

An Investigation of the Thermal Decomposition of the Methohydroxides and Methodeuterio-oxides of Some 5-*N,N*-Dimethylaminopent-1-enes

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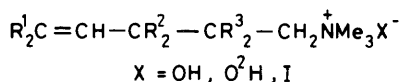
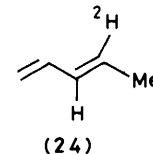
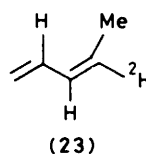
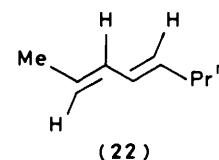
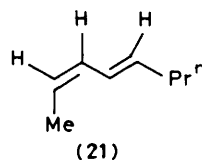
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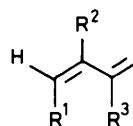
The base-catalysed thermal decomposition of a number of quaternary bases of the type $(R^1)_2C=CHC(R^2)_2C(R^3)_2CH_2^+NMe_3X^-$ ($R^1 = H, Me$; $R^2 = H, ^2H$; $R^3 = H, ^2H, Me$; $X = OH, O^2H$) has been investigated. It is shown that the reaction is initiated by attack of base (OH , O^2H , ylide) on an allylic proton or [2H]. A mechanism for the reaction is suggested.

Little attention seems to have been given to the thermal decomposition of trimethylpent-4-enylammonium hydroxides, e.g. (1; $X = OH$), where the hydrocarbon products are (*Z*)- and (*E*)-penta-1,3-dienes (7) and (11) in 80 and 20% yields, respectively. The thermal reaction involves the Hofmann-type formation of a double bond and isomerisation of a double bond to give a conjugated diene. These reactions may proceed in several ways, which may be simultaneous, namely (a) by initial elimination of trimethylamine and water followed by isomerisation of the existing double bond, (b) by initial



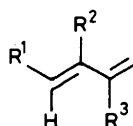
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- (2) $R^1 = R^3 = H, R^2 = ^2H$
- (3) $R^1 = R^2 = H, R^3 = ^2H$
- (4) $R^1 = R^2 = H, R^3 = Me$
- (5) $R^1 = Me, R^2 = R^3 = H$
- (6) $R^1 = Me, R^2 = H, R^3 = ^2H$

(*Z*)- and (*Z,E*)-Series

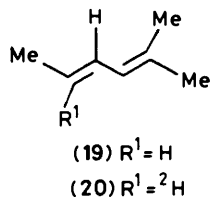
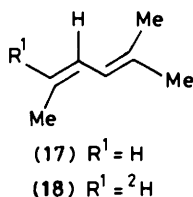
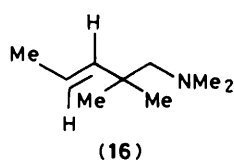
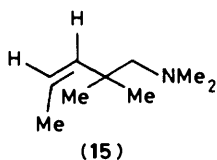


- (7) $R^1 = Me, R^2 = R^3 = H$
- (8) $R^1 = CH_2^2H, R^2 = R^3 = H$
- (9) $R^1 = Me, R^2 = ^2H, R^3 = H$
- (10) $R^1 = Me, R^2 = H, R^3 = ^2H$

(*E*)- and (*E,E*)-Series



- (11) $R^1 = Me, R^2 = R^3 = H$
- (12) $R^1 = CH_2^2H, R^2 = R^3 = H$
- (13) $R^1 = CH_2^2H, R^2 = ^2H, R^3 = H$
- (14) $R^1 = Me, R^2 = H, R^3 = ^2H$



isomerisation of the existing double bond followed by the elimination reaction, (c) by initial Hofmann elimination followed by isomerisation of the double bond so formed. In our work on the identity of conylene (see preceding paper) we were struck by the apparent ease with which the conjugated diene is formed, and stereoselectively, when the correct temperature, and presumably hydroxide concentration is reached.

In order to throw light on the mechanism of these reactions we have investigated the thermal decomposition of the methohydroxide and metho[2H]hydroxide of 5-*N,N*-dimethylaminopent-1-ene and a number of its derivatives disubstituted by 2H at C-3 or C-4, or by methyl groups at C-1 or C-4 (see Table).

Results

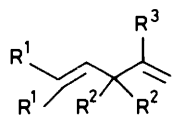
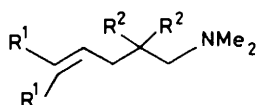
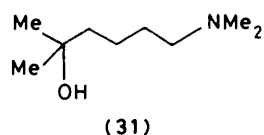
Thermal decomposition of the simplest compound (1; $X = OH$) gave a hydrocarbon mixture consisting of (*Z*)-penta-1,3-diene (7) and its (*E*)-isomer (11) in the ratio of *ca.* 4:1. This preponderance of the (*Z*)-isomer was repeated when the metho[2H]hydroxide (1; $X = O^2H$) was thermally decomposed, the hydrocarbon products then being (*Z*)-[5- 2H]penta-1,3-diene (8) and its (*E*)-isomer (12) in the ratio (1H n.m.r.), 5.3:1. The trimethylamine was also deuteriated (*ca.* 25%).

The identities of the undeuteriated piperlylenes were established by g.l.c. on a silver nitrate-ethylene glycol column, the (*E*)-isomer (11) having the shorter retention time,^{1,2} and by reaction of each with maleic anhydride. The (*Z*)-isomer (7) was largely polymerised while the (*E*)-isomer (11) gave (\pm)-(3*aS*,4*S*,7*aR*)-4-methyl-3*a*,4,7,7*a*-tetrahydrobenzo[*c*]furan-1,3-dione (32).³

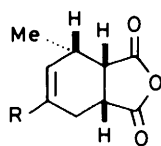
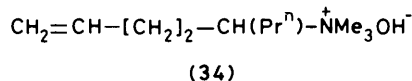
The (*Z*)- and (*E*)-[5- 2H]penta-1,3-dienes (8) and (12) were separated by g.l.c. on a 25 m capillary column (OVI) at 20–30 °C, the (*E*)-isomer (16%) being eluted first.^{1,2} The 1H n.m.r. spectrum of the dienes at 360 MHz showed, beside other

Table. Products of the thermal decomposition of quaternary bases; $(R^1)_2C=CHC(R^2)_2C(R^3)_2CH_2 \overset{+}{N}Me_3 \bar{O}H$

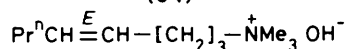
Base	Products (relative amounts of principal products)
<i>N,N,N</i> -Trimethyl- <i>N</i> -pent-4-enylammonium Hydroxide (1 ; X = OH)	(<i>Z</i>)-Penta-1,3-diene (7) (80%); (<i>E</i>)-isomer (11) (20%)
<i>N,N,N</i> -Trimethyl- <i>N</i> -pent-4-enylammonium [2H]hydroxide (1 ; X = O 2H)	(<i>Z</i>)-[5-^2H]Penta-1,3-diene (8) (84%); (<i>E</i>)-isomer (12) (16%); deuterated NMe $_3$
<i>N,N,N</i> -Trimethyl- <i>N</i> -[3,3- 2H_2]pent-4-enylammonium hydroxide (2 ; X = OH)	(<i>Z</i>)-[3-^2H]Penta-1,3-diene (9); [3,3- 2H_2]penta-1,4-diene (25); (<i>E</i>)-[3,5- 2H_2]penta-1,3-diene (13); NMe $_3$ (1%) deuterated
<i>N,N,N</i> -Trimethyl- <i>N</i> -[2,2- 2H_2]pent-4-enylammonium hydroxide (3 ; X = OH)	(<i>Z</i>)-[2-^2H]Penta-1,3-diene (10) (80%); (<i>E</i>)-isomer (14) (20%)
<i>N</i> -2,2-Dimethylpent-4-enyl- <i>N,N,N</i> -trimethylammonium hydroxide (4 ; X = OH)	(<i>E</i>)-5- <i>N,N</i> -dimethylamino-4,4-dimethylpent-2-ene (16) (60%); (<i>Z</i>)-isomer (15) (7%); 5- <i>N,N</i> -dimethylamino-4,4-dimethylpent-1-ene (28) (33%)
<i>N</i> -2,2-Dimethylpent-4-enyl- <i>N,N,N</i> -trimethylammonium [2H]hydroxide (4 ; X = O 2H)	Amines (16) (54%); (15) (9%); (28) (36%) highly deuterated in their NMe $_2$ groups
<i>N,N,N</i> -Trimethyl- <i>N</i> -5-methylhex-4-enylammonium hydroxide (5 ; X = OH)	5-Methylhexa-1,4-diene (26) (47%); (<i>Z</i>)-2-Methylhexa-2,4-diene (17) (25.5%); (<i>E</i>)-isomer (19) (27.5%); base: 6- <i>N,N</i> -dimethylamino-2-methylhex-2-ene (29)
<i>N,N,N</i> -Trimethyl- <i>N</i> -5-methyl[2,2- 2H_2]hex-4-enylammonium hydroxide	5-Methyl[2-^2H]hexa-1,4-diene (27); (<i>Z</i>)-2-methyl[5-^2H]hexa-2,4-diene (18); (<i>E</i>)-isomer (20); 6- <i>N,N</i> -dimethylamino-2-methyl[5,5- 2H_2]hex-2-ene (30)
<i>N,N,N</i> -Trimethyl- <i>N</i> -oct-7-en-4-ylammonium hydroxide (34) (see preceding paper)	(2 <i>E,4E</i>)-Octa-2,4-diene (22) (13.5%); (2 <i>Z,4E</i>)-Octa-2,4-diene (21) (55%); (<i>E</i>)-Octa-1,4-diene (37) (10%); probably (<i>E</i>)-octa-1,5-diene (38) (21.5%)
<i>N,N,N</i> -Trimethyl- <i>N</i> -(<i>E</i>)-oct-4- and -5-en-1-ylammonium hydroxides (35) and (36)	(2 <i>E,4E</i>)-Octa-2,4-diene (22) (45%); (2 <i>Z,4E</i>)-octa-2,4-diene (21) (32%); (<i>E</i>)-octa-1,4-diene (37) (23%)

(25) $R^1 = H, R^2 = ^2H, R^3 = H$ (26) $R^1 = Me, R^2 = R^3 = H$ (27) $R^1 = Me, R^2 = H, R^3 = ^2H$ (28) $R^1 = H, R^2 = Me$ (29) $R^1 = Me, R^2 = H$ (30) $R^1 = Me, R^2 = ^2H$ 

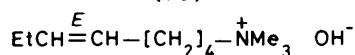
(31)

(32) $R = H$ (33) $R = ^2H$ 

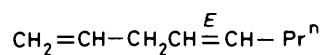
(34)



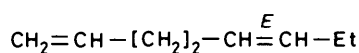
(35)



(36)



(37)



(38)

expected signals (see Experimental section), for the major component (**8**) a multiplet at δ 5.53 which on irradiation at δ 1.75 collapsed to a broad doublet at δ 5.53, J 10 Hz ($^2HCH_2CH=CH$). The corresponding multiplet for the minor component (**12**) collapsed to a doublet at δ 5.72, J 15.5 Hz

($^2HCH_2CH=CH$). The multiplet at δ 1.75 (2HCH_2) integrated for 2.2 protons corresponding to about 80% mono-deuteration. In the noise decoupled ^{13}C n.m.r. spectrum of the mixture of (**8**) and (**12**), the triplet (J 20 Hz) of the 2HCH_2 group of (**8**) could be seen partially overlapping the singlet at δ 13.32 derived from the undeuterated analogue (**7**). The i.r. spectrum of the mixture of (**8**) and (**12**) was similar to that of the undeuterated dienes (**7**) and (**11**), but a strong band at 2160 cm^{-1} in (**8**) and (**12**) can be assigned to the C^2H group. The trimethylamine formed from (**1**; X = O 2H) was converted into benzyltrimethylammonium iodide which showed about 25% deuteration (1H n.m.r.) of its NMe $_3$ group (*i.e.* ca. 2.25 2H).

Thermal decomposition of *N,N,N*-trimethyl-*N*-[3,3- 2H_2]pent-4-enylammonium hydroxide (**2**; X = OH) gave a mixture of (*Z*)-[3-^2H]penta-1,3-diene (**9**), [3,3- 2H_2]penta-1,4-diene (**25**), (*E*)-[3,5- 2H_2]penta-1,3-diene (**13**) and a small amount of the (*E*)-isomer of (**9**). The trimethylamine formed was deuterated; there was about 10% transfer of deuterium from (**2**; X = OH) to NMe $_3$. The presence of the 1,4-diene (**25**) amongst the products is noteworthy since the corresponding unlabelled diene is not found in the products of decomposition of the corresponding undeuterated base (**1**; X = OH).

The position of the deuterium atom in (**9**) is confirmed by a broad signal at δ 6.1 in the 2H n.m.r. spectrum (55 MHz) of the mixture. A signal at δ 2.7 corresponds to $CH_2=CHC^2H_2CH=CH_2$ of (**25**) (about 10% of the mixture) and a weak signal at δ 1.77 is in the expected position for (*E*)- $^2HCH_2CH=CH$ of (**13**). The percentage enrichment of the $MeCH=C$ group of (**13**) with [2H] is about 2.9. The 90 MHz 1H n.m.r. spectrum of the mixture, in dilute solution in chloroform, showed signals which confirmed the presence of (**9**) and its (*E*)-isomer. Quartets at δ 5.53 (J 8 Hz) and 5.75 (J 10 Hz) can be assigned to the $MeCH=C^2H$ protons of (**9**) and its (*E*)-isomer, respectively, while overlapping signals at δ 4.95–5.3 can be assigned to the methylene groups of these compounds and (**25**). Unfortunately the overlapping methyl doublets of (**9**) and its (*E*)-isomer at δ 1.75 were not sufficiently resolved to give a measure of the amounts of each, but on the basis of the quartets mentioned the (*E*)-isomer is present in 20–40% of the quantity of the (*Z*)-isomer.

N,N,N-Trimethyl-*N*-[2,2-²H₂]pent-4-enylammonium hydroxide (**3**; X = OH) gave a mixture of effectively completely monodeuteriated (*Z*)- and (*E*)-[2-²H]penta-1,3-dienes (**10**) and (**14**) in which the former predominated (>80%; g.l.c., ¹H n.m.r.). The mixture showed two broad singlets, each of 1 H at δ 5.09 and 5.16 derived from the deuteriated vinyl group (CH₂=C²H) as well as other expected signals (see Experimental section). With maleic anhydride the major component (**10**) was largely polymerised, but the (*E*)-diene (**14**) gave (±)-(3*a*S,4*S*,7*a*R)-4-methyl[6-²H]-3*a*,4,7,7*a*-tetrahydrobenzo[*c*]furan-1,3-dione (**33**). The mass spectra of the adduct (**33**) and the mixture of dienes (**10**) and (**14**) confirmed the presence of one deuterium atom in these compounds.

We next investigated the thermal decomposition of *N*,2,2-dimethylpent-4-enyl-*N,N,N*-trimethylammonium hydroxide (**4**; X = OH) and its [2-²H]hydroxide (**4**; X = O²H), systems which cannot undergo the normal Hofmann elimination reaction. The products from the former (**4**; X = OH) were (i.r., ¹H n.m.r.) (*E*)-5-*N,N*-dimethylamino-4,4-dimethylpent-2-ene (**16**) (60%), its (*Z*)-isomer (**15**) (7%), and 5-*N,N*-dimethylamino-4,4-dimethylpent-1-ene (**28**) (33%). These yields are based upon the areas of the Me₂C signals at δ 0.98, 1.13, and 0.87, respectively in the ¹H n.m.r. spectrum of the mixture of the compounds mentioned. The composition of the mixture was later confirmed by the intensity of the resolved olefinic signals in its 360 MHz ¹H n.m.r. spectrum. The major vinylic signal was the doublet, *J* 16 Hz of the 3 H of the (*E*)-isomer (**16**). In the ¹³C n.m.r. spectrum of the mixture, signals at δ 18.1 (C-1), 120.7 (C-2), 141.2 (C-3), 37.7 (C-4), 72.0 (C-5), 26.2 (MeC), and 48.5 (MeN) can be attributed to the major component (**16**).⁴ The large amount of the (*E*)-isomer (**16**) compared with the (*Z*)-isomer (**15**) is noteworthy.

5-*N,N*-Dimethylamino-4,4-dimethylpent-1-ene (**28**) was largely (ca. 77%) isomerised to (*E*)-5-*N,N*-dimethylamino-4,4-dimethylpent-2-ene (**16**) when heated with potassium hydroxide in dimethyl sulphoxide. The quaternary [2-²H]hydroxide (**4**; X = O²H) gave the amines (**16**) (54%), (**15**) (9%), and (**28**) (36%) highly deuteriated in their dimethylamino groups. There was little evidence of deuteriation in their 1-methyl groups.

N,N,N-Trimethyl-*N*-5-methylhex-4-enylammonium hydroxide (**5**; X = OH), in which the double bond is stabilised by methyl groups is thermally decomposed to a mixture of 5-methylhexa-1,4-diene (**26**) (47%),⁵ (*Z*)-2-methylhexa-2,4-diene (**17**) (25.5%),⁶ and its (*E*)-isomer (**19**) (27.5%).⁶ The i.r. spectrum of the mixture showed bands at 990 and 910 (CH₂=CH), 960 (*trans*-CH=CH), and 720 cm⁻¹ (*cis*-CH=CH). Its ¹³C n.m.r. spectrum⁴ showed the presence of eight methyl groups, the nine non-quaternary olefinic carbon atoms, and the triplet of the allylic methylene group of (**26**) (see Experimental section). This demonstrates the presence of the three dienes. G.l.c. on a 30 m silicone column revealed the three dienes, the unconjugated diene being eluted first.

The basic fraction formed from (**5**; X = OH) was a mixture (g.l.c., i.r., ¹H n.m.r.) of 6-*N,N*-dimethylamino-2-methylhex-2-ene (**29**) and 6-*N,N*-dimethylamino-2-methylhexan-2-ol (**31**), the latter being formed from (**29**) under the acidic conditions of the work-up procedure. The amine (**29**) was formed in high yield when (**5**; X = I) was treated with silver carbonate and the product thermally decomposed. We found this procedure to be an effective means of forming tertiary amines, free from hydrocarbons, from quaternary iodides.

N,N,N-Trimethyl-*N*-5-methyl[2,2-²H₂]hex-4-enylammonium hydroxide (**6**; X = OH) afforded 5-methyl[2-²H]hexa-1,4-diene (**27**), (*Z*)-2-methyl[5-²H]hexa-2,4-diene (**18**), and its (*E*)-isomer (**20**) in the proportions, 30:31:32, and 6-*N,N*-dimethylamino-2-methyl[5,5-²H₂]hex-2-ene (**30**). The i.r. spectrum of the mixture of dienes was similar to that of the undeuteriated analogues, but the peaks at 990, 910, and 960 cm⁻¹ of the former were weaker than those of the latter, and

there was a strong peak at 2 240 cm⁻¹ (C²H) in the former. In the ¹H n.m.r. spectrum of the mixture of dienes, a prominent feature was the doublet (2 H) at δ 2.69 of the allylic methylene group of the 1,4-diene (**27**). The ¹H n.m.r. spectrum of the pure amine (**30**) which showed a doublet, 2 H, at δ 1.94 (*J* 7 Hz) (C=CHCH₂C²H₂) and a singlet at δ 2.12 (CH₂N), confirmed the position of the deuterium label.

These results are summarised in the Table which also includes for comparison the results, described in the preceding paper, obtained on thermal decomposition of *N,N,N*-trimethyl-*N*-oct-7-en-4-ylammonium hydroxide (**34**) and the mixture of *N,N,N*-trimethyl-1-*N*-(*E*)-oct-4- and -5-en-1-ylammonium hydroxides (**35**) and (**36**).

Discussion

There are three possible points of attack of base on unsubstituted systems of type (1), namely on an allylic methylene proton, on a proton β to the quaternary nitrogen, and on the nitrogen methyl groups. The order in which the attack takes place will influence the nature of the products. Initial attack at the allylic centre is likely to lead to an isomerised double bond, while a simple Hofmann elimination will result from attack of base at the β-position to the quaternary nitrogen. This will afford an unconjugated diene which may then isomerise. Attack of hydroxide on the nitrogen methyl group will afford either an ylide or methanol and a tertiary base. Two bases may also be involved namely, hydroxide/deuterioxide or the ylide mentioned.

Reference has already been made to the apparently spontaneous formation of conjugated dienes in the thermal decomposition of systems of type (1), when the appropriate reaction temperature has been reached. ¹H n.m.r. spectra of the quaternary bases show no change during the pre-heating period, nor even when decomposition of the base has started, and treatment of undecomposed base with hydrogen iodide affords the initial quaternary iodide.

It is possible to envisage an attack by base at the β-position to the ammonium group leading to a 1,4-diene followed by isomerisation to a 1,3-diene even though during the overall reaction hydroxide is replaced by trimethylamine. There should be sufficient hydroxide present for the duration of the reaction for this isomerisation to occur. However, we have been unable to isomerise penta-1,4-diene to any significant extent either with tetra-*n*-butylammonium hydroxide or with saturated aqueous potassium hydroxide by heating in a bomb calorimeter at 130–150 °C for 30 min, but these are not the exact conditions of the Hofmann elimination reaction.

So far as the nature of the base is concerned, the formation of highly deuteriated trimethylamine, and the deuteriated amines (**16**), (**15**), and (**28**) from the metho[²H]hydroxides (**1**; X = O²H) and (**4**; X = O²H), respectively, shows that an ylide is formed. Whether or not this is the base involved in the formation of the conjugated dienes from (**1**; X = OH, O²H) is not clear from the above evidence.

A number of workers^{7,8} have proposed that an ylide is the base in simple Hofmann eliminations. Others for example, Weygand, Daniel, and Simon⁸ proposed that an ylide competes with hydroxide as base in the Hofmann elimination in ethyl-trimethylammonium hydroxide tritiated in various positions.

The formation of (*Z*)- and (*E*)-[2-²H]penta-1,3-dienes (**10**) and (**14**) rather than (*Z*)- and (*E*)-[4-²H]penta-1,3-dienes (**23**) and (**24**) or a mixture of the four isomers from *N,N,N*-trimethyl-*N*-[2,2-²H]pent-4-enylammonium hydroxide (**3**; X = OH) suggests that initial attack of base takes place at the allylic proton. This leads to isomerisation of the vinylic double bond which occurs prior to the Hofmann elimination reaction. We may also deduce that, under the experimental conditions, a 1,5-

hydrogen shift in (10) and (14) does not occur as this would lead to a mixture of the 2- and 4-deuteriated products. Furthermore, had the reaction proceeded by an initial Hofmann elimination to give a 1,4-diene followed by hydrogen abstraction to afford the pentadienyl anion and its subsequent protonation then we would also expect a mixture of four deuteriated products.

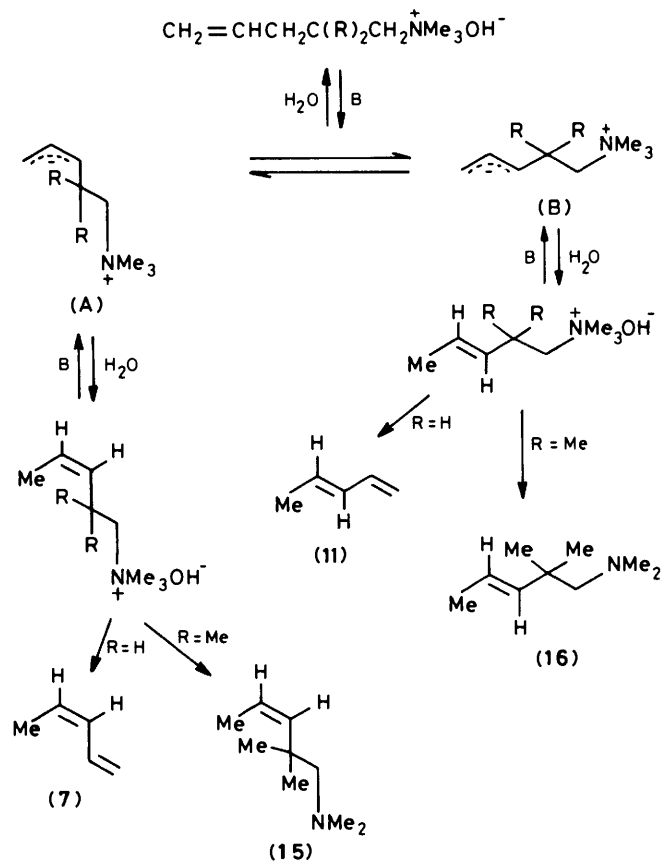
Thermal decomposition of *N,N,N*-trimethyl-*N*-[3,3-²H₂]-pent-4-enylammonium hydroxide (2; X = OH) gave trimethylamine whose deuterium content was only about 10% of one [²H]-transfer. Weygand *et al.*⁸ found a similar amount of tritium incorporated in the trimethylamine from the Hofmann elimination in [2-³H]ethyltrimethylammonium hydroxide on heating in superheated steam at 150 °C. These authors⁸ explained the result by invoking a dual mechanism involving both hydroxide and ylide as bases. Our result can be similarly explained, but it is also possible that the small amount of deuterium incorporated in the trimethylamine derived from (2; X = OH) comes *via* its ylide from the HO²H formed by attack of hydroxide on a C-3-deuterium atom of (2; X = OH). This could also explain the results of Weygand *et al.*⁸ since the use of superheated steam as a source of heat would give an environment rich in water. A similar uncertainty exists for the formation of (*E*)-[3,5-²H₂]penta-1,3-diene (13). It might also be argued that deuterium transferred from C-3 to the ylide is rapidly lost to water present in the environment. The question therefore as to whether an ylide is the base which attacks the allylic protons is therefore not answered.

The main hydrocarbon product derived from (2; X = OH) was (*Z*)-[3-²H]penta-1,3-diene (9), but the unconjugated [3,3-²H₂]penta-1,4-diene (25) and (*E*)-[3,5-²H₂]penta-1,3-diene (13) were also formed. The corresponding undeuteriated unconjugated diene [(25) without ²H] was not evident in the products of decomposition of (1; X = OH). This can be explained by the deuterium isotope effect; when deuterium is present at the 3-position as in (2; X = OH), a simple Hofmann elimination competes with deuterium abstraction from the allylic position.

We turn now to the question of the stereochemistry of the isomerised double bond. It will be noticed that in the mixtures of products derived from the quaternary bases (1)–(3), the (*Z*)-pentadiene is the predominant diene. These results fall into line with those expected from results of a number of workers⁹ who have shown that the *cisoid* anion of a simple allylic system is more stable than the *transoid* anion and that rapid protonation of the anion will yield the kinetically favoured *cis*-isomerised double bond. However as the bulk of the substituting group adjacent to the allylic system increases, kinetic control decreases and the thermodynamically controlled formation of the *trans*-isomer is increasingly favoured⁹ (see below). We gather the facts outlined above in Scheme 1.

In the case of (1; X = OH), the more stable anion is the *cisoid* anion (A). Protonation of (A) from the environment gives the kinetically favoured (*Z*)-olefin which rapidly undergoes Hofmann elimination to yield (7). The less stable anion (B) leads in a similar way to the (*E*)-isomer (11). That protonation of the anions (A) and (B) takes place from the environment is shown by the fact that when the [²H]hydroxide (1; X = O²H) in D₂O is decomposed deuterium appears at C-5 in the products (8) and (12). The degree of deuteriation at C-5 will however depend upon reaction conditions and will vary from experiment to experiment. We do not know the exact amount of water or HO²H retained when decomposition of the quaternary base begins.

The second stage of the diene synthesis is a base-catalysed Hofmann elimination reaction, either by hydroxide (deuterioxide) or ylide. We presume that this is rapid since there is no evidence of change in the ¹H n.m.r. spectrum of the quaternary base even when its decomposition has commenced. The

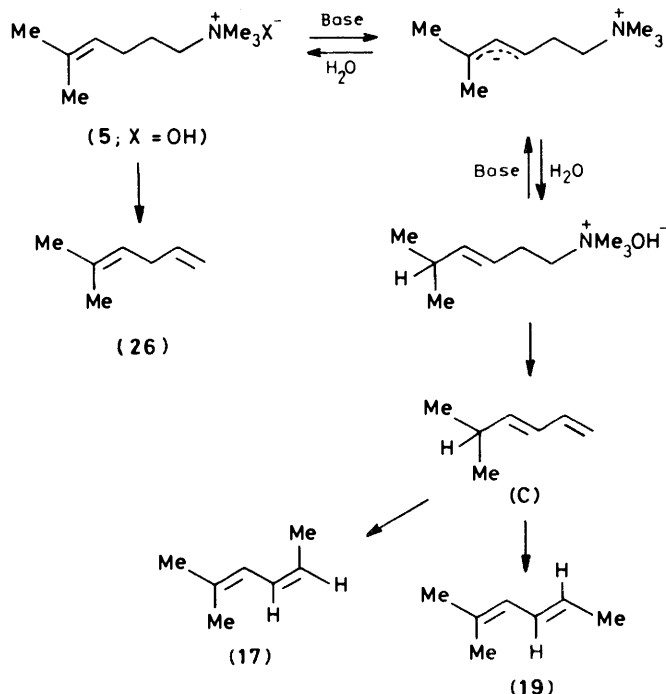


elimination will be facilitated by the fact that the hydrogen atom β to the ammonium ion, of the intermediate, is also allylic.

Thermal decomposition of *N,N,N*-trimethylpent-4-enyl-*N,N,N*-trimethylammonium hydroxide (4; X = OH) yields tertiary bases with loss of methanol. The major product was (*E*)-5-*N,N*-dimethylamino-4,4-dimethylpent-2-ene (16), its (*Z*)-isomer (15) being formed only in about 7%. This result can be explained by the fact that the *gem*-dimethyl group will encourage⁹ the formation of the *transoid*-anion (B) (Scheme 1) which will yield the (*E*)-isomer (16), rather than the anion (A), the precursor of the (*Z*)-isomer (15). There was a substantial amount of the un-isomerised amine (28). Its formation is a result of competitive reaction between *N*-demethylation with consequent loss of hydroxide and abstraction of a C-3-proton which requires hydroxide.

Decomposition of (4; X = O²H) yields the amines (16), (15), and (28), highly deuteriated in their *N*-methyl groups, but with little deuteriation at their C-5 positions.

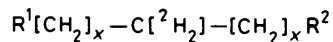
The major product of the decomposition of *N,N,N*-trimethyl-*N*-5-methylhex-4-enylammonium hydroxide (5; X = OH) is the unconjugated, 5-methylhexa-1,4-diene (26). This can be explained as follows (see Scheme 2). The base-catalysed equilibrium between (5; X = OH) and the other quaternary ammonium hydroxide shown in Scheme 2 must clearly lie in favour of the former, the common anion^{9b} being formed by abstraction of an allylic proton from (5; X = OH). Hofmann elimination reactions will yield the unconjugated diene (26) from (5; X = OH), and the conjugated diene (C) in lower yield than that of (26). Base catalysed rearrangement of the diene (C) will yield the thermodynamically more stable dienes (17) and (19). Alternatively these dienes may be formed by isomerisation of the 1,4-diene (26).



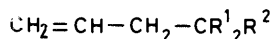
Substitution of deuterium for hydrogen in the 2-position of (5; X = OH) to give (6; X = OH) will reduce the rate of the simple Hofmann elimination in the latter. As a result, a higher proportion of the conjugated dienes (18) and (20) compared with the unconjugated diene (27) will be formed. This is the experimental result, based on analysis of the n.m.r. spectrum of the diene mixture. Another product from (6; X = OH) is 6-*N,N*-dimethylamino-2-methyl[5,5-²H₂]hex-2-ene (30). The corresponding undeuteriated amine (29) was not formed from (5; X = OH). Thus as a result of the deuterium isotope effect, in the decomposition of (6; X = OH) demethylation of its ammonium group is more competitive with the Hofmann elimination reaction than in the decomposition of (5; X = OH).

The mechanism shown in Scheme 1 can be applied to the thermal decomposition of *N,N,N*-trimethyl-*N*-oct-7-en-4-ylammonium hydroxide (34) which yields (2*Z*,4*E*)-octa-2,4-diene (21) as the predominant product (see preceding paper). In many respects the system of (34) can be compared with (1; X = OH). (2*E*,4*E*)-Octa-2,4-diene (22) is the largest but not the predominant product arising from the thermal decomposition of the mixture of *N,N,N*-trimethyl-*N*-(*E*)-oct-4- and -5-en-1-ylammonium hydroxides [mainly (35)] and (36). The system of (35) is similar to that of (5; X = OH) and the experimental results can be explained in a similar manner to those of (5; X = OH).

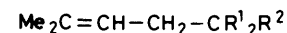
Materials.—*N,N,N*-Trimethyl-*N*-[3,3-²H₂]pent-4-enylammonium hydroxide (2; X = OH) was prepared by modification and extension of the method used by Lambert and Keske¹⁰ for the preparation of [4,4-²H₂]cyclohexanone. The deuteration of diethyl malonate with D₂O in pyridine is more convenient and economical than the method used by these workers. In the conversion of 1,3-dibromo[2,2-²H₂]propane (40), obtained from the diol (39), into the corresponding dinitrile (41) by Vogel's method,¹¹ 4-cyano[3,3-²H₂]butanamide (42) was a by-product. The mixture of dinitrile and amido-nitrile hydrolysed with acid gave [3,3-²H₂]glutaric acid (43). This was reduced to the diol (44) which was converted into the dibromide (45). 1,1-Dimethyl[4,4-²H₂]piperidinium iodide (46) was obtained from 1,5-dibromo[3,3-²H₂]pentane (45) by



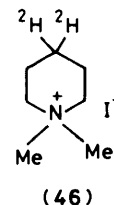
- (39) R¹ = R² = OH, x = 1
 (40) R¹ = R² = Br, x = 1
 (41) R¹ = R² = CN, x = 1
 (42) R¹ = CONH₂, R² = CN, x = 1
 (43) R¹ = R² = CO₂H, x = 1
 (44) R¹ = R² = OH, x = 2
 (45) R¹ = R² = Br, x = 2



- (47) R¹ = ²H, R² = CO₂H
 (48) R¹ = ²H, R² = CH₂OH
 (49) R¹ = ²H, R² = CH₂I
 (50) R¹ = Me, R² = CHO
 (51) R¹ = Me, R² = CH₂NH₂
 (52) R¹ = Me, R² = CH₂OH
 (53) R¹ = Me, R² = CH₂I



- (54) R¹ = H, R² = CO₂H
 (55) R¹ = ²H, R² = CO₂H



reaction with methylamine followed by halogen exchange. The quaternary salt (46) was converted into (2; X = OH) in the usual way.

N,N,N-Trimethyl-*N*-[2,2-²H₂]pent-4-enylammonium hydroxide (3; X = OH) was prepared by the route: allylmalonic acid → [2,2-²H₂]pent-4-enoic acid (47) → [2,2-²H₂]pent-4-enol (48) → mixture of toluene-*p*-sulphonate and chloride → [2,2-²H₂]pent-4-enyl iodide (49) → (3; X = I) → (3; X = OH).

N-2,2-Dimethylpent-4-enyl-*N,N,N*-trimethylammonium hydroxide (4; X = OH) was obtained by the route: 2,2-dimethylpent-4-enal (50)¹² → its oxime → 2,2-dimethylpent-4-enylamine¹³ (51) → (4; X = I) → (4; X = OH). An alternative method of preparing (4; X = I) from the aldehyde (50), *via* the alcohol (52) and 2,2-dimethylpent-4-enyl iodide (53) was abandoned, since this latter compound—a neopentyl iodide—failed to react with methylamine.

N,N,N-Trimethyl-*N*-5-methylhex-4-enylammonium hydroxide (5; X = OH) and its [2,2-²H₂]-derivative (6; X = OH) were prepared in a similar manner to (3; X = OH) from 3,3-dimethylallylmalonic acid → 5-methylhex-4-enoic acid (54)¹⁴ and its [2,2-²H₂]-derivative (55), respectively.

Experimental

Elementary analyses were carried out by g.l.c. ¹³C N.m.r. assignments were confirmed by off-resonance decoupling experiments.

General conditions for the thermal decomposition of the quaternary bases were as follows. A solution of the corresponding quaternary iodide in water, or in deuterium oxide, was stirred at 15 °C with freshly prepared silver oxide, added in portions until no iodide remained in the mother liquor. The mixture was filtered, the silver iodide was washed with water or deuterium oxide and the combined solutions were evaporated to a thick syrup at 15 °C and 0.1 mmHg. This was heated as rapidly as possible to 150–160 °C (bath temp.), and the products were collected in an ice-cold receiver and washed with 10% hydrochloric acid from which amine was recovered.

Tertiary amines, free from hydrocarbons were obtained by

the general procedure described using silver carbonate in place of silver oxide.

Ether refers to diethyl ether throughout.

N,N,N-Trimethyl-*N*-pent-4-enylammonium Iodide (1; X = I).—Thermal decomposition of *N*-methylpiperidine methoxide, from the quaternary iodide (62 g), gave 5-*N,N*-dimethylaminopent-1-ene (19 g), b.p. 117 °C (cf. ref. 15); ν_{\max} (liq. film) 2 760 (MeN), 1 638, 990, and 913 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.21 (s, Me_2N) and 4.7—6.2 (3 H, m, $\text{CH}_2=\text{CH}$); m/z 113 (M^+ , 4%). Its methiodide (1; X = I), needles (ethyl acetate-ethanol), had m.p. 225—226 °C; $\delta(\text{D}_2\text{O})$ 2.07 (4 H, m, $[\text{CH}_2]_2\text{CH}=\text{CH}_2$), 3.08 (s, Me_3N), 3.28 (t, CH_2N), 5.19 (m, $\text{CH}_2=\text{CH}$), and 5.72 (m, $\text{CH}=\text{CH}_2$) (Found: C, 37.9; H, 7.0; I, 49.9; N, 5.5. $\text{C}_8\text{H}_{18}\text{IN}$ requires C, 37.8; H, 7.1; I, 49.8; N, 5.5%).

(*Z*)- and (*E*)-Penta-1,3-dienes (7) and (11).—Thermal decomposition of (1; X = OH) derived from (1; X = I) (41 g) gave an oil (7.5 g), b.p. 41—43 °C. G.l.c. on a silver nitrate-ethylene glycol column revealed a 4:1 mixture of (*Z*)- and (*E*)-penta-1,3-dienes (7) and (11), the latter being eluted first. The mixture showed ν_{\max} (liq. film) 1 643, 1 597, 997, 955, 905, and 778 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.77 (d, J 5.9 Hz, Me), and 4.7—7.1 (5 H, m, olefinic H); comparable with the spectrum of a commercial sample of penta-1,3-diene (piperylene).

(±)-(3aS,4S,7aR)-4-Methyl-3a,4,7,7a-tetrahydrobenzo[*c*]furan-1,3-dione (32).—The mixture of dienes (7) and (11) (4.1 g) was stirred with maleic anhydride at 50—55 °C for 1 h, and the unpolymerised (*Z*)-diene (7) was then removed by distillation. This had b.p. 43—44 °C, ν_{\max} (liq. film) 3 010, 1 784, 1 643, 1 594, 999, 908, and 755 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.76 (d, J 6.2 Hz, Me) and 4.7—7.0 (5 H, m). It was used (g.l.c.) to identify the (*Z*)-diene (7) of the mixture. The residue had m.p., and mixed m.p. 61 °C with an authentic specimen¹⁶ of the adduct of (*E*)-penta-1,3-diene (11) with maleic anhydride.

Thermal Decomposition of *N,N,N*-Trimethyl-*N*-pent-4-enylammonium [²H]Hydroxide (1; X = O²H).—The quaternary salt (1; X = I) (14.4 g) in D_2O was stirred with silver oxide (7.5 g) giving the [²H]hydroxide (1; X = O²H). This was decomposed in the usual way giving a mixture of mainly (*Z*)-[²H]penta-1,3-diene (8) (ca. 85%), and its (*E*)-isomer (12) (ca. 15%), ν_{\max} (liq. film) 2 160 (C^2H), 1 810, 1 645, 1 597, 1 000, 970, 910, 775, and 640 cm^{-1} ; for the (*Z*)-isomer (8) δ (360 MHz; CDCl_3), 1.75 (2 H, br s, $^2\text{HCH}_2$), 5.10 (1 H, d, J 10 Hz, $\text{H}(\text{H})\text{C}=\text{CHCH}=\text{C}$), 5.17 [1 H, d, J 16.5 Hz, $\text{H}(\text{H})\text{C}=\text{CHCH}=\text{C}$], 5.53 (1 H, m, $^2\text{HCH}_2\text{CH}=\text{C}$), 6.03 (1 H, t, J 10 Hz, $^2\text{HCH}_2\text{CH}=\text{CH}$), and 6.66 (1 H, dt, J 16.5 and 10 Hz, $\text{CH}=\text{CH}_2$); for the (*E*)-isomer (12) δ (360 MHz; CDCl_3) 4.93 [1 H, d, J 10 Hz, $\text{H}(\text{H})\text{C}=\text{CHCH}=\text{C}$], 5.72 (1 H, m, $^2\text{HCH}_2\text{CH}=\text{C}$), and 6.32 (1 H, dt, J 17.5 and 10 Hz, $\text{CH}=\text{CH}_2$). Other signals are hidden below those of the (*Z*)-isomer. Signals in the ^{13}C n.m.r. spectrum of the mixture were seen at δ 137.5 [C-2, (12)], 132.9 [C-3, (12)], 132.3 [C-2, (8)], 130.5 [C-3, (8)], 129.8 [C-4, (12)], 126.9 [C-4, (8)], 116.6 [C-1, (8)], 114.4 [C-1, (12)], 17.9 [C-5, (12)], 13.3 [C-5, (8)], and 13.1 [t, J 20 Hz, $^2\text{HCH}_2$, (8)].

The basic fraction from the thermal decomposition extracted into chloroform (100 ml) was set aside with benzyl chloride (5 g) for several days and then evaporated to dryness at 40 °C, 20 mmHg. The hygroscopic solid (5 g) was washed with ether and then refluxed with sodium iodide (5 g) in acetone (5 ml). Sodium chloride was removed and the solvent distilled off giving deuteriated *N*-benzyl-*N,N,N*-trimethylammonium iodide, m.p. 176—177 °C (acetone) (lit.¹⁷ m.p. 177—178 °C for the undeuteriated salt); $\delta(\text{D}_2\text{O})$ 3.08 (s, MeN⁺), 4.50 (2 H, s, CH_2N^+),

and 7.59 (5 H, s, ArH). In three spectra the proton contents of the signal at δ 3.08 were 6.7, 6.86, and 6.75.

N,N,N-Trimethyl-*N*-[3,3-²H₂]pent-4-enylammonium Iodide (2; X = I)

Diethyl [²H₂]Malonate.—A mixture of diethyl malonate (50 g), anhydrous pyridine (80 ml), and deuterium oxide (33 ml) was stirred for 24 h, and a mixture of water and pyridine (110 ml), b.p. 95—115 °C, was carefully removed by distillation. The residue was again treated with pyridine (75 ml) and deuterium oxide (33 ml) over 24 h, and water and pyridine (113 ml) removed. The residue was washed with deuterium oxide, dried, and distilled giving the deuteriated ester (35.7 g), b.p. 32 °C at 0.1 mmHg; ^1H n.m.r. measurements showed complete deuteration.

[2,2-²H₂]Propane-1,3-diol (39).—The ester (22.4 g), reduced by Lambert's method¹⁰ using lithium aluminium hydride, gave the diol (8.5 g), b.p. 78 °C at 1 mmHg; ν_{\max} (liq. film) 3 350 (br), 2 210, and 2 135 cm^{-1} (C^2H); $\delta(\text{D}_2\text{O})$, 4.68 (s, CH_2OH).

1,3-Dibromo[2,2-²H₂]propane (40).—The diol (14.7 g) was added with stirring to freshly distilled phosphorus tribromide (20.4 g) in benzene (50 ml) at 0 °C, and stirring was continued for 1 h, giving the dibromide (25.2 g), b.p. 65 °C at 15 mmHg; ν_{\max} (liq. film) 2 200 and 2 120 cm^{-1} (C^2H); $\delta(\text{CCl}_4)$ 3.53 (s, CH_2Br).

[2,2-²H₂]Glutaric-1,3-dinitrile (41).—The dibromo compound (37.1 g) in ethanol (75 ml) was added over 30 min to a hot, stirred solution of sodium cyanide (22 g) in water (22 ml). The mixture was refluxed for 35 h, and worked up as previously described¹¹ giving the dinitrile (7.6 g), b.p. 100 °C at 1 mmHg. The higher boiling residue solidified and was crystallised from ethyl acetate-hexane giving 4-cyano[3,3-²H₂]butanamide (42), m.p. 65 °C (lit.¹⁸ gives m.p. 68—69 °C for the undeuteriated compound); ν_{\max} (Nujol) 3 480, 3 370, 3 220 (CONH_2), 2 248 (CN), 2 142 (C^2H), 1 680, and 1 615 cm^{-1} (CONH_2); $\delta(\text{CDCl}_3)$ 2.38 and 2.45 (4 H, 2 s, CH_2CONH_2 and CH_2CN) and 5.77 (2 H, br s, CONH_2) (Found: C, 52.55; H, 7.3; N, 24.3. $\text{C}_5\text{H}_6[{}^2\text{H}_2]\text{N}_2\text{O}$ requires C, 52.6; H, 7.0; N, 24.6%).

[3,3-²H₂]Glutaric Acid (43).—Hydrolysis of the mixture of the dinitrile (41) and the amide (42) (21 g) with sulphuric acid (315 ml; 50% w/v) gave the acid (10.1 g), m.p. 93 °C (ethyl acetate-hexane); ν_{\max} (Nujol) 2 230 and 2 140 (C^2H) and 1 700 cm^{-1} (CO_2H); $\delta(\text{D}_2\text{O})$ 2.4 (s, $\text{CH}_2\text{CO}_2\text{H}$) (Found: C, 44.7; H, 6.1. Calc. for $\text{C}_5\text{H}_6[{}^2\text{H}_2]\text{O}_4$: C, 44.8; H, 6.0%).

[3,3-²H₂]Pentane-1,5-diol (44).—Reduction of the preceding compound (10 g) with lithium aluminium hydride (cf. ref. 10) gave the diol (5.3 g), b.p. 90 °C at 0.3 mmHg; ν_{\max} (liq. film) 3 350 (br), 2 185, and 2 110 cm^{-1} ; $\delta(\text{D}_2\text{O})$ 1.57 (4 H, t, J 7 Hz, $\text{HOCH}_2\text{CH}_2\text{C}^2\text{H}_2$) and 3.63 (4 H, t, J 7 Hz, CH_2OH).

1,5-Dibromo[3,3-²H₂]pentane (45).—Bromination of the diol (44) by the method used for (40) gave the bromo compound, b.p. 86—88 °C at 10 mmHg; ν_{\max} (liq. film) 2 200 and 2 100, 1 275 and 1 220s (cf. ref. 19), and 630 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.88 (4 H, t, J 7 Hz, $^2\text{CH}_2\text{CH}_2\text{CH}_2$) and 3.42 (4 H, t, J 7 Hz, $\text{CH}_2\text{CH}_2\text{Br}$).

1,1-Dimethyl[4,4-²H₂]piperidinium Iodide (46).—The bromo compound (45) (8.8 g) in methanol (22 ml), initially cooled in ice, was stirred at room temperature for 24 h, with methylamine (15.2 g, 36%), then basified at 0 °C with saturated aqueous potassium hydroxide, and extracted several times with

methylene chloride. Removal of solvents from the dried extract gave an oil which was treated at 0 °C with methyl iodide in methanol. Removal of solvent gave the required quaternary salt (46) (5 g), m.p. 355 °C (ethyl acetate-ethanol); δ (360 MHz; D₂O) 1.95 (4 H, br s, C²H₂CH₂), 3.14 (6 H, s, NMe₂), and 3.39 (4 H, t, J 6 Hz, NCH₂).

N,N,N-Trimethyl-N-[3,3-²H₂]pent-4-enylammonium Iodide (2; X = I).—The quaternary salt (46) (5 g) was treated with silver oxide and the amine, 5-*N,N*-dimethylamino[3,3-²H₂]pent-1-ene (1.6 g) was isolated in the usual way. It was not purified, but was treated with methyl iodide in methanol giving the methiodide (2; X = I) (2.5 g), m.p. 221 °C (ethyl acetate-ethanol); δ (360 MHz; D₂O) 1.96 (2 H, m, C²H₂CH₂), 3.16 (9 H, s, NMe₃), 3.36 (2 H, m, NCH₂), 5.14 and 5.18 (2 H, two overlapping d, J 11 and 17 Hz, H₂C=C), and 5.94 (1 H, dd, J 11 and 17 Hz, C²H₂CH=CH₂).

The ¹H n.m.r. spectra of the above compounds show that deuteration at the allylic position is at least 95%.

Deuterated Benzyltrimethylammonium Iodide.—The quaternary salt (2; X = I) (2.25 g) was treated with silver oxide in the usual way and the quaternary base decomposed. The trimethylamine and piperynes formed were collected in chloroform, and benzyl chloride (1.5 g) was added. After 24 h, solvent containing piperynes was removed by distillation and collected. The residue was washed with acetone, suspended in acetone (15 ml), stirred and refluxed with sodium iodide. Sodium chloride was removed by filtration and solvent was removed by distillation giving the quaternary iodide (0.2 g), m.p. 175–176 °C (acetone); δ (55 MHz; D₂O) 2.95 (NMe₂CH₂⁺H). The abundance of ²H in the quaternary iodide relative to the natural abundance of ²H in H₂O is 0.2155:1. Using 20.00 mg of quaternary iodide in 2.0 ml H₂O, monodeuteration is 9.93%.

N,N,N-Trimethyl-N-[2,2-²H₂]pent-4-enylammonium Hydroxide (3; X = OH)

[2,2-²H₂]Pent-4-enoic Acid (47).—Diethyl allylmalonate (20 g) was stirred with sodium hydroxide (16 g) in water (50 ml) until homogeneity was attained (15–20 h). The mixture was diluted with water, carefully acidified at 0–5 °C, saturated with ammonium sulphate, and extracted with ether (5 × 50 ml) to give allylmalonic acid (12 g), m.p. 105 °C (plates, hexane-ethyl acetate) (lit.,¹⁴ m.p. 102 °C); ν_{\max} 3 010 (CH₂=CH), 1 710, 1 645, 990, and 910 cm⁻¹. The acid (3 g) was stirred for 16 h with deuterium oxide (1.5 ml) and anhydrous pyridine (15 ml) and then concentrated to a syrup at 15 °C, 0.1 mmHg. The exchange was repeated on two further occasions when the ¹H n.m.r. spectrum showed complete deuteration. The product was refluxed for 2 h, with pyridine (6 ml) and deuterium oxide (1 ml) giving [2,2-²H₂]pent-4-enoic acid (47) (1.7 g), b.p. 51 °C at 0.25 mmHg (lit.,¹⁴ gives b.p. 90 °C at 16 mmHg for the undeuterated acid); ν_{\max} (liq. film) 2 140 (C²H), 1 710, 1 645, 995, and 915 cm⁻¹; δ (CCl₄) 2.28 (d, J 7 Hz, CH₂CH=CH₂), 4.94 (m, CH₂=CH), and 5.73 (m, CH=CH₂).

[2,2-²H₂]Pent-4-enol (48).—A stirred solution of the acid (47) (29 g) in ether (100 ml) was slowly treated with lithium aluminium hydride (9.5 g) and the mixture was refluxed for 1 h. The usual work-up gave the alcohol (20.5 g), b.p. 134–135 °C; 28–29 °C at 0.5 mmHg (lit.,²⁰ gives b.p. 136 °C for the undeuterated alcohol prepared by a different method); ν_{\max} (liq. film) 3 350, 2 200, 2 125, 1 643, 997, and 915 cm⁻¹; δ (CCl₄) 2.05 (d, J 6 Hz, CH₂C=C), 3.0 (CH₂OH), 3.5 (s, CH₂OH), 4.97 (m, CH₂=C), and 5.78 (m, CH=C).

N,N,N-Trimethyl-N-[2,2-²H₂]pent-4-enylammonium Iodide (3; X = I).—Reaction of the alcohol (48) (3 g) in pyridine (20 ml) with toluene-*p*-sulphonyl chloride (7 g) gave a mixture of the toluene-*p*-sulphonate and chloride, ν_{\max} (liq. film) 2 200, 2 150 (C²H), 1 645 (C=C), 1 600 and 1 500 (Ar), 1 365 and 1 200 (SO₂), 1 000 and 910 (CH=CH₂), and 660 cm⁻¹ (Cl). This was refluxed in acetone (50 ml) with sodium iodide (15 g) giving [2,2-²H₂]pent-4-enyl iodide (49).²¹ The iodide was stirred with an excess of trimethylamine (33%) until homogeneous, and the solution was evaporated to dryness at 40 °C, 20 mmHg. The quaternary iodide (3; X = I) was obtained as needles (ethyl acetate-acetone), m.p. 210–211 °C (decomp.) (lit.,²² gives m.p. 227–229 °C for the undeuterated salt); ν_{\max} (Nujol) 2 220, 2 100, 1 640, 990, and 910 cm⁻¹; δ (D₂O) 2.05 (d, J 6 Hz, CH₂CH=C), 3.05 (s, Me₃N⁺), 3.22 (s, CH₂N⁺), 5.0 (m, CH₂=CH), 5.8 (m, CH=CH₂) (Found: C, 37.2; H, 7.5; I, 49.3; N, 5.4. C₈H₁₆[²H₂]IN requires C, 37.4; H, 7.0; I, 49.4; N, 5.4%).

(*Z*)- and (*E*)-[2-²H]Penta-1,3-dienes (10) and (14).—Thermal decomposition of the quaternary base (3; X = OH) from (3; X = I) (20.6 g) gave hydrocarbon (4 g) and amine (0.2 g) fractions. The hydrocarbon fraction, virtually completely monodeuterated, consisted mainly (>80% by g.l.c., n.m.r.) of (*Z*)-[2-²H]penta-1,3-diene (10), b.p. 42–45 °C; ν_{\max} (liq. film) 2 245, 2 000, 1 640, 1 590, 995, 970, 905, 725, and 675 cm⁻¹; δ (CCl₄; 360 MHz) 1.77 [d, J 7 Hz, (*Z*)-MeCH=CH], 5.09 [br s, ²HC=C(H)H], 5.16 [br s, ²HC=C(H)H] 5.54 [dq, J 10.5, 7 Hz, (*Z*)-MeCH=CHC²H=C], 5.71 [dq, J 15, 7 Hz, (*E*)-MeCH=CHC²H=C], and 6.02 [d, J 10.5 Hz, (*Z*)-MeCH=CHC²H=C].

Adduct with maleic anhydride. The mixture of (10) and (14) (1 g) and maleic anhydride (1.5 g) was kept at 50 °C for 1 h, and (*Z*)-[2-²H]penta-1,3-diene (0.1 g), b.p. 43 °C, ν_{\max} 670 cm⁻¹ removed by distillation. The adduct, (±)-(3aS,4S,7aR)-4-methyl[6-²H]-3a,4,7a-tetrahydrobenzo[*c*]furan-1,3-dione (33) (20 mg), extracted from polymeric material with hot benzene, had m.p. 57 °C (needles; benzene-hexane) (lit.,¹⁶ m.p. 61 °C for the undeuterated adduct); ν_{\max} (Nujol) 1 840 and 1 770 cm⁻¹; δ (CDCl₃) 2.3 (d, J 6 Hz, MeCH), 2.11 (m, 7-H), 2.45 (m, 4-H), 2.6 (m, 7-H), 3.02 (d, J 6 Hz, 3a-H), 3.22 (m, 7a-H), and 6.0 (br s, 5-H); *m/z* 139 (*M*⁺ – CO, 28%), 95 (*M*⁺ – C₂O₃, 58), 94 (*M*⁺ – C₂O₃ – H, 44), 80 (*M*⁺ – Me – C₂O₃, 100), and 69 (C₅H₇²H, 8). The undeuterated adduct shows *m/z* 138 (33%), 94 (64), 93 (72), 79 (100), and 68 (10).

The basic fraction (0.2 g) formed from the decomposition of (3; X = OH) was 5-*N,N*-dimethylamino[4,4-²H₂]pent-1-ene, ν_{\max} (liq. film) 2 200, 2 100, 1 645, 1 000, and 915 cm⁻¹; *m/z* 115 (*M*⁺, 38%), 114 (*M*⁺ – H, 26), 79 (100), 58 (CH₂NMe, 26), and 52 (70).

For comparison purposes, the following compounds were prepared by the route used for (3; X = I): pent-4-enoic acid, b.p. 50 °C at 0.5 mmHg (cf. ref. 14) and pent-4-enol, b.p. 45 °C at 15 mmHg (cf. ref. 20). Reaction of this alcohol (2 g) in pyridine (20 ml) with toluene-*p*-sulphonyl chloride (4.9 g) gave pent-4-enyl chloride (2.1 g), b.p. 110 °C (lit.,²¹ gives b.p. 102–104 °C); ν_{\max} (liq. film) 1 645, 1 000, 920, and 705 cm⁻¹. Pent-4-enyl iodide,²¹ not purified, gave the methiodide of 5-*N,N*-dimethylaminopent-1-ene, m.p. 225–226 °C (cf. ref. 22).

N-2,2-Dimethylpent-4-enyl-N,N,N-trimethylammonium Iodide (4; X = I)

2,2-Dimethylpent-4-enylamine (51).—2,2-Dimethylpent-4-enal (50)¹² gave by Bousquet's method¹³ its oxime, b.p. 46–47 °C at 0.3 mmHg (lit.,²³ b.p. 85 °C at 17 mmHg); ν_{\max} 3 330, 1 645, 995, 950, and 920 cm⁻¹; δ (CDCl₃) 9.25 (s, C=NOH), 1.18

(s, Me₂C), 2.17 (d, *J* 7 Hz, CH₂CH=C), and 4.85–6.0 (4 H, m, olefinic CH₂=CH and HC=N). The oxime (19 g) in ethanol (300 ml) was reduced with sodium (75 g) (*cf.* ref. 24) giving the required amine (51), b.p. 48–49 °C at 20 mmHg (lit.,²⁵ gives b.p. 130–133.5 °C); ν_{\max} (Nujol) 3 400 and 3 320 cm⁻¹ (NH); δ (80 MHz; CDCl₃), 0.85 (s, Me₂C), 1.06 (s, NH₂), 1.97 (dt, *J* 1.1 and 7.3 Hz, CH₂CH=C), 2.38 (s, CH₂NH₂), 4.82 and 4.98 (2 m, CH₂=CH), and 5.7 (m, CH=CH₂) (Found: C, 74.2; H, 13.7; N, 12.7. Calc. for C₇H₁₅N: C, 74.3; H, 13.3; N, 12.4%). Its *toluene-p-sulphonyl derivative* (needles; ethanol–water) had m.p. 71–72 °C (Found: C, 62.6; H, 8.0; N, 5.3. C₁₄H₂₁NO₂S requires C, 62.9; H, 7.9; N, 5.2%).

Methiodide (4; X = I).—A stirred mixture of the amine (51) (9.3 g), ethanol (40 ml), and anhydrous potassium carbonate (16.6 g) was slowly treated with methyl iodide (19 ml) and stirring was continued for 18 h. The solid was collected, washed with hot ethanol (2 × 10 ml), and the combined filtrate and washings was evaporated to dryness at 40 °C, 20 mmHg. The solid product was crystallised from ethyl acetate–ethanol giving the *quaternary iodide* (4; X = I) (17.5 g) as rhombs, m.p. 219–220 °C (decomp.); δ (D₂O) 1.33 (s, Me₂C), 2.23 (dt, *J* 1.1, 7 Hz, CH₂CH=C), 3.23 (s, Me₃N⁺), 3.33 (s, CH₂N⁺), 5.0 and 5.26 (2 m, CH₂=CH), and 5.7 (m, CH=C) (Found: C, 42.5; H, 7.85; I, 44.6; N, 4.8. C₁₀H₂₂IN requires C, 42.4; H, 7.8; I, 44.9; N, 4.9%).

Thermal Decomposition of (4; X = OH).—The base from the quaternary iodide (4; X = I) (5 g) gave a mixture of amines (1.5 g), b.p. 58–59 °C at 20 mmHg, consisting (*i.e.*, ¹H n.m.r.) of (*E*)-5-*N,N*-dimethylamino-4,4-dimethylpent-2-ene (16) (60%), its (*Z*)-isomer (15) (7%), and 5-*N,N*-dimethylamino-4,4-dimethylpent-1-ene (28) (33%). The mixture showed ν_{\max} (liq. film) 3 090, 3 020, 2 770 (MeN), 1 645, 1 000 and 920 (CH₂=CH), and 980 cm⁻¹ (*trans*-CH=CH); δ (CDCl₃) 0.98 [*ca.* 3.6 H, s, Me₂C (16)], 1.13 [*ca.* 0.42 H, s, Me₂C (15)], 0.87 [*ca.* 1.98 H, s, Me₂C (28)], 1.65 (d, MeCH=C), 1.81 (d, CH₂C=C), 2.2 (s, Me₂N), 2.22 (s, CH₂N), 4.99 and 5.15 (2 m, CH₂=C), and 5.7 (m, CH=CH₂); δ_c (CDCl₃) 18.1 [C-1 (16)], 116.7 [C-1 (28)], 120.7 [C-2 (16)], 136.0 [C-2 (28)], 141.2 [C-3 (16)], 45.1 [C-3 (28)], 37.7 [C-4 (16)], 35.8 [C-4 (28)], 72.0 [C-5 (16)], 70.8 [C-5 (28)], 26.2 [MeC (16)], 27.5 [MeC (15)], 25.6 [MeC (28)], 48.5 [MeN (16)], and 48.9 [MeN (28)].

5-*N,N*-Dimethylamino-4,4-dimethylpent-1-ene (28).—The quaternary iodide (4; X = I) (5 g) in water (10 ml) was stirred with silver carbonate in excess, the mixture was filtered, the filtrate evaporated to a syrup under reduced pressure and then heated at 150–155 °C (bath temp.) giving the pure *amine* (28) (2.2 g), b.p. 60 °C at 20 mmHg; ν_{\max} 3 085, 3 005, 2 780, 1 645, 1 000, and 915 cm⁻¹; δ (CDCl₃) 0.86 (s, Me₂C), 2.06 (dt, *J* 8 and 1 Hz, CH₂C=C), 2.11 (s, CH₂N), 2.28 (s, Me₂N), 4.12 and 5.07 (2 m, CH₂=CH), and 5.7 (m, CH=C); δ_c (CDCl₃) 25.6 (q, MeC), 35.8 (s, C-4), 45.1 (t, C-3), 48.9 (q, Me₂N), 70.8 (t, C-5), 116.7 (t, C-1), and 136.0 (d, C-2) (Found: C, 76.1; H, 13.4; N, 9.7. C₉H₁₉N requires C, 76.6; H, 13.5; N, 9.9%).

Isomerisation of 5-*N,N*-Dimethylamino-4,4-dimethylpent-1-ene (28) to mainly (*E*)-5-*N,N*-Dimethylamino-4,4-dimethylpent-2-ene (16).—The amine (28) (0.8 g), potassium hydroxide (0.9 g), and dimethyl sulphoxide (4 ml) were heated for 6 h, at 140 °C. The usual work-up gave an oil (0.6 g) whose *i.e.* spectrum showed a major peak at 975 cm⁻¹ (*trans*-CH=CH) and reduced intensity in the peaks at 3 085, 1 000, and 915 cm⁻¹. Its ¹H and ¹³C n.m.r. spectra (CDCl₃) provided an identification of the products.

2,2-Dimethylpent-4-enyl Iodide (53).—The corresponding alcohol (52) was prepared from the aldehyde (50) (43.6 g) which

was reduced in ethanol (100 ml) and water (25 ml) with sodium borohydride (6.1 g). The alcohol (52) (40 g) had b.p. 72 °C at 20 mmHg (lit.,¹² b.p. 152.5–153 °C); ν_{\max} (liq. film) 3 350, 3 085, 3 000, 1 640, 997, and 912 cm⁻¹; δ (CDCl₃) 0.88 (s, Me₂C), 2.02 (d, *J* 7.3 Hz, CH₂CH=CH₂), 3.21 (s, CH₂OH), 4.95 and 5.11 (2 m, CH₂=CH), and 5.5 (m, CH=CH₂).

The alcohol (52) (21 g) in pyridine (150 ml) and toluene-*p*-sulphonyl chloride (53 g) gave, after 72 h, the toluene-*p*-sulphonate as a thick oil (45 g), ν_{\max} (liq. film) 1 640, 1 600, 1 500, 1 370, 1 190, 1 005, and 915 cm⁻¹ which was refluxed for 18 h in acetone (180 ml) with sodium iodide (91 g, 3.3 mol). The *iodide* (53) (18.5 g) thus obtained had b.p. 92–93 °C at 20 mmHg; ν_{\max} (liq. film) 3 090, 3 010, 1 645, 1 005, and 920 cm⁻¹; δ (CCl₄) 1.05 (s, Me₂C), 2.1 (d, *J* 7 Hz, CH₂CH=CH₂), 3.13 (s, CH₂I), 4.9 and 5.12 (2 m, CH=CH₂), and 5.5 (m, CH=CH₂) (Found: C, 37.9; H, 6.1; I, 56.6. C₇H₁₃I requires C, 37.5; H, 5.8; I, 56.7%).

Thermal Decomposition of the Metho[²H]hydroxide (4; X = O²H).—The quaternary iodide (4; X = I) (10 g) reacted with silver oxide in D₂O (20 ml) to give the metho[²H]hydroxide which at 150 °C (bath temp.) afforded a mixture of deuterated amines (3 g), b.p. 65–66 °C at 20 mmHg; ν_{\max} 3 080, 2 870, 2 840, 2 800, 2 180vs, 2 050vs, 1 640, 1 000, 975, and 915 cm⁻¹. The NMe region (2 800–2 900 cm⁻¹) was much simpler than that of the undeuterated amines and its ¹H n.m.r. spectrum showed the presence of deuterium in the *N*-methyl groups.

***N,N,N*-Trimethyl-*N*-5-methylhex-4-enylammonium
iodide (5; X = I)**

5-Methylhex-4-enoic Acid (54).—Diethyl sodiomalonate[ester (48 g), sodium (6.9 g) in ethanol (150 ml)] was rapidly treated at 0 °C with 3,3-dimethylallyl bromide (44 g) in ethanol (50 ml), stirred for 6 h at 15 °C and refluxed for 0.5 h, giving diethyl 3,3-dimethylallylmalonate (40 g), b.p. 136–138 °C at 15 mmHg (*cf.* ref. 14). The ester was stirred with sodium hydroxide (16 g) in water (50 ml) until homogeneity was attained. The usual work-up gave 3,3-dimethylallylmalonic acid (16 g), m.p. 96 °C (hexane–ethyl acetate) (lit.,¹⁴ 96 °C); ν_{\max} 2 650, 1 730, and 1 710 cm⁻¹. The malonic acid (16 g) was refluxed for 2 h in pyridine (35 ml) and water (2 ml) giving 5-methylhex-4-enoic acid (54) (11.7 g), b.p. 67 °C at 0.3 mmHg (lit.,¹⁴ b.p. 95 °C at 1 mmHg); ν_{\max} (liq. film) 2 680, 1 710, and 830 cm⁻¹; δ (CCl₄) 1.67, 1.62 (2 s, Me₂C=C), 2.3 (m, *J* 3.5 Hz, CH₂CH=C), and 5.0 (br s, CH=CMe₂). Its *methyl ester*²⁶ had b.p. 60–61 °C at 12 mmHg; ν_{\max} (liq. film) 1 745, 1 675, and 830 cm⁻¹; δ (CCl₄) 1.60 and 1.67 (2 s, Me₂C=C), 2.22 (4 H, m, CH₂CH₂CH=C), 3.58 (s, OMe), and 5.0 (br s, HC=C) (Found: C, 68.1; H, 9.8. C₈H₁₄O₂ requires C, 67.6; H, 9.8%).

5-Methylhex-4-en-1-ol.—The hexenoic acid (54) (22.9 g) in ether (50 ml) was added slowly to a stirred suspension of lithium aluminium hydride (8 g) in ether (30 ml) kept at 0 °C, and then refluxed for 1 h, giving the alcohol (18.4 g), b.p. 39–40 °C at 0.2 mmHg (lit.,¹⁵ gives b.p. 82–83 °C at 20 mmHg for this alcohol prepared by a different method); ν_{\max} (liq. film) 3 350, 1 670, and 832 cm⁻¹; δ (CCl₄) 1.6 and 1.65 (2 s, Me₂C=C), 2.05 (m, CH₂CH₂C=C), 2.43 (OH), 3.65 (t, *J* 7 Hz, CH₂OH), and 5.01 (t, *J* 7 Hz, CH=C) (Found: C, 73.5; H, 12.2. Calc. for C₇H₁₄O: C, 73.7; H, 12.3%).

5-Methylhex-4-enyl iodide.—The preceding alcohol (18.4 g), stirred for 24 h with toluene-*p*-sulphonyl chloride (34 g) in pyridine (50 ml), gave (*i.e.*) a mixture (36 g) of the toluene-*p*-sulphonate and chloride. This mixture was refluxed for 16 h in acetone (50 ml) with sodium iodide (48 g) giving 5-methylhex-4-

enyl iodide (19.1 g), b.p. 45 °C at 0.5 mmHg (lit.,¹⁵ b.p. 50—52 °C at 5 mmHg); ν_{\max} 1 675 and 835 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.63 and 1.67 (2 s, $\text{Me}_2\text{C}=\text{C}$), 1.83—2.13 (4 H, m, $[\text{CH}_2]_2$), 3.1 (t, J 7 Hz, CH_2I), and 5.0 (t, J 7 Hz, $\text{CH}=\text{C}$) (Found: C, 37.3; H, 5.9. Calc. for $\text{C}_7\text{H}_{13}\text{I}$: C, 37.5; H, 5.8%).

Methiodide (5; X = I).—The preceding iodide (19 g), stirred with trimethylamine (75 ml; 33%) until homogeneity was attained and the solution then evaporated to dryness, gave the *quaternary iodide* (5; X = I) (24 g), m.p. 143—144 °C (shrinking 138—139 °C) (rhombs; ethyl acetate–ethanol); $\delta(\text{D}_2\text{O})$ 1.78 and 1.87 (2 s, Me_2), 2.0—2.42 (4 H, m, $[\text{CH}_2]_2$), 3.23 (s, Me_3N^+), 3.43 (t, J 8 Hz, CH_2N^+), and 5.3 (t, J 7 Hz, $\text{CH}=\text{C}$) (Found: C, 42.1; H, 7.8; I, 45.1; N, 4.85. $\text{C}_{10}\text{H}_{22}\text{IN}$ requires C, 42.4; H, 7.8; I, 44.9; N, 4.9%).

5-Methylhexa-1,4-diene (26)⁵ and (Z)- and (E)-2-Methylhexa-2,4-dienes (17)⁶ and (19),⁶ respectively.—The quaternary base (5; X = OH) from the iodide (5; X = I) (20 g) gave hydrocarbons (3.6 g), b.p. 98—102 °C and amines (1.15 g), b.p. 120 °C at 30 mmHg. The hydrocarbon product had i.r. bands at 3 080, 3 030, and 1 815 ($\text{CH}_2=\text{CH}$), 1 640 (isolated $\text{C}=\text{C}$), 1 625 and 1 610 ($\text{C}=\text{C}=\text{C}$), 990 and 910 ($\text{CH}_2=\text{CH}$), 960 (*trans*- $\text{CH}=\text{CH}$), and 720 cm^{-1} (*cis*- $\text{CH}=\text{CH}$); $\delta(\text{CDCl}_3)$ 1.67 (d, J 8 Hz, $\text{MeCH}=\text{C}$), 1.61, 1.72, 1.76, and 1.79 (4 s, $\text{Me}_2\text{C}=\text{C}$), 2.65 (*ca.* 0.7 H, t, J 7 Hz, $\text{CH}_2\text{C}=\text{C}$), and 4.63—6.3 ($\text{CH}=\text{C}$ and $\text{CH}_2=\text{C}$); $\delta_c(\text{CDCl}_3)$ 13.2 [Me, C-6 of (19)], 17.7 (Me), 17.9 (Me), 18.1 [Me, C-6 of (17)], 18.6 [Me, C-6 of (26)], 25.0 (Me), 25.5 [Me, C-1 of (19)], 26.0 [C-5—Me of (26)], 21.6 [t, C-3 of (26)], 114.2 [C-1 of (26)], 137.7 [C-2 of (26)], 130.1, 126.6, 126.5, 126.0, 125.0, 123.4, and 121.7; m/z 96 (M^+), 81 ($M^+ - \text{Me}$, 100%), 55 ($M^+ - \text{C}_3\text{H}_5$), and 41 ($\text{CH}_2\text{CH}=\text{CH}_2^+$). G.l.c. on a 15% D.C. 200 Chromosorb P column afforded a separation into two entities. The peak of lower retention time corresponded to that of pure 5-methylhexa-1,4-diene (26), $\delta(\text{CDCl}_3)$ 1.61 and 1.72 (2 s, Me_2C), 2.65 (t, J 7 Hz, $\text{CH}_2\text{CH}=\text{C}$), 4.7—5.15 (3 H, m, $\text{CH}_2=\text{CH}$), and 5.38—5.95 (1 H, m, $\text{CH}=\text{C}$). The peak of higher retention time corresponded to that of a mixture of (17) and (19). Three peaks were displayed on a 30 m methyl silicone column at 70 °C with a flame ionisation detector, elution being in the order (26) (47%), (17) (25.5%), and (19) (27.5%). The dienes (17) and (19) were not fully characterised. By g.c.-mass spectrometry they displayed similar spectra varying only in the quantity of the ions excepting $M^+ - \text{Me}$ which was 100% in each case.

6-N,N-Dimethylamino-2-methylhex-2-ene (29) and 6-N,N-Dimethylamino-2-methylhexan-2-ol (31).—The amines were extracted from the decomposition products of (5; X = OH) with 10% hydrochloric acid and the extract was evaporated to dryness at 50 °C (20 mmHg). The product was basified giving an oil which showed two spots on t.l.c., ν_{\max} (liq. film) 3 350 (OH), 2 820 and 2 780 (NMe_2), 1 650, and 840 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.2 (s, Me_2COH), 1.62 and 1.68 (2 s, $\text{Me}_2\text{C}=\text{C}$), 1.9 and 1.45 (m, CH_2), 2.23 (s, Me_2N), 2.33 (t, J 7 Hz, CH_2N), 2.63 (OH), and 5.1 (t, J 7 Hz, $\text{CH}=\text{C}$). The compound of lower polarity was 6-N,N-dimethylamino-2-methylhex-2-ene (29) (see below). The other compound was 6-N,N-dimethylamino-2-methylhexan-2-ol (31). A similar mixture was formed (t.l.c., i.r., n.m.r.) when the unsaturated amine (29) was stirred overnight with 10% hydrochloric acid.

6-N,N-Dimethylamino-2-methylhex-2-ene (29).—The quaternary iodide (5; X = I) (4.3 g) was stirred with silver carbonate, filtered, the aqueous solution evaporated to dryness and then heated at 150 °C (bath temp.) giving the *amine* (29) (1.5 g), b.p. 87 °C at 30 mmHg; ν_{\max} (liq. film) 2 780, 2 760, 1 670, and 845

cm^{-1} ; $\delta(\text{CCl}_4)$ 1.62 and 1.7 (2 s, $\text{Me}_2\text{C}=\text{C}$), 1.83—2.2 (4 H, m, $[\text{CH}_2]_2$), 2.33 (s, Me_2N), 2.38 (t, J 8 Hz, CH_2N), and 5.1 (t, J 7 Hz, $\text{CH}=\text{CMe}_2$) (Found: C, 76.6; H, 13.3; N, 10.1. $\text{C}_9\text{H}_{19}\text{N}$ requires C, 76.6; H, 13.5; N, 9.9%).

N,N,N-Trimethyl-N-5-methyl[2,2-²H₂]hex-4-enylammonium Iodide (6; X = I)

5-Methyl[2,2-²H₂]hex-4-enoic acid (55).—This acid, prepared from 3,3-dimethylallylmalonic acid by the method used for the preparation of [2,2-²H₂]pent-4-enoic acid (47), had b.p. 67 °C at 0.3 mmHg; ν_{\max} 2 140 (C^2H), 1 710, and 830 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.63 and 1.70 (2 s, Me_2C), 2.28 (d, J 6 Hz, $\text{CH}_2\text{CH}=\text{CMe}_2$), and 5.07 (t, J 6 Hz, $\text{CH}=\text{CMe}_2$). Its *methyl ester* had b.p. 60—61 °C at 12 mmHg; ν_{\max} (liq. film) 2 140, 2 100, 1 735, and 820 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.58 and 1.63 (2 s, Me_2C), 2.24 (d, J 6 Hz, $\text{CH}_2\text{CH}=\text{CMe}_2$), 3.57 (s, CO_2Me), and 5.0 (t, J 6 Hz, $\text{CH}=\text{CMe}_2$) (Found: C, 66.8; 'H', 9.9. $\text{C}_8\text{H}_{12}[^2\text{H}_2]\text{O}_2$ requires C, 66.7; 'H', 9.7%).

5-Methyl[2,2-²H₂]hex-4-en-1-ol.—This alcohol had b.p. 45 °C at 0.5 mmHg; ν_{\max} (liq. film) 3 340, 2 195, 2 115, 1 600, and 825 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.62 and 1.70 (2 s, Me_2C), 2.05 (d, J 7 Hz, $\text{CH}_2\text{CH}=\text{CMe}_2$), 2.85 (s, CH_2OH), 3.61 (s, CH_2OH), and 5.14 (t, J 7 Hz, $\text{CH}=\text{CMe}_2$).

5-Methyl[2,2-²H₂]hex-4-enyl Iodide.—This iodide was prepared from the mixture of the toluene-*p*-sulphonate and chloride obtained from the 5-methylhex-4-en-1-ol, but was not purified, ν_{\max} (liq. film) 2 190, 2 105, 1 670, 1 645, and 820 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.63 and 1.67 (2 s), 2.05 (d, J 7 Hz), 3.08 (s, CH_2I), and 5.0 (t, J 7 Hz).

Methiodide (6; X = I).—The preceding iodide was stirred with trimethylamine as described above giving the *quaternary iodide* (6; X = I), m.p. 142 °C (shrinking 138 °C) (ethyl acetate–ethanol); ν_{\max} (Nujol) 2 210 (C^2H), 1 670, and 820 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.62 and 1.67 (2 s, Me_2C), 2.1 (d, J 7 Hz, $\text{CH}_2\text{CH}=\text{CMe}_2$), 3.43 (s, Me_3N^+), 3.57 (s, CH_2N^+), and 5.01 (t, J 7 Hz, $\text{CH}=\text{CMe}_2$). It was virtually completely deuteriated at C-2.

Thermal Decomposition of (6; X = OH).—The base (6; X = OH) from the quaternary iodide (3.5 g) gave a hydrocarbon fraction (0.5 g), b.p. 82—85 °C; ν_{\max} (liq. film) 3 080, 3 020 ($\text{CH}_2=\text{CH}$), 2 240 (C^2H), 1 650, 1 625, 990, 970, 910, and 720 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.59 and 1.68 (2 s, $\text{Me}_2\text{C}=\text{C}$), 1.76 (s, $\text{MeC}^2\text{H}=\text{C}$), 2.69 (d, J 7 Hz, $\text{Me}_2\text{C}=\text{CHCH}_2\text{C}^2\text{H}=\text{CH}_2$), 4.61 and 4.85 (2 s, $\text{CH}_2=\text{C}^2\text{H}$), and 5.75 and 6.13 (2 d, J 10 Hz, $\text{Me}_2\text{C}=\text{CHCH}=\text{C}^2\text{HMe}$). The basic fraction (0.1 g) consisted of 6-N,N-dimethylamino-2-methyl[5,5-²H₂]hex-2-ene (30), a pure specimen of which was prepared from the quaternary iodide (6; X = I) (3.7 g) and silver carbonate and thermal decomposition of the product. The amine (30) (1.6 g) had b.p. 98—99 °C at 15 mmHg; ν_{\max} (liq. film) 2 820, 2 770, 2 200, 2 120, 1 670, 1 650, and 830 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.60 and 1.67 (2 s, $\text{Me}_2\text{C}=\text{C}$), 1.94 (d, J 7 Hz, $\text{Me}_2\text{C}=\text{CHCH}_2\text{C}^2\text{H}_2$), 2.12 (two overlapping s, CH_2N and Me_2N), and 5.01 (t, J 7 Hz, $\text{Me}_2\text{C}=\text{CHCH}_2$).

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