5.37 (3H, m, =CH), 5.17–4.72 (2H, m, $=CH_2$), 4.27 (2H, s, OH), 3.77 (2H, m, C-CH-O), 3.13 (2H, d, J 4 Hz, N-CH_2-C=), 2.43 (4H, m, N-CH_2-C), 2.06 (4H, m, =C-CH_2-C-CH_2-C=) 1.51 (2H, m, C-CH_2-C), 1.07 (6H, split doublet, J 6 Hz, C-CH_3). IR (neat) ν cm^{-1} 3400, 3080, 2970, 2935, 1665, 1640, 1455, 1415, 1375, 1340, 1140, 1065, 990, 975, 955, 915, 840. GC/MS as bis TMS ether (RT 22.3 min), *m/e* 385 (M 1%), 370

Table 3. N-(2,7-octadienyl) aminoalcohols

	B.P./mm	n_D^{21}	Purity*	Found %			Required %		
				C	H	N	C	H	N
1a	124/13	1.4734	98	72.4	11.4	7.7	72.1	11.5	7.6
1b	130/13	1.4722	98.5	72.9	11.7	7.2	73.1	11.7	7.1
1c	120/0.5	1.4687	98	74.5	11.9	6.4	74.7	12.0	6.2
1d	128/0.5	1.4735	99	74.8	12.1	6.3	74.7	12.0	6.2
1g	152/13	1.4840	98	67.9	10.8	6.4	67.6	10.8	6.6
4g	150/0.5	1.4850	98	74.5	10.8	4.5	74.8	10.9	4.4
1h	130/0.5	1.4722	98	69.8	11.5	5.6	69.7	11.2	5.8

* The impurity is the corresponding branched chain isomer.

Table 4. Acetyl derivatives of the N-(2,7-octadienyl) aminoalcohols

Acetate of	B.P./mm	n_D^{21}	Purity*	Found % C	H	N	Required % C	H	N
1a	137/12	1.4575	98	69.1	10.4	6.2	69.3	10.3	6.2
1b	143/13	1.4570	98.5	70.4	10.5	5.7	70.25	10.5	5.8
1c	158/13	1.4567	98	72.1	10.7	5.2	71.9	10.9	5.2
1d	160/13	1.4607	99	71.9	10.7	5.3	71.9	10.9	5.2
1g	185/13	1.4627	99	64.3	9.0	4.8	64.6	9.15	4.7
1h	130/0.5	1.4556	99	66.7	9.2	4.1	66.5	9.54	4.3

* Impurity being the corresponding N-1,7 octadien-3-yl amino acetate derivative.

Table 5.

R	Retention time(min)[a] br	str	(M-69)%[b] branched	straight	(109)% branched	straight
CH_3	16.1	18.4	35	2	15	30
C_2H_5	17.1	19.6	27	4	12	20
$n\text{-}C_4H_9$	21.6	24.1	26	3	7	15
$t\text{-}C_4H_9$		22.5		2		16
C_6H_5		34		1		25
$C_6H_5\text{-}CH_2$	30.6	38.2	25	2	8	15
CH_2CH_2OTMS	19.2	19.8	13	1	8	25

b) Base Peaks (100%) are M-103 in all cases

a) 1.5 m x 4 mm 3% SP2250 on
supelcoport 100-120. He:30 ml/min
80° x 5°/min to 260°

(15%), 316 (1%), 269 (70%), 268 (M-117, 100%), 160 (10%), 144 (20%), 130 (7%), 109 (15%), 73 (60%), 67 (70%), 55 (30%).

Mass spectrometry

The mass spectra of the TMS derivatives of the isomeric pairs N-2,7-octadienyl (straight chain) and N-1,7-octadien-3-yl (branched) aminoalcohols are similar.[8] However, in each case, the branched chain isomer has a shorter retention time, and the relative intensities of the M-69 ion and the 109 ion are characteristically different.

Acetylation of the N-octadienyl alkanolamines

Each reaction was carried out on a *ca* 50 mmole scale. The N-octadienylalkanolamine was dissolved in AC_2O (50 ml) and heated under reflux for approx 1 hr and then distilled. The yields of pure product were about 80–90%. A low-boiling fraction (80°/13 mm) was obtained in each case and was shown to consist of 1,7-octadien-3-yl acetate and 2,7-octadienyl acetate by comparison with pure samples. The physical properties and elemental analyses of the acetyl derivatives of **1a–1h** are presented in Table 4.

Reaction of excess butadiene with diethanolamine

Diethanolamine (20 mmole) was heated with butadiene (180 mmole) in the presence of $Pdacac_2$ (0.1 mmole) and PPh_3 (0.2 mmole) at 90° to constant volume (~30 hr). GLC analysis showed the presence of octatriene, (48%, 52 mmole). **1g** (5%, 2.7 mmole). **2g** (0.1%) and **4g** (47% 17.2 mmole). Distillation afforded the pure ether **4g** (4.1 g) b.p. 150°/0.5 mm n_d^{21} 1.4850. NMR δ (CCl_4) 6.2–5.3 (6H, m), 5.2–4.74 (4H, m), 3.87 (2H, d, J 4 Hz), 3.47 (4H, split triplet, J 6 Hz), 3.13 (2H, d, J 5 Hz), 3.0 (1H, s), 2.63 (4H, m), 3.05 (8H, m), 1.55 (4H, m). GC/MS as TMS ether (RT 30 min), *m/e* 393 (M^+ 1%), 324 (1%), 291 (15%), 290 (75%), 268 (2%), 255 (20%), 254 (100%), 166 (15%), 146 (10%), 130 (21%), 109 (15%), 73 (15%), 67 (50%), 55 (20%).

Attempted telomerisation of N-methyl-N-(2,7-octadienyl) amino ethanol **1a** *with butadiene*

The aminoalcohol (25 mmole) with butadiene (115 mmole) were

heated in the presence of PD $acac_2$ (0.1 mmole) and PPh_3 (0.2 mmole) at 80° in a graduated tube until constant volume was attained (60 hr). GLC analysis showed the mixture to consist of octa-1,3,7-triene and unreacted starting material. Distillation afforded octa-1,3,7-triene (5.2 g, 48 mmoles) and the starting **1a** (4.1 g, 22 mmole).

Synthesis of N-*methyl*-N-(2,7-*octadienyl*) *amino ethyl*, (2,7-*octadienyl*) *ether* **4a**

N-methylaminoethanol (25 mmol) in the presence of Pd $(acac)_2$ (0.1 mmole), $(C_6H_5)_2$ P $(C_6H_4$. $mSO_3Na)$ **5** (0.2 mmole) and butadiene (150 mmole) were heated at 80° in a graduated tube during 60 hr. Distillation of the crude product afforded **4a** (7 g, 95%, b.p. 140°/0.5 mm). Purity 100% by GLC analysis. NMR δ (CCl_4) 6.1–5.2 (6H, m), 5.1–4.65 (4H, m), 3.83 (2H, d, J 4 Hz), 3.48 (2H, t, J 5 Hz), 2.93 (2H, d, J 5 Hz), 4.43 (2H, t, J 5 Hz), 2.17 (3H, 2), 2.0 (8H, m), 1.53 (4H, m). IR (neat) ν cm^{-1} 3400, 2980, 2780, 1670, 1640, 1455, 1110, 970, 910. GC/MS (RT 31 min), *m/e* 291 (M^+ 0.4%), 182 (0.3%), 152 (100%), 138 (1.1%), 109 (7.2%), 67 (29.9%), 55 (10.2%), 44 (36.7%). n_D^{21} 1.4735.

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