Base Catalysed Rearrangements involving Ylide Intermediates. Part 2.[1] The Stevens [1,2] and [3,2] Sigmatropic Rearrangements of Allylic Ammonium Ylides

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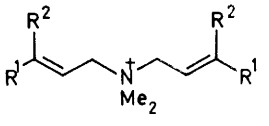
The base catalysed rearrangement of the quaternary ammonium salts (9) usually gives the [3,2] sigmatropic rearrangement product (10) rather than the Stevens [1,2] rearrangement product (11). An earlier claim has been corrected: the corresponding reaction of the acetylenic ammonium chloride (16) gives the allene (18). These results are discussed in terms of a competition between the symmetry-allowed [3,2] sigmatropic rearrangement and the non-allowed Stevens [1,2] rearrangement which is formulated either as proceeding *via* a radical pair intermediate or as being a concerted symmetry-forbidden process.

THE base catalysed transformations of diallylammonium cations (1) and allylpropynylammonium cations (2) are believed to involve rearrangement of the intermediate ylides.[1] Two main types of reaction pathway are observed. The preferred pathways may be regarded as



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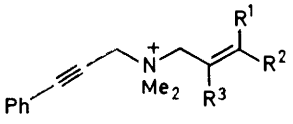

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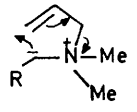

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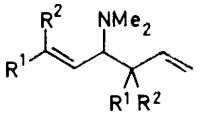

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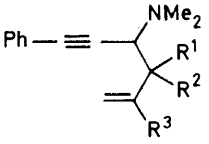

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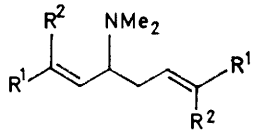

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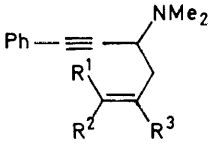

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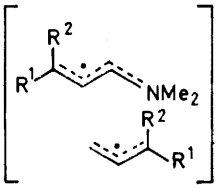

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intramolecular S_N2' reactions (3) associated with participation of six electrons. The transformations (1) ⟶ (4) and (2) ⟶ (5) are [3,2] sigmatropic rearrangements.[2] The competing but minor route is the [1,2] Stevens rearrangement [3] which leads to the amines (6) and (7). A mechanism for the Stevens rearrangement (1) ⟶ (6) involving homolysis of the ylide to an intermediate radical pair (8), followed by recombination, accounts for the observed products. Alternatively a concerted–forbidden † pathway may be proposed [4] for the Stevens [1,2] rearrangement.

The base catalysed rearrangements of monoallylammonium cations (9) [5,6] were investigated by Millard and Stevens [7] in 1963. Products from two different rearrangement pathways, the [3,2] rearrangement product (10) and the [1,2] Stevens rearrangement product (11) were obtained in two cases (9c and d). In four other cases (9b) (9; $R^1 = p$-$MeOC_6H_4$, $R^2 = R^3 = H$), (9; $R^1 = p$-$O_2NC_6H_4$, $R^2 = R^3 = H$), and (9; R^1 = 1-naphthyl, $R^2 = R^3 = H$), the [3,2] rearrangement product was formed exclusively.[7] This difference in chemical behaviour was difficult to explain, as the variation in the constitution of five of the precursors was limited only to their aryl substituents.

It will be appreciated that when this investigation was made,[7] it was necessary to rely upon chemical degradation such as ozonolysis to discriminate between the isomers (10) and (11). Furthermore, the determination of the product ratio (10 : 11) involved their separation by crystallisation of mixtures of structural isomers and diastereoisomers. Our interest in the competition between the [3,2] sigmatropic rearrangement and the Stevens [1,2] rearrangement encouraged us to examine further [8] the base catalysed transformations of quaternary ammonium derivatives of ketones and esters. N.m.r. spectroscopy was used to determine the product ratio directly. During the study now reported in full, it became clear that a direct isomerisation (10) ⟶ (11) could be brought about thermally.[8] This isomerisation (10) ⟶ (11) is a new [1,3] sigmatropic rearrangement and its implications in relation to the present investigations are discussed in this paper. The more general and mechanistic aspects of the reaction are considered in Part 3 [9] and Part 4.[10]

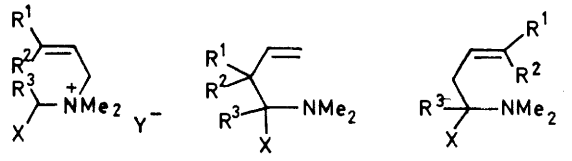
The base catalysed rearrangement was usually carried out by treatment of the quaternary salt (9) with aqueous sodium hydroxide for a few hours at room temperature;

† The term ' concerted–forbidden ' is used here as defined in ref. 4. The use of the description ' concerted,' which will be discussed in later papers of this series, is commented upon in ref. 1.

in those cases where the quaternary salt was insoluble, some ethanol was added. For the quaternary salts (9e, f, h, and j) the basic reagent was sodium methoxide in dimethyl sulphoxide solution. The total yields of products are listed in the Table. The product ratios (10) : (11) were deduced from the n.m.r. spectra of the total reaction product.

From the results given in the Table, it is clear that the base catalysed rearrangement at room temperature of the quaternary salts (9) usually proceeds in very good yield and, with the exception of salts (9e, f, j, and k), the [3,2] sigmatropic rearrangement product (10) is formed exclusively. The constitution of the rearrangement

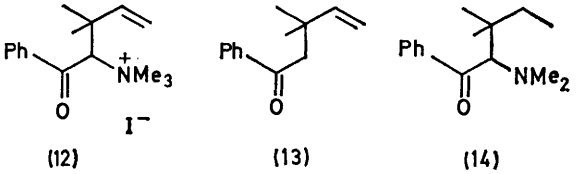
The total yields and the ratio of products (10) and (11) obtained by the base catalysed rearrangement of the quaternary ammonium salts (9) at room temperature



(9) (10) (11)

	Quaternary ammonium salt (9)					Yield of basic products (10)+(11)	Product ratio	
	R^1	R^2	R^3	X	Y	(%)	(10) : (11)	
(a)	Me	Me	H	PhCO	Cl	98	100	0
(b)	Me	H	H	PhCO	Br	96	100	0
(c)	Ph	H	H	PhCO	Br	98	100	0
(d)	*o*-MeC_6H_4	H	H	PhCO	Br	97	100	0
(e)	Me	Me	H	*p*-$O_2NC_6H_4$	Br	54	40	60
(f)	Ph	H	H	*p*-$O_2NC_6H_4$	Br	80	77	23
(g)	Me	Me	H	CH_3CO	Cl	60	100	0
(h)	Me	Me	H	MeO_2C	Br	93	100	0
(j)	Me	Me	Me	MeO_2C	Br	94	94	6
(k)	Me	Me	Me	PhCO	Br	95	40	60

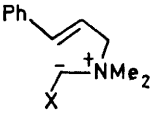
product (10a) was firmly established by spectroscopic and chemical evidence. The n.m.r. spectrum showed the presence of a single uncoupled proton, τ 5.97, an ABX system for three vinylic protons, and two diastereotopic methyl groups, τ 8.78 and 8.87. The amine (10a) gave a methiodide (12) which was reduced with zinc and dilute sulphuric acid to the unsaturated ketone (13). The amine (10a) also gave a dihydro-derivative (14) by catalytic hydrogenation.



(12) (13) (14)

The constitutions of the rearrangement products (10b—k) were similarly established from spectral data. When the substituents R^1 and R^2 in the rearrangement products (10) are different, two substances could be formed which are diastereoisomerically related. From the base catalysed rearrangements of the salts (10b—d and f) two diastereoisomeric racemates were obtained in each case. The relative configurations of these diastereoisomers are unknown and they are, therefore, just labelled as diastereoisomers *A* and *B* in the Experimental section. The separation of the product (10b) into its diastereoisomeric components was not achieved, but duplication of signals in the n.m.r. spectrum of the reaction product clearly showed that it was a mixture.

The rearrangement product (10c) (98%) was separated into two crystalline compounds, diastereoisomer *A* (57%), m.p. 101° (picrate, m.p. 177°), and diastereoisomer *B* (21%), m.p. 103° (picrate, m.p. 166°). These two substances are believed to be identical with the substances described by Millard and Stevens [7] as 1-dimethylamino-2-phenylbut-3-enyl phenyl ketone, m.p. 100—101° (picrate, m.p. 173°), and 1-dimethylamino-4-phenylbut-3-enyl phenyl ketone, m.p. 101—102° (picrate, m.p. 165°). Rearrangement of the quaternary salt (9d) similarly yields two products (10d) (98%) identified as diastereoisomer *A* (46%), m.p. 108° (picrate, m.p. 175°), and diastereoisomer *B* (12%), an oil (picrate, m.p. 178°). These two diastereoisomers are considered to be identical with substances reported [7] as 1-dimethylamino-2-*o*-tolylbut-3-enyl phenyl ketone, m.p. 107—108° (picrate, m.p. 180°), and 1-dimethylamino-4-*o*-tolylbut-3-enyl phenyl ketone, an oil (picrate, m.p. 184—185°), respectively.



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Rearrangement of the compounds (9e, f, j, and k) gave the Stevens [1,2] rearrangement products (11) in addition to the products (10) formed by the [3,2] sigmatropic rearrangement. Two factors may be considered as having an important role in determining the product ratio associated with the [1,2] and [3,2] rearrangements. It was noted in Part 1 [1] that the proportion of Stevens rearrangement was higher in the rearrangement of the cinnamylammonium salts. Thus the relative yield of the Stevens [1,2] rearrangement product appears to be directly related to the stability of the intermediate ylide which is itself controlled by the nature of the adjacent grouping X. The stability of the ylides (15) should decrease in the order X = PhCO > PhC≡C > PhCH=CH > $NO_2C_6H_4$ [11] which is in the order of increasing proportion of Stevens rearrangement product.

The second factor which will influence the relative proportions of Stevens [1,2] rearrangement product (11) is steric interaction in the transition state for the [3,2] rearrangement (see Part 1, Scheme 5). Thus in the salts (9j and k) in which $R^1 = R^2 = R^3 = Me$, the increased steric interactions will raise the activation energy of the transition state associated with the [3,2] rearrangement and allow the Stevens [1,2] rearrangement pathway to compete rather more effectively.

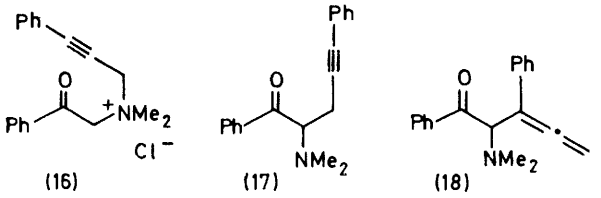
From the results summarised in the Table it is clear there is a very strong preference for the base catalysed rearrangement of the quaternary salts (9) to take the course (9) ⟶ (10) associated with [3,2] sigmatropic rearrangement. In this respect, the behaviour of these monoallyl derivatives is identical with that shown by diallylammonium cations (1) and allylpropynylammonium cations (2).[1]

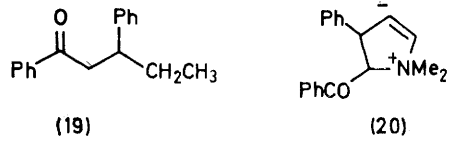
During this study it was found that many compounds of the type (10) undergo a remarkably facile thermal [1,3] sigmatropic rearrangement yielding the isomers (11).[9,10] The possibility that the Stevens rearrangement products (11) were produced by a thermal [1,3] sigmatropic rearrangement was considered. However, for those reactions yielding (11e, f, j, and k), it is clear that the [1,3] sigmatropic reaction (10) ⟶ (11) is not responsible for their formation. No change in product ratios with time was observed and the temperatures at which an acceptable rate could be established for the transformations (10e, f, j, and k) ⟶ (11e, f, j, and k) are much higher than those at which the base catalysed rearrangements were carried out.

The base catalysed rearrangement of dimethylphenacyl-(3-phenylprop-2-ynyl)ammonium chloride (16) was described [12] as yielding the acetylenic dimethylaminoketone (17). This reaction has been frequently quoted [13] to support the view that the 3-phenylprop-2-ynyl grouping migrates directly to give the Stevens [1,2] rearrangement product. This opinion [12] is not correct. In fact, the quaternary salt (16) with aqueous sodium carbonate at room temperature is transformed in high yield to the allene (18). The constitution of the rearrangement product was firmly established as the allene (18) from spectroscopic and chemical evidence. Its i.r. spectrum showed bands at 1 935 and 860 cm^{-1}, highly characteristic of the $>C=C=CH_2$ grouping and aryl-ketone absorption (ν_{CO} 1 687 cm^{-1}. Its n.m.r. spectrum showed an ABC system (τ_A 4.84, τ_B 4.90, τ_C 5.14; J_{BC} 13 Hz; $J_{AC} = J_{AB} = 2$ Hz) assignable to the $CH_CH_B=C=C-CH_A-CO$ grouping. Long-range coupling is well authenticated in allene derivatives [14a] and high values have been reported [14b] for their geminal coupling constants. The allene (18) was characterised as a crystalline methiodide which showed allenic spectral properties. Catalytic hydrogenation of the allene (18) gave the ketone (19) characterised as its 2,4-dinitrophenylhydrazone. Now that the constitution of the product has been revised to the allene (18) we are unable to account for the claim [12] that its reduction yields 1,3-dibenzoylpropane.

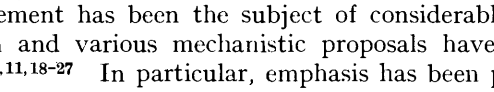
The base catalysed transformation (16) ⟶ (18) could formally be considered as a further example of the concerted [3,2] sigmatropic rearrangement.[15] However, this view may not necessarily be correct. On the present evidence,[16,17] the intermediate betaine (20) is more likely to be involved in the transformation (16) ⟶ (18).

One additional example of the Stevens [1,2] rearrangement which has been examined further is the base catalysed rearrangement of dimethyldiphenacyl ammonium bromide (21).[5] The formation of the product (22) (yield 69%) is of interest in that, in this case, it is the phenacyl group rather than a methyl group which migrates. This claim [5] has been fully confirmed. The product (22) previously obtained as an oil [5] has now been obtained crystalline. Its n.m.r. spectrum showed an ABX system assignable to the $CO-CH_X-CH_AH_B-CO$ grouping.





The competition between the symmetry allowed [3,2] rearrangement and the symmetry forbidden Stevens [1,2] rearrangement is of mechanistic interest, since the activation energies associated with both processes are obviously similar. The mechanism of the [1,2] rearrangement has been the subject of considerable discussion and various mechanistic proposals have been made.[3,11,18-27] In particular, emphasis has been placed upon the observation of CIDNP associated with the rearrangement and this has been discussed briefly.[28] The relationship of these results to other mechanistic studies



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of the Stevens rearrangement will form the subject of a future paper in this series: some discussions have been reported in preliminary form.[29] It is of interest to note that a theoretical study [30] of the Stevens rearrangement favours a pericyclic antiaromatic concerted process.

EXPERIMENTAL

The general experimental directions used are given in Part 1.[1]

Dimethyl-(3,3-dimethylallyl)phenacylammonium Chloride (9a).—*NN*-Dimethyl-3,3-dimethylallylamine [31] (15 g) and phenacyl chloride (21.2 g) in ether (250 ml) were heated under reflux for 24 h. After cooling, the precipitate was collected, and crystallisation from ethyl acetate–methanol gave *dimethyl-(3,3-dimethylallyl)phenacylammonium chloride* (9a) (25 g, 69%) as prisms, m.p. 151° (Found: C, 67.1; H, 8.1; N, 5.4. $C_{15}H_{22}ClNO$ requires C, 67.3; H, 8.2; N, 5.2%); τ (CF_3CO_2H) 1.9—2.5 (m, 5 aromatic H), AX_2 system, τ_A 4.50, τ_X 5.62 [J_{AX} 8 Hz, $=CH_A-C(H_X)_2-\overset{+}{N}$], 5.00 (s, CH_2-CO), 6.56 (s, $\overset{+}{N}Me_2$), and 8.07 and 8.12 (s, two vinylic Me).

Base Catalysed Rearrangement of Dimethyl-(3,3-dimethylallyl)phenacylammonium Chloride (9a). *Formation of* 3,3-*Dimethyl-2-dimethylamino-1-phenylpent-4-en-1-one* (10a).—Dimethyl-(3,3-dimethylallyl)phenacylammonium chloride (5.2 g) in ethanol (50 ml) was mixed with 2N-sodium hydroxide (10 ml) and set aside for 1 h. The mixture was then extracted with ether (2 × 50 ml) and evaporation yielded 3,3-*dimethyl-2-dimethylamino-1-phenylpent-4-en-1-one* (10a) (4.4 g, 98%) as a pale yellow oil (Found: C, 78.0; H, 9.2; N, 6.0. $C_{15}H_{21}NO$ requires C, 77.9; H, 9.1; N, 6.1%); τ 2.0—2.2 (m, aromatic H), 2.4—2.7 (m, 3 aromatic H), ABX system, τ_X 3.75, τ_A 4.97, τ_B 5.02 (J_{AX} 17, J_{BX} 10, J_{AB} 2 Hz, $CH_AH_B{=}CH_X{-}$), 5.97 (s, CH–CO), 7.62 (s, NMe_2), 8.78 and 8.87 (two s, CMe_2).

3,3-*Dimethyl-2-dimethylamino-1-phenylpent-4-en-1-one Methiodide* (12).—3,3-Dimethyl-2-dimethylamino-1-phenylpent-4-en-1-one (10a) (1.5 g) and methyl iodide (10 ml) were heated under reflux for 12 h. Ether (20 ml) was then added and the precipitate was collected and crystallised from ether–ethyl acetate–methanol giving 3,3-*dimethyl-2-dimethylamino-1-phenylpent-4-en-1-one methiodide* (12) (2 g, 83%) as prisms, m.p. 183° (Found: C, 52.0; H, 6.5; N, 3.8. $C_{15}H_{21}NO,CH_3I$ requires C, 51.5; H, 6.4; N, 3.8%).

3,3-*Dimethyl-1-phenylpent-4-en-1-one* (13).—A mixture of 3,3-dimethyl-2-dimethylamino-1-phenylpent-4-en-1-one methiodide (12) (5 g), 2N-sulphuric acid (50 ml), and zinc powder (10 g) was steam-distilled until oily droplets ceased to appear in the distillate. The organic phase was separated, dried ($CaCl_2$), and distillation gave 3,3-*dimethyl-1-phenylpent-4-en-1-one* (13) (2.2 g, 88%), b.p. 86—87° at 1 mmHg (Found: C, 83.2; H, 8.3. $C_{13}H_{16}O$ requires C, 83.0; H, 8.5%); τ 2.0—2.7 (m, 5 aromatic H), ABX system, τ_X 4.00, τ_A 5.05, τ_B 5.08 (J_{AX} 18, J_{BX} 10, J_{AB} 1.5 Hz, $CH_AH_B{=}CH_X{-}$), 7.05 (s, CH_2CO), and 8.84 (s, $>CMe_2$). Its 2,4-*dinitrophenylhydrazone* crystallised from ethanol as red prisms, m.p. 144° (Found: C, 61.7; H, 5.5; N, 15.0. $C_{19}H_{20}N_4O_4$ requires C, 62.0; H, 5.4; N, 15.2%).

3,3-*Dimethyl-2-dimethylamino-1-phenylpentan-1-one* (14). — 3,3-Dimethyl-2-dimethylamino-1-phenylpent-4-en-1-one (10a) (5 g), palladised carbon (5%, 500 mg), and ethanol (50 ml) were hydrogenated until 1 mol. equiv. of hydrogen had been absorbed. After filtration and evaporation, distillation of the residue gave 3,3-*dimethyl-2-dimethylamino-1-phenylpentan-1-one* (14) (4.5 g, 90%) as an oil, b.p. 94° at 0.2 mmHg (Found: C, 77.1; H, 10.1; N, 5.7. $C_{15}H_{23}NO$ requires C, 77.2; H, 9.9; N, 6.0%); τ 2.0—2.7 (m, 5 aromatic H), 6.03 (s, COCH), 7.62 (s, NMe_2), 8.92 and 9.02 (two s, $>CMe_2$), A_3X_2 system, τ_A 9.17, τ_X 8.54 [J_{AX} 7 Hz, $C(H_X)_2{-}C(H_A)_3$].

Base Catalysed Rearrangement of But-2-enyldimethylphenacylammonium Bromide (9b). *Formation of Diastereoisomers* A *and* B *of* 2-*Dimethylamino-3-methyl-1-phenylpent-4-en-1-one* (10b).—Crotyl bromide (27 g) and *NN*-dimethylphenacylamine [32] (32.6 g) in ether (500 ml) were heated under reflux for 24 h. The ether was decanted from the precipitated gum which was dissolved in water (100 ml) and shaken with ether (2 × 100 ml). Aqueous 10N-sodium hydroxide was added to the aqueous layer and after 2 h at room temperature the solution was extracted with ether (2 × 100 ml) and the ethereal extracts were shaken with 5N-hydrochloric acid (2 × 50 ml). Neutralisation with 10N-sodium hydroxide followed by extraction with ether (2 × 100 ml), evaporation, and distillation of the residue, yielded 2-*dimethylamino-3-methyl-1-phenylpent-4-en-1-one* (10b) as a mixture of diastereoisomers *A* and *B* (20 g, 96%), b.p. 143—145° at 11 mmHg (lit.,[7] 145—150° at 18 mmHg), τ 1.9—2.7 (m, 5 aromatic H), 3.7—5.3 (m, $CH{=}CH_2$), *ca.* 6.00 (m, $COCHNMe_2$), 6.8—7.3 (m, CH_3CH), 7.67 (s, NMe_2), and 8.89 and 9.13 (two d, *J* 7 Hz, non-equivalent Me of diastereoisomers *A* and *B*).

Cinnamyldimethylphenacylammonium Bromide (9c).—*NN*-Dimethylphenacylamine (17.3 g) and cinnamyl bromide (19.7 g) in ether (500 ml) were heated under reflux for 12 h. After cooling, the precipitate was collected and crystallisation from ether–ethyl acetate–methanol gave cinnamyldimethylphenacylammonium bromide (9c) (28 g, 74%) as prisms, m.p. 156° (lit.,[7] 159°); τ (CF_3CO_2H) 1.9—2.9 (m, 5 aromatic H), ABX_2 system, τ_A 2.97, τ_B 3.60, τ_X 5.49 [J_{AB} 16, J_{BX} 7 Hz, $PhCH_A{=}CH_B{-}C(H_X)_2{-}\overset{+}{N}$], 4.92 (s, $CH_2{-}CO$), and 6.48 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of Cinnamyldimethylphenacylammonium Bromide (9c). *Formation of Diastereoisomers* A *and* B *of* 2-*Dimethylamino-1,3-diphenylpent-4-en-1-one* (10c).—A solution of cinnamyldimethylphenacylammonium bromide (9c) (5 g), water (50 ml), and 2N-sodium hydroxide solution (20 ml) was kept at 60—70° for 15 min, cooled, and extracted with ether (2 × 50 ml). Evaporation yielded a yellow crystalline residue (3.6 g, 98%) which was fractionally crystallised from light petroleum (b.p. 60—80°) giving 2-*dimethylamino-1,3-diphenylpent-4-en-1-one* (diastereoisomer *A*) (2.2 g, 57%) as pale yellow needles, m.p. 101° (lit.,[7] 100—101°); τ 2.2—3.0 (m, 10 aromatic H), ABMXY system, τ_A 4.82, τ_B 4.87, τ_M 3.66, τ_X 5.95, τ_Y 5.34 (J_{AB} 2, J_{AM} 10, J_{BM} 17, J_{MX} 8, J_{XY} 11 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y{-}CO$), and 7.58 (s, NMe_2). The *picrate* crystallised from ethanol as yellow prisms, m.p. 177° (lit.,[7] 173°) (Found: C, 59.2; H, 4.6; N, 11.1. $C_{25}H_{24}N_4O_8$ requires C, 59.1; H, 4.7; N, 11.0%). Concentration of the mother liquors gave 2-*dimethylamino-1,3-diphenylpent-4-en-1-one* (diastereoisomer *B*) (0.8 g, 21%) as yellow prisms, m.p. 103° (lit.,[7] 101—102°); τ 1.9—2.8 (m, 10 aromatic H), ABMXY system, τ_A 5.08, τ_B 5.15, τ_M 4.09, τ_X 5.91, τ_Y 5.31 (J_{AB} 2, J_{BM} 10, J_{AM} 17, J_{MX} 7, J_{XY} 11 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y{-}CO$), and 7.80 (s, NMe_2). The *picrate* crystallised from ethanol as yellow prisms, m.p. 166° (lit.,[7] 165°) (Found: C, 59.0; H, 4.8; N, 10.9. $C_{25}H_{24}N_4O_8$ requires C, 59.1; H, 4.7; N, 11.0%).

Dimethylphenacyl-[3-(o-tolyl)prop-2-enyl]ammonium Bromide (9d).—*NN*-Dimethylphenacylamine (7.7 g) and 3-(*o*-tolyl)prop-2-enyl bromide [33] (10 g) in ether (250 ml) were heated under reflux for 12 h. After cooling, the precipitate was collected and crystallised from ethanol–ether giving dimethylphenacyl-[3-(*o*-tolyl)prop-2-enyl]ammonium bromide (9d) (13 g, 78%), m.p. 143° (lit.,[7] 150—151°); τ (CF_3CO_2H) 1.9—3.0 (m, 9 aromatic H), ABX_2 system, τ_A 1.9—3.0, τ_B 3.75, τ_X 5.44 [J_{AB} 16, J_{BX} 7 Hz, $CH_A{=}CH_B{-}C(H_X)_2{-}\overset{+}{N}$], 4.90 (s, $COCH_2{-}\overset{+}{N}$), 6.45 (s, $\overset{+}{N}Me_2$), and 7.78 (s, aromatic Me).

Base Catalysed Rearrangement of Dimethylphenacyl-[3-(o-tolyl)prop-2-enyl]ammonium Bromide (9d). *Formation of Diastereoisomers* A *and* B *of* 2-*Dimethylamino-1-phenyl-3-(o-tolyl)pent-4-en-1-one* (10d).—2N-Sodium hydroxide (10 ml) was added to a solution of dimethylphenacyl-[3-(*o*-tolyl)-prop-2-enyl]ammonium bromide (9d) (5 g) in ethanol (50 ml) and the mixture was set aside for 3 h. Extraction with ether (2 × 50 ml) and evaporation gave a yellow oil (3.8 g, 97%) which was fractionally crystallised from light petroleum (b.p. 60—80°) giving 2-*dimethylamino-1-phenyl-3-(o-tolyl)-pent-4-en-1-one* (diastereoisomer *A*) (1.8 g, 46%) as thick yellow prisms, m.p. 108° (lit.,[7] 107—108°); τ 1.9—3.0 (m,

9 aromatic H), ABMXY system, τ_A 5.18, τ_B 5.16, τ_M 4.26, τ_X 5.78, τ_Y 5.23 (J_{AB} 1, J_{AM} 18, J_{BM} 10, J_{MX} 7, J_{XY} 10.5 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y{-}CO$), 7.60 (s, aromatic Me), and 7.82 (s, NMe_2). The picrate crystallised from methanol as yellow needles, m.p. 175° (lit.,[7] 180°) (Found: C, 59.9; H, 4.7; N, 10.9. $C_{26}H_{26}N_4O_8$ requires C, 59.8; H, 5.0; N, 10.7%). Evaporation of the mother liquors yielded *2-dimethylamino-1-phenyl-3-(o-tolyl)pent-4-en-1-one* (diastereoisomer *B*) (0.5 g, 12%) as a yellow oil; τ 2.2—3.2 (m, 9 aromatic H), ABMXY system, τ_A 5.07, τ_B 4.99, τ_M 3.80, τ_X 5.74, τ_Y 5.34 (J_{AB} 2, J_{AM} 17, J_{BM} 11, J_{MX} 7.5, J_{XY} 11 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y{-}CO$), 7.67 (s, NMe_2), and 7.70 (s, aromatic Me). The *picrate* crystallised from ethanol as yellow prisms, m.p. 178° (lit.,[7] 184—185°) (Found: C, 59.9; H, 5.0; N, 10.5. $C_{26}H_{26}N_4O_8$ requires C, 59.8; H, 5.0; N, 10.7%).

Dimethyl-(3,3-dimethylallyl)-(p-nitrobenzyl)ammonium Bromide (9e).—*NN*-Dimethyl-3,3-dimethylallylamine (10.3 g) and *p*-nitrobenzyl bromide (21.6 g) were mixed in ether (250 ml) and after 2 h the precipitate was collected. Crystallisation from ethanol–ether gave *dimethyl-(3,3-dimethylallyl)-(p-nitrobenzyl)ammonium bromide* (9e) (22 g, 70%), m.p. 160° (Found: C, 51.3; H, 6.6; N, 8.4. $C_{14}H_{21}BrN_2O_2$ requires C, 51.1; H, 6.4; N, 8.5%); n.m.r. (CF_3CO_2H): AA'BB' system, τ_A 1.53, τ_B 2.10 (J_{AB} 7.5 Hz, 4 aromatic H), AX_2 system, τ_A 4.40, τ_X 5.78 [J_{AX} 7 Hz, $>C{=}CH_A{-}C(H_X)_2$], 5.27 (s, $ArCH_2{-}\overset{+}{N}$), 6.85 (s, $\overset{+}{N}Me_2$), and 7.98 and 8.08 (two s, vinylic Me).

Base Catalysed Rearrangement of Dimethyl-(3,3-dimethylallyl)-(p-nitrobenzyl)ammonium Bromide (9e). *Formation of 4-Dimethylamino-3,3-dimethyl-4-(p-nitrophenyl)but-1-ene* (10e) *and 5-Dimethylamino-2-methyl-5-(p-nitrophenyl)pent-2-ene* (11e) (*with* D. J. Yarrow).—Sodium methoxide solution prepared from sodium hydride (0.36 g), dimethyl sulphoxide (25 ml), and methanol (2 ml) was added during 10 min at room temperature to a stirred solution of dimethyl-(3,3-dimethylallyl)-(*p*-nitrobenzyl)ammonium bromide (5 g) in dimethyl sulphoxide (75 ml). After the addition was complete, the solution was diluted with water and extracted with ether (2 × 75 ml). The extracts were shaken with 5N-hydrochloric acid (50 ml) and neutralisation of the aqueous phase with 10N-sodium hydroxide, extraction with ether (2 × 50 ml), and evaporation of the ethereal extracts yielded a brown oil (2.0 g, 54%) which was fractionated by preparative t.l.c. (silica gel, chloroform–ether, 1 : 1) giving fraction (i) (higher R_F component) and fraction (ii) (lower R_F component).

Fraction (i) (32%), a yellow oil, was *5-dimethylamino-2-methyl-5-(p-nitrophenyl)pent-2-ene* (11e); n.m.r.: AA'BB' system, τ_A 1.82, τ_B 2.54 (J_{AB} 8 Hz, 4 aromatic H), AMNX system, τ_A 5.05, τ_M,τ_N 7.3—7.7, τ_X 6.71 (J_{AM}, J_{AN} 7, J_{MX} 5, J_{NX} 8 Hz, $=CH_A{-}CH_MH_N{-}CH_X{-}NMe_2$), 7.77 (s, NMe_2), and 8.40 and 8.57 (two s, two vinylic Me). Its *picrate* crystallised from ethanol as yellow prisms, m.p. 148° (Found: C, 50.1; H, 4.8; N, 14.8. $C_{20}H_{23}N_5O_9$ requires C, 50.3; H, 4.9; N, 14.7%).

Fraction (ii) (21%), a yellow oil, was *4-dimethylamino-3,3-dimethyl-4-(p-nitrophenyl)but-1-ene* (10e); n.m.r.: AA'BB' system, τ_A 1.82, τ_B 2.55 (J_{AB} 9 Hz, 4 aromatic H), ABX system, τ_A 4.90, τ_B 4.95, τ_X 3.74 (J_{AB} 2, J_{AX} 10, J_{BX} 17 Hz, $CH_AH_B{=}CH_X$), 6.65 (s, ArC*H*), 7.82 (s, N*Me*$_2$), and 8.88 and 9.05 (s, $>CMe_2$). It was characterised as the *picrate* which crystallised from ethanol in yellow needles, m.p. 145° (Found: C, 50.0; H, 4.7; N, 14.9. $C_{20}H_{23}N_5O_9$ requires C, 50.3; H, 4.9; N, 14.7%).

Cinnamyldimethyl-(p-nitrobenzyl)ammonium Bromide (9f) (*with* K. Reynard).—*NN*-Dimethylcinnamylamine [1] (12 g) and *p*-nitrobenzyl bromide (16.2 g) in methyl cyanide (10 ml) were heated under reflux for 30 min, cooled, and diluted with ether (200 ml). The precipitate was collected and crystallisation from ethanol–ethyl acetate gave *cinnamyldimethyl-(p-nitrobenzyl)ammonium bromide* (9f) (25 g, 86%) as prisms, m.p. 192° (Found: C, 57.6; H, 5.8; N, 7.6; Br, 21.4. $C_{18}H_{21}BrN_2O_2$ requires C, 57.3; H, 5.6; N, 7.4; Br, 21.2%); n.m.r. (CF_3CO_2H): AA'BB', τ_A 1.49, τ_B 2.06 (J_{AB} 8.5 Hz, 4 aromatic H), 2.3—2.7 (m, 5 aromatic H), ABX_2 system, τ_A 2.83, τ_B 3.50, τ_X 5.66 [J_{AB} 16, J_{BX} 7 Hz, $CH_A{=}CH_B{-}C(H_X)_2$], 5.15 (s, $CH_2{-}\overset{+}{N}$), and 6.73 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of Cinnamyldimethyl-(p-nitrobenzyl)ammonium Bromide (9f). *Formation of Diastereoisomers* A *and* B *of 4-Dimethylamino-4-(p-nitrophenyl)-3-phenylbut-1-ene* (10f) *and 4-Dimethylamino-4-(p-nitrophenyl)-1-phenylbut-1-ene* (11f).—Sodium methoxide solution prepared from sodium hydride (360 mg), dimethyl sulphoxide (20 ml), and methanol was added dropwise during 10 min at room temperature to a stirred solution of cinnamyldimethyl-(*p*-nitrobenzyl)ammonium bromide (9f) (24 g) in dimethyl sulphoxide (200 ml). Dilution with water and extraction with ether (3 × 150 ml) gave extracts which were shaken with 2N-hydrochloric acid (2 × 100 ml). Neutralisation of the acidic extracts with 10N-sodium hydroxide, extraction with ether (3 × 150 ml), and evaporation of the ethereal extracts gave a yellow oil (15.1 g, 80%) which was separated by preparative t.l.c. [silica gel, benzene–chloroform–ether (1 : 1 : 1)] into three fractions.

Fraction (i) (31%), a yellow oil, was *4-dimethylamino-4-(p-nitrophenyl)-3-phenylbut-1-ene* (10f) (diastereoisomer *A*), τ 1.9—3.0 (m, 9 aromatic H), ABMXY system, τ_A 5.02, τ_B 5.08, τ_M 4.10, τ_X 5.99, τ_Y 6.32 (J_{AB} 1, J_{AM} 10, J_{BM} 17, J_{MX} 7, J_{XY} 9 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y{-}NMe_2$), and 7.83 (s, NMe_2). It was characterised as the *picrate*, which crystallised from acetic acid as yellow prisms, m.p. 186° (Found: C, 54.6; H, 4.2; N, 13.2. $C_{24}H_{23}N_5O_9$ requires C, 54.9; H, 4.4; N, 13.3%).

Fraction (ii) (30%), a yellow oil, was *4-dimethylamino-4-(p-nitrophenyl)-3-phenylbut-1-ene* (10f) (diastereoisomer *B*), n.m.r.: AA'BB' system, τ_A 1.91, τ_B 2.80 (J_{AB} 8.5 Hz, 4 aromatic H), 2.90 (s, 5 aromatic H), ABMXY system, τ_A 4.80, τ_B 4.85, τ_M 3.4—4.0, τ_X,τ_Y 5.9—6.1 (J_{AB} 2, J_{AM} 10, J_{BM} 17 Hz, $CH_AH_B{=}CH_M{-}CH_X{-}CH_Y$), and 7.78 (s, NMe_2). It was characterised as its *picrate* which crystallised from ethanol as yellow needles, m.p. 184° (Found: C, 55.0; H, 4.5; N, 13.3%).

Fraction (iii) (19%), a yellow oil, was *4-dimethylamino-4-(p-nitrophenyl)-1-phenylbut-1-ene* (11f); n.m.r.: AA'BB' system, τ_A 1.79, τ_B 2.53 (J_{AB} 8.5 Hz, 4 aromatic H), 2.75br (s, 5 aromatic H), ABMNX system, τ_A 3.66, τ_B 4.10, τ_M,τ_N 7.2—7.5, τ_X 6.58 (J_{AB} 15.5, $J_{BM} = J_{BN} = 7$, J_{MX} 6, J_{NX} 8 Hz, $CH_A{=}CH_B{-}CH_MH_N{-}CH_X{-}NMe_2$), and 7.78 (s, NMe_2). It was characterised as the *picrate* which crystallised from ethanol as yellow needles, m.p. 110° (Found: C, 54.6; H, 4.2; N, 13.1. $C_{24}H_{23}N_5O_9$ requires C, 54.9; H, 4.4; N, 13.3%).

Acetonyldimethyl-(3,3-dimethylallyl)ammonium Chloride (9g).—*NN*-Dimethyl-3,3-dimethylallylamine (12.7 g) and chloroacetone (10.4 g) in methyl cyanide (200 ml) were heated under reflux for 10 min, cooled, and ether (200 ml) was added. The hygroscopic precipitate (18 g, 79%) was collected, washed with ether (3 × 20 ml), and stored in a desiccator over potassium hydroxide. The extreme de-

liquescence of *acetonyldimethyl-(3,3-dimethylallyl)ammonium chloride* (9g) precluded analysis; n.m.r. (CF_3CO_2H): AX_2 system, τ_A 4.60, τ_X 5.80 [J_{AX} 8 Hz, $\gtrless C{=}CH_A{-}C(H_X)_2{-}$], 6.80 (s, $\overset{+}{N}Me_2$), 7.68 (s, CH_3CO), and 8.07 and 8.15 (two s, vinylic Me).

Base Catalysed Rearrangement of Acetonyldimethyl-(3,3-dimethylallyl)ammonium Chloride (9g). *Formation of 4,4-Dimethyl-3-dimethylaminohex-5-en-2-one* (10g).—10N-Sodium hydroxide (15 ml) was added at room temperature to a solution of acetonyldimethyl-(3,3-dimethylallyl)-ammonium chloride (9g) (16 g) in water (20 ml) and after 1 h the mixture was extracted with ether (2 × 50 ml). Evaporation of the ethereal extracts gave *4,4-dimethyl-3-dimethylaminohex-5-en-2-one* (10g) (7.9 g, 60%) as an oil, b.p. 74° at 10 mmHg (Found: C, 71.3; H, 11.4; N, 8.2. $C_{10}H_{19}NO$ requires C, 71.0; H, 11.2; N, 8.3%); n.m.r.: ABX system, τ_A 5.01, τ_B 5.03, τ_X 3.87 (J_{AB} 2, J_{AX} 18, J_{BX} 10.5 Hz, $CH_AH_B{=}CH_X$), 6.94 (s, COCH), 7.55 (s, NMe_2), 7.90 (s, CH_3CO), and 8.88 and 8.92 (two s, $\gtrless CMe_2$). It was characterised as the *picrate* which crystallised from ethanol as yellow needles, m.p. 114° (Found: C, 47.4; H, 5.2; N, 13.9. $C_{16}H_{22}N_4O_8$ requires C, 48.2; H, 5.2; N, 14.1%).

Dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylmethyl)-ammonium Bromide (9h).—Methyl bromoacetate (30.6 g) in ether (200 ml) was added dropwise at room temperature to a stirred solution of *NN*-dimethyl-3,3-dimethylallylamine (20.6 g) in ether (250 ml). The precipitate was collected and crystallisation from ethanol–ether gave *dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylmethyl)ammonium bromide* (9h) (46 g, 89%) as prisms, m.p. 149° (Found: C, 44.9; H, 7.5; N, 5.0. $C_{10}H_{20}BrNO_2$ requires C, 45.1; H, 7.5; N, 5.3%); n.m.r. (CF_3CO_2H): AX_2 system, τ_A 4.55, τ_X 5.77 [J_{AX} 7.5 Hz, $\gtrless C{=}CH_A{-}C(H_X)_2{-}\overset{+}{N}$], 5.78 (s, $COCH_2{-}\overset{+}{N}$), 6.07 (s, CO_2Me), 6.65 (s, $\overset{+}{N}Me_2$), and 8.03 and 8.12 (two s, vinylic Me).

Base Catalysed Rearrangement of Dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylmethyl)ammonium Bromide (9h). *Formation of Methyl 3,3-Dimethyl-2-dimethylaminopent-4-enoate* (10h).—Dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylmethyl)ammonium bromide (9h) (7.0 g) in dimethyl sulphoxide (60 ml) was added to a solution prepared from sodium hydride (1.2 g), dimethyl sulphoxide (60 ml), and methanol. After 30 min the mixture was diluted with water and extracted with ether (2 × 100 ml). The ethereal extracts were shaken with 2N-sulphuric acid (2 × 50 ml) and the acidic extracts were neutralised with 10N-sodium hydroxide and extracted with ether (2 × 100 ml). Evaporation of the ethereal extracts gave an oil which on distillation yielded *methyl 3,3-dimethyl-2-dimethylaminopent-4-enoate* (10h) (4.3 g, 93%), b.p. 82° at 13 mmHg (Found: C, 64.9; H, 10.0; N, 7.6. $C_{10}H_{19}NO_2$ requires C, 64.9; H, 10.3; N, 7.6%); n.m.r.: ABX system, τ_A 4.98, τ_B 5.00, τ_X 3.84 (J_{AB} 2, J_{AX} 18, J_{BX} 10 Hz, $\gtrless CH_AH_B{=}CH_X{-}$), 6.30 (s, CO_2Me), 7.03 (s, $COCH_2$), 7.65 (s, NMe_2), and 8.85 and 8.90 (two s, $\gtrless CMe_2$).

Dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylethyl)-ammonium Bromide (9j).—Methyl 2-bromopropionate (16.7 g) and *NN*-dimethyl-3,3-dimethylallylamine (11.3 g) were mixed in methyl cyanide (25 ml) and set aside for 12 h. After dilution with ether (250 ml), the precipitate was collected and washed with ether (3 × 25 ml) giving *dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylethyl)ammonium bromide* (9j) (23 g, 82%), m.p. 119° (Found: C, 47.4; H, 7.8; N, 4.8. $C_{11}H_{22}BrNO_2$ requires C, 47.1; H, 7.9; N, 5.0%); n.m.r. (D_2O): AX_2 system, τ_A 4.46; τ_X 5.82 [J_{AX} 7.5 Hz, $C{=}CH_A{-}C(H_X)_2{-}$], AX_3 system, τ_A 5.52, τ_X 8.24 (J_{AX} 7 Hz, $CO{-}CH_A{-}C(H_X)_3$], 6.05 (s, CO_2Me), 6.75 (s, $\overset{+}{N}Me_2$), and 8.03 and 8.12 (two s, $HC{=}CMe_2$).

Base Catalysed Rearrangement of Dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylethyl)ammonium Bromide (9j). *Formation of Methyl 2-Dimethylamino-2,3,3-trimethylpent-4-enoate* (10j) *and Methyl 2,5-Dimethyl-2-dimethylaminohex-4-enoate* (11j).—Dimethyl-(3,3-dimethylallyl)-(1-methoxycarbonylethyl)ammonium bromide (9j) (12.4 g) in dimethyl sulphoxide (25 ml) was added at room temperature to a solution of sodium methoxide prepared from sodium hydride (1.8 g), dimethyl sulphoxide (25 ml), and methanol. After 12 h, the mixture was diluted with water and extracted with ether (2 × 75 ml). The ethereal extracts were shaken with 2N-hydrochloric acid (2 × 50 ml) and the acidic extract was neutralised with 10N-sodium hydroxide and extracted with ether (2 × 75 ml). Evaporation of the dried ethereal extracts yielded an oil (7.9 g, 94%) which was separated by preparative t.l.c. [silica gel, benzene–chloroform–ether (1 : 1 : 1)] into two fractions.

Fraction (i) (88%), an oil, was *methyl 2-dimethylamino-2,3,3-trimethylpent-4-enoate* (10j), n.m.r.: ABX system, τ_A 4.95, τ_B 4.98, τ_X 3.70 (J_{AB} 2, J_{AX} 18, J_{BX} 10 Hz, $CH_AH_B{=}CH_X{-}$), 6.27 (s, CO_2Me), 7.78 (s, NMe_2), 8.83 (s, $\gtrless CMe_2$), and 8.92 (s, $O{=}C{-}C{-}CH_3$). The *picrate* crystallised from benzene as yellow prisms, m.p. 120° (Found: C, 47.8; H, 5.4; N, 13.3. $C_{17}H_{24}N_4O_9$ requires C, 47.7; H, 5.6; N, 13.1%).

Fraction (ii) (6%), an oil, was *methyl 2,5-dimethyl-2-dimethylaminohex-4-enoate* (11j); n.m.r.: AX_2 system, τ_A 4.94, τ_X 7.59 [J_{AX} 7.5 Hz, $C{=}CH_A{-}C(H_X)_2{-}$], 6.28 (s, CO_2Me), 7.72 (s, NMe_2), 8.28br and 8.38br (two s, ${=}CMe_2$), and 8.72 (s, $O{=}C{-}C{-}CH_3$). The *picrate* crystallised from benzene as yellow prisms, m.p. 119° (Found: C, 47.8; H, 5.4; N, 13.2. $C_{17}H_{24}N_4O_9$ requires C, 47.7; H, 5.6; N, 13.1%).

Dimethyl-(3,3-dimethylallyl)-(2-methylphenacyl)ammonium Bromide (9k).—3,3-Dimethylallyl bromide[34] (14.9 g) in methyl cyanide (10 ml) was added to a solution of 2-dimethylaminopropiophenone[35] (17.7 g) in methyl cyanide (15 ml) with cooling, and the solution was set aside for 1 h. Ether (200 ml) was added and the precipitate was collected. Crystallisation from ethyl acetate–methanol gave *dimethyl-(3,3-dimethylallyl)-(2-methylphenacyl)ammonium bromide* (9k) (28 g, 86%), m.p. 127° (Found: C, 58.9; H, 7.3; N, 4.4. $C_{26}H_{24}BrNO$ requires C, 58.9; H, 7.4; N, 4.3%), τ (D_2O) 2.0—2.7 (m, 5 aromatic H), ABX system, τ_X *ca.* 4.7, τ_A,τ_B 5.6—6.2 ($={CH_X}{-}{CH_AH_B}{-}\overset{+}{N}$), AX_3 system, τ_A 4.67, τ_X 8.44 [J_{AX} 7 Hz, $CH_A{-}C(H_X)_3$], 6.70 and 6.77 (two s, $\overset{+}{N}Me_2$), and 8.64 and 8.71 (two s, $={CMe_2}$).

Base Catalysed Rearrangement of Dimethyl-(3,3-dimethylallyl)-(2-methylphenacyl)ammonium Bromide (9k). *Formation of 2-Dimethylamino-2,3,3-trimethyl-1-phenylpent-4-en-1-one* (10k) *and 2,5-Dimethyl-2-dimethylamino-1-phenylhex-4-en-1-one* (11k).—10N-Sodium hydroxide (6 ml) was added to a solution of dimethyl-(3,3-dimethylallyl)-(2-methylphenacyl)ammonium bromide (9k) (9.8 g) in water (50 ml) and after 1 h the mixture was extracted with ether (2 × 50 ml). The ethereal extracts were shaken with 2N-sulphuric acid (2 × 50 ml) and the acidic extract was neutralised with 10N-sodium hydroxide and extracted with ether (2 × 50 ml). Evaporation of the ethereal extract gave a dark yellow oil (7.0 g, 95%) which was shown by n.m.r. to consist of *2-dimethylamino-2,3,3-trimethyl-1-phenylpent-4-en-1-one*

(10k) (40%), τ 1.4—2.8 (m, 5 aromatic H), ABX system, τ_A,τ_B 4.9—5.3, τ_X *ca.* 3.8 (CH_X=CH_AH_B), 7.63 (s, NMe_2), 8.62 (s, CH_3–C–NMe_2), and 8.93 and 8.98 (two s, >CMe_2), and 2,5-*dimethyl*-2-*dimethylamino*-1-*phenylhex*-4-*en*-1-*one* (11k) (60%), τ 1.4—2.8 (m, 5 aromatic H), ABX system, τ_X 5.15, τ_A,τ_B 7.3—7.7 (J_{AX} = J_{BX} = 7 Hz, =CH_X–CH_AH_B), 7.71 (s, NMe_2), 8.45 and 8.72 (two s, =CMe_2), and 8.82 (s, CH_3–C–NMe_2). Attempts to separate this mixture were unsuccessful.

Dimethylphenacyl-(3-phenylprop-2-ynyl)ammonium Bromide (16).—*NN*-Dimethyl-3-phenylprop-2-ynylamine [36] (15.9 g) and phenacyl bromide (19.7 g) in ether (150 ml) were heated under reflux for 4 h. The precipitate was collected and crystallisation from ether–ethyl acetate gave prisms of dimethylphenacyl-(3-phenylprop-2-ynyl)ammonium bromide (16) (30 g, 84%), m.p. 160° (lit.,[12] 162°); τ (CF_3CO_2H) 1.8—3.2 (m, 10 aromatic H), 4.75 (s, $CO–CH_2$), 5.13 (s, $C{\equiv}C–CH_2$), and 6.37 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of Dimethylphenacyl-(3-phenylprop-2-ynyl)ammonium Bromide (16). *Formation of 2-Dimethylamino-1,3-diphenylpenta-3,4-dien-1-one* (18).—Sodium carbonate solution (10%, 20 ml) was added to a solution of dimethylphenacyl-(3-phenylprop-2-ynyl)-ammonium bromide (16) (3.58 g) in water (10 ml) and the mixture was set aside for 1 h, then extracted with ether (2 × 50 ml). The ethereal extracts were shaken with 2N-hydrochloric acid (2 × 50 ml) and the acidic extract was neutralised with aqueous sodium carbonate solution (10%) and extracted into ether (2 × 50 ml). Evaporation of the dried ethereal extracts yielded 2-*dimethylamino*-1,3-*diphenylpenta*-3,4-*dien*-1-*one* (18) (2.3 g, 83%), a yellow oil, $\nu_{max.}$ (liquid film) 1 935, 1 687, and 860 cm^{-1}; τ 1.9—2.8 (m, 10 aromatic H), ABC system, τ_A 4.84, τ_B 4.90, τ_C 5.14 (J_{AB} = J_{AC} = 2, J_{BC} 13 Hz, CH_A=C=CH_BH_C), and 7.43 (s, NMe_2). It was characterised as its *methiodide* which crystallised from ethyl acetate as prisms, m.p. 137° (decomp.) (Found: C, 57.1; H, 5.3; N, 3.3. $C_{20}H_{22}INO$ requires C, 57.3; H, 5.3; N, 3.3%); τ (CF_3CO_2H) 1.7—2.7 (m, 10 aromatic H), 3.35 (s, COCH), AB system, τ_A 4.65, τ_B 4.45 (J_{AB} 15 Hz, C=C=CH_AH_B), and 6.45 (s, NMe_2).

Hydrogenation of 2-Dimethylamino-1,3-diphenylpenta-3,4-dien-1-one (18). *Formation of 1,3-Diphenylpentan-1-one* (19).— 2-Dimethylamino-1,3-diphenylpenta-3,4-dien-1-one (18) (1.3 g), palladised carbon (5%, 500 mg), and ethanol (10 ml) were stirred under hydrogen at room temperature until three molar equivalents (315 ml) had been absorbed. Filtration and evaporation gave a brown oil (1.2 g) which was dissolved in methanol (10 ml) and added to an excess of an acidic solution of 2,4-dinitrophenylhydrazine. The precipitate was collected and crystallised from acetic acid giving 1,3-*diphenylpentan*-1-*one* 2,4-*dinitrophenylhydrazone* (1.5 g, 72%) as red needles, m.p. 161° (Found: C, 66.0; H, 5.0; N, 13.5. $C_{23}H_{22}N_4O_4$ requires C, 66.0; H, 5.3; N, 13.4%); τ −1.23 (s, NH), AMX system, τ_A 0.92, τ_M 1.7, τ_X 2.05 [J_{AM} 2, J_{MX} 9 Hz, 2,4-$(NO_2)_2C_6H_3$], 2.1—2.9 (m, 10 aromatic H), and $ABCM_2X_3$ system, τ_A, τ_B, τ_C 6.6—7.3, τ_M 7.8—8.3, τ_X 9.17 [J_{MX} = J_{CM} = 7 Hz, CH_AH_B–CH_C–$C(H_M)_2$–$C(H_X)_3$].

Dimethyldiphenacylammonium Bromide (21).—Phenacyl bromide (19.9 g) and *NN*-dimethylphenacylamine (16.3 g) in ether (200 ml) were heated under reflux for 12 h. The precipitate was collected and crystallisation from ethanol–ether gave dimethyldiphenacylammonium bromide (21) (24 g, 66%) as prisms, m.p. 158° (lit.,[37] 159—161°); τ (CF_3CO_2H) 1.8—2.7 (m, 10 aromatic H), 4.28 (s, two $CO–CH_2$), and 6.29 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of Dimethyldiphenacylammonium Bromide (21). *Formation of 2-Dimethylamino-1,4-diphenylbutane-1,4-dione* (22) (*with* E. Dickinson).—4N-Sodium hydroxide (10ml) was added to dimethyldiphenacylammonium bromide (21) (8 g) in water (20 ml) and after 2 h the mixture was extracted with ether (2 × 75 ml). The ethereal extracts were shaken with 2N-hydrochloric acid (2 × 50 ml) and the acidic extract was neutralised with 10N-sodium hydroxide and extracted with ether (2 × 75 ml). Evaporation of the dried extracts yielded a dark oil which crystallised from light petroleum (b.p. 60—80°) giving 2-dimethylamino-1,4-diphenylbutane-1,4-dione (4.8 g, 69%) as prisms, m.p. 63° (lit.,[5] previously reported as an oil) (Found: C, 76.9; H, 6.7; N, 4.8. $C_{18}H_{19}NO_2$ requires C, 76.9; H, 6.8; N, 5.0%); τ 1.8—2.8 (m, 10 aromatic H), ABX system, τ_A 6.23, τ_B 6.85, τ_X 5.10 (J_{AB} 17, J_{BX} 4, J_{AX} 10 Hz, CH_X–CH_AH_B), and 7.68 (s, NMe_2). It gave a picrate which crystallised from ethanol as yellow prisms, m.p. 125° (lit.,[5] 128—130°).

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REFERENCES

[1] Part 1, R. W. Jemison, T. Laird, W. D. Ollis, and I. O. Sutherland, preceding paper.
[2] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781; Nguyên Trong Anh, 'Die Woodward–Hoffmann–Regeln und ihre Anwendung,' Verlag Chemie, Weinheim, 1972, pp. 96—98.
[3] S. H. Pine, *Org. Reactions*, 1970, **18**, 403; A. R. Lepley and A. Giumanini in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Interscience, New York, 1971, vol. 3, 297; T. S. Stevens and W. E. Watts, 'Selected Molecular Rearrangements,' van Nostrand–Reinhold, London, 1973, p. 81.
[4] W. Schmidt, *Tetrahedron Letters*, 1972, 581; N. D. Epiotis, *J. Amer. Chem. Soc.*, 1972, **94**, 1924; J. A. Berson and L. Salem, *ibid.*, p. 8917; J. A. Berson, *Accounts Chem. Res.*, 1972, **5**, 406; J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, jun., *ibid.*, p. 402; J. A. Berson and R. W. Holder, *J. Amer. Chem. Soc.*, 1973, **95**, 2037.
[5] T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 1932, 1932.
[6] W. Heffe, *Helv. Chim. Acta*, 1964, **47**, 1289.
[7] B. J. Millard and T. S. Stevens, *J. Chem. Soc.*, 1963, 3397.
[8] For a preliminary account see R. W. Jemison and W. D. Ollis, *Chem. Comm.*, 1969, 294.
[9] R. W. Jemison, T. Laird, W. D. Ollis, and I. O. Sutherland, following paper.
[10] R. W. Jemison, W. D. Ollis, I. O. Sutherland, and J. Tannock, *J.C.S. Perkin I*, 1980, 1462.
[11] A. W. Johnson, 'Ylide Chemistry,' Academic Press, New York, 1966.
[12] J. L. Dunn and T. S. Stevens, *J. Chem. Soc.*, 1934, 279.
[13] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1969, p. 788; 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 279; J. March, 'Advanced Organic Chemistry,' McGraw-Hill, New York, 1968, p. 285.
[14] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance in Organic Chemistry,' Pergamon, Oxford, 1969, (*a*) p. 328; (*b*) p. 278 and references cited therein.
[15] J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Comm.*, 1968, 1083.
[16] S. Mageswaran, W. D. Ollis, and I. O. Sutherland, *Chem. Comm.*, 1971, 1493.
[17] W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *J.C.S. Chem. Comm.*, 1973, 657.
[18] T. S. Stevens, *Progr. Org. Chem.*, 1968, **7**, 48.
[19] E. F. Jenny and J. Druey, *Angew. Chem. Internat. Edn.*, 1962, **1**, 152.

[20] E. F. Jenny and K. Schenker, *Angew. Chem. Internat. Edn.*, 1965, **4**, 441.
[21] H. E. Zimmerman in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1963, Part 1, p. 378.
[22] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 223.
[23] R. K. Hill and T. H. Chan, *J. Amer. Chem. Soc.*, 1966, **88**, 866.
[24] E. Grovenstein, jun., and G. Wentworth, *J. Amer. Chem. Soc.*, 1967, **89**, 1852.
[25] H. Joshua, R. Gans, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4884.
[26] J. H. Brewster, and R. S. Jones, jun., *J. Org. Chem.*, 1969, **34**, 354.
[27] J. E. Baldwin, W. F. Ericson, R. E. Hackler, and R. M. Scott, *Chem. Comm.*, 1970, 576.
[28] U. H. Dolling, G. L. Closs, A. H. Cohen, and W. D. Ollis, *J.C.S. Chem. Comm.*, 1975, 545.
[29] W. D. Ollis, M. Rey, I. O. Sutherland, and G. L. Closs, *J.C.S. Chem. Comm.*, 1975, 543.
[30] M. J. S. Dewar and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 1839.
[31] G. T. Martirosyan, E. A. Grigoryan, and A. T. Babayan, *Izvest. Akad. Nauk Arm. S.S.R. Khim. Nauk*, 1965, **18**, 161 (*Chem. Abs.*, 1965, **63**, 14,686b).
[32] R. L. Letsinger and R. Collat, *J. Amer. Chem. Soc.*, 1952, **74**, 621.
[33] R. A. Mitsch and N. H. Cromwell, *J. Org. Chem.*, 1960, **25**, 1719.
[34] H. L. Simon, Ad. Kaufmann, and H. Schinz, *Helv. Chim. Acta*, 1946, **29**, 1133.
[35] I. N. Nazarov, E. M. Cherkasova, and G. S. Erkomaishvili, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1959, 1605 (*Chem. Abs.*, 1960, **54**, 8698).
[36] I. Iwai and T. Hiroaka, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 1564.
[37] F. Kröhnke, *Chem. Ber.*, 1957, **90**, 2236.