Base Catalysed Rearrangements involving Ylide Intermediates. Part 4.[1] [1,3] Sigmatropic Rearrangements of 4-Dimethylaminobutenes and [3,3] Sigmatropic Rearrangements of 3-Dimethylaminohexa-1,5-dienes

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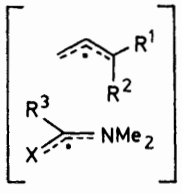
The [1,3] sigmatropic rearrangement (11) ⟶ (12) of the 9-dimethylamino-9-(1-phenylallyl)fluorene is a stereoselective process (84 : 16) at 170°. Analogous [1,3] rearrangements (16) ⟶ (17) of other fluorene derivatives show that the reaction rate is increased by electron donating 9-substituents in the order O^- > NMe_2 > OMe. Similar substituent effects are observed for the [3,3] Cope rearrangement (25) ⟶ (26) of hexa-1,5-dienes. 4-Phenyl, 4,4-dimethyl, and 3-dimethylamino substituents are particularly effective in accelerating the rate of the rearrangement (25) ⟶ (26).

In Part 3[1] the [1,3] sigmatropic rearrangements of suitably activated 4-dimethylaminobutenes (1; X = COR or *p*-$O_2NC_6H_4$) to give the amines (2) were described. In view of the continuing interest in [1,3] rearrangements [2-21] we now report further studies of this reaction, together with a brief comparison of substituent effects in related [1,3] and [3,3] sigmatropic processes.

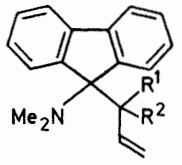
(1) (2)



(3)

For a symmetry allowed,[22] and therefore 'concerted' † process (1) ⟶ (2) the stereochemistry must be of the [$_\sigma 2_s + {}_\pi 2_a$] or [$_\sigma 2_a + {}_\pi 2_s$] types,[3,6,7] and of these alternatives the latter, involving inversion [3,14] at the migration terminus C-1 [see (1) and (2)], is the more likely process. For symmetry forbidden processes [22] some stereochemical preference for the [$_\sigma 2_s + {}_\pi 2_s$] pathway may still be retained.[2,4,12,24] Alternatively the reaction could take a pathway, involving the radical pair (3),[25] which would not be expected to show stereoselectivity unless radical coupling is fast compared with stereochemical re-orientation. Our initial investigation of the reaction (1) ⟶ (2) was therefore centred upon its stereoselectivity.

The stereochemistry of simple processes analogous to (1) ⟶ (2) proved difficult to study, but the fluorenyl derivatives (4) are highly crystalline compounds so that diastereoisomeric compounds required for stereochemical studies may potentially be readily separated. The amines (4a—c) were obtained by [3,2] sigmatropic rearrangements of the corresponding ylides,[23,26] formed by treating the quaternary salts (5a—c) with base. Two of these amines (4b and c) underwent a clean [1,3] rearrangement at 79°, giving the isomers (6b and c),



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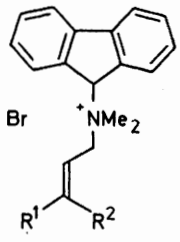
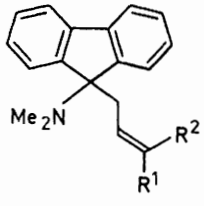


(5)

a ; $R^1 = R^2 = H$
b ; $R^1 = R^2 = Me$
c ; $R^1 = Ph$, $R^2 = H$



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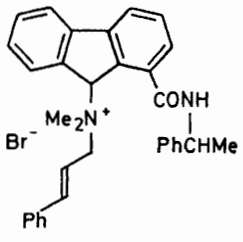

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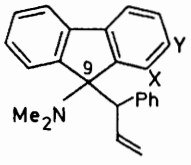
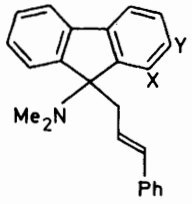


(7) X = H, Y = COPh
(8) X = CO_2CHMe_2, Y = H
(11) X = CONHCHMePh, Y = H



(9) X = H, Y = COPh
(10) X = CO_2CHMe_2, Y = H
(12) X = CONHCHMePh, Y = H

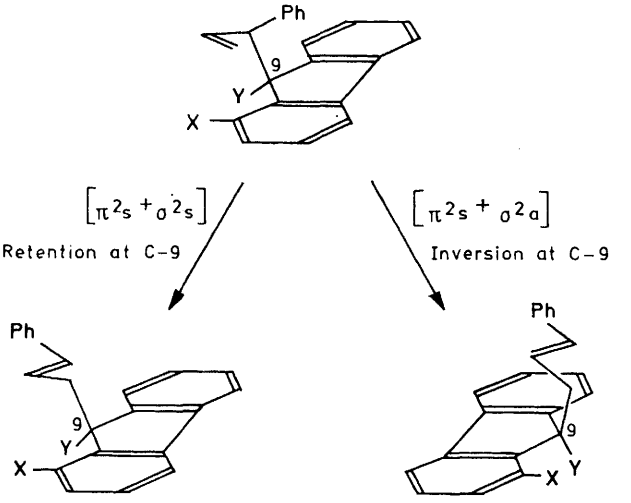
† For a discussion of the use of the term 'concerted' see Part 1.[23]

respectively. The rearrangements both showed first-order kinetics and reaction rates were readily followed by n.m.r. analysis of reactant and product concentrations.

These reactions (4) ⟶ (6) were, however, unsuitable for an examination of the stereoselectivity of the reaction, and accordingly the fluorenylamines (7) and (8) were synthesised and a single pure racemic diastereoisomer of each compound was isolated by crystallisation. These diastereoisomers rearranged giving the chiral cinnamylfluorenes (9) and (10) as racemates. However, optical resolution of (7) and (8), required for stereochemical analysis of the [1,3] rearrangement, proved difficult and a different approach to the problem was therefore investigated.

The fluorenylamine (11) contains three centres of chirality and the corresponding [1,3] rearrangement product (12) contains two centres of chirality: the rearrangement of a single racemic diastereoisomer of (11) would therefore provide stereochemical information if the stereochemical purity of the product (12) were examined. A single pure racemic diastereoisomer of (11), m.p. 169°, was obtained by fractional crystallisation of the mixture of products obtained from the treatment of the quaternary salt (13) with base. The homogeneity of this isomer of (11) was checked by examination of its 220 MHz n.m.r. spectrum which was entirely consistent with the presence of a single pure racemic diastereoisomer. Thermal rearrangement of (11) at 170° gave the cinnamylfluorene (12) which was shown by its 220 MHz n.m.r. spectrum to consist of two racemic diastereoisomers of (12) in the ratio 16 : 3. Both diastereoisomers had a *trans*-double bond in the cinnamyl substituent and the configuration of the phenylethyl substituent would remain unchanged during the rearrangement (11) ⟶ (12). We conclude therefore that the formation of two racemic diastereoisomers (12) involves the chiral centre at C-9 and that some retention and inversion at this centre occurs during the rearrangement process (11) ⟶ (12). The relative configurations of (11) and (12) have not been established, so our result for the rearrangement (11) ⟶ (12) may be interpreted as proceeding either with 84% retention and 16% inversion or with 16% retention and 84% inversion of the configuration of the migrating centre of chirality of the fluoren-9-yl residue. This conclusion is consistent with (i) a radical pair mechanism [22,25] for the rearrangement or (ii) a combination of allowed $[_{\pi}2_{s} + {}_{\sigma}2_{a}]$ and non-allowed $[_{\pi}2_{a} + {}_{\sigma}2_{s}]$ processes [3,4,14,24] (see Scheme). The observation of a relatively high degree of stereoselectivity in this reaction (11) ⟶ (12) carried out at 170° is of interest and may be related to the observation [12] of high stereoselectivity (*ca.* 90% retention of configuration at the migrating centre) in the thermal rearrangement (14) ⟶ (15) carried out at 250°. These results and ours, indicating relatively high stereoselectivity in [1,3] rearrangements, are consistent with recently published views concerning reactions of this type.[3,4,12,24] It is possible that the thermal transformations (11) ⟶ (12) and (14) ⟶ (15) [12] represent orbital symmetry forbidden reactions which proceed by concerted pathways associated with high stereoselectivity because these are energetically more favourable than reactions involving radical pair intermediates. However, further speculation about the mechanism for the transformation (11) ⟶ (12) is inappropriate until the relation between the stereochemical configurations of precursor (11) and products (12) can be established. The precursor (11) is crystalline but the two racemic diastereoisomers (12) have not been separated and crystallised.

In view of the fact that [1,3] rearrangements analogous to (1) ⟶ (2) represent processes that are formally symmetry forbidden, it was of interest to examine substituent effects on the rate of the rearrangement. Effects of this type have recently been discussed [24] in terms of increased opportunity for configuration interaction in the transition state for a $[_{\pi}2_{s} + {}_{\sigma}2_{s}]$ rearrangement. The rearrangement of the 9-(1-phenylallyl)fluorenyl system is a convenient reaction for the study of such effects so a number



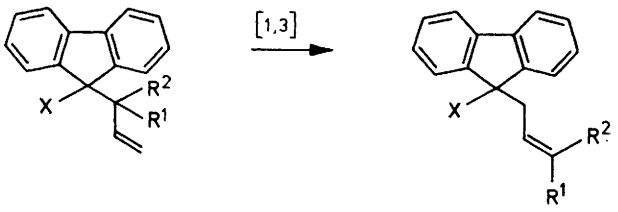
SCHEME Stereochemical aspects of the [1,3] rearrangement of chiral 9-(1-phenylallyl)fluorene derivatives

of 9-(1-phenylallyl)fluorenes (16) was synthesised and the rates of the thermal [1,3] rearrangement (16) ⟶ (17) were measured.

The results of this study are summarised in Table 1, and it is clear that the rate of the reaction increases in the order X = OMe < NMe_2 < O^-. The rapid base catalysed rearrangement of the 9-hydroxyfluorene (16; X = OH) in methanolic sodium methoxide clearly accounts for the reported isolation of 9-cinnamylfluoren-9-ol (17; X = OH) from the Wittig rearrangement of cinnamyl fluoren-9-yl ether; [27] the base catalysed [3,2] rearrangement of other allylic ethers at low temperatures is well known.[28] The thermal [1,3] rearrangement of the hydroxyfluorene (16; X = Ph) was not observed since at 170° a retroene reaction [29] occurred and a mixture of fluorenone and *trans*-1-phenylpropene was obtained. Similar fragmentation reactions have been reported as side reactions in the oxy-Cope rearrangement of 3-hydroxyhexa-1,5-dienes.[30] Pyrolysis of the deuteriated fluorenol (16; X = OD) gave 3-deuterio-1-phenylpropene as expected from the six-centre retroene

TABLE 1

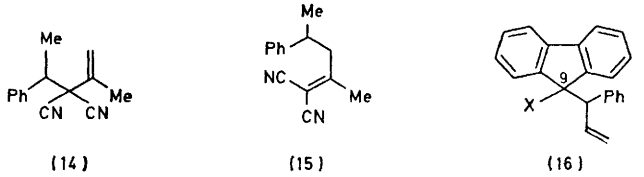
[1,3] Rearrangement of 9-prop-2-enylfluorenes [a]



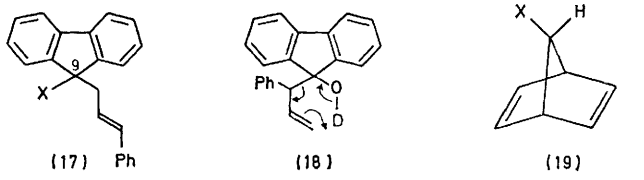
Compound	X	R^1	R^2	T/°C	$t_{\frac{1}{2}}$/s	k/s^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1}
(4b)	Me_2N	Me	Me	79	2.85×10^3	2.4×10^{-4}	26.5
(4c)	Me_2N	Ph	H	79	7.25×10^3	9.6×10^{-5}	27.3
(16; X = OMe)	MeO	Ph	H	125	4.9×10^5	1.4×10^{-6}	34.2
(16; X = O$^-$)	O$^-$	Ph	H	24	3.26×10^5	2.1×10^{-6}	25.1

[a] Data refer to pure liquids except for the case X = O$^-$ which was examined in 1M methanolic sodium methoxide.

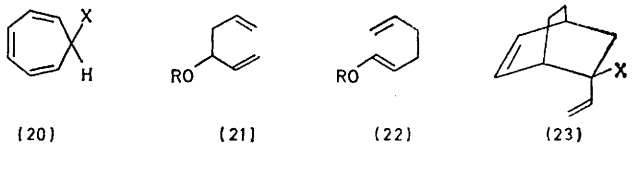
mechanism [see arrows in (18)]. It is of interest that the thermal rearrangement [15,31] of the norbornadiene derivatives (19) to the cycloheptatriene derivatives (20) also proceeds at a much faster rate for the anion (19; X = O$^-$)



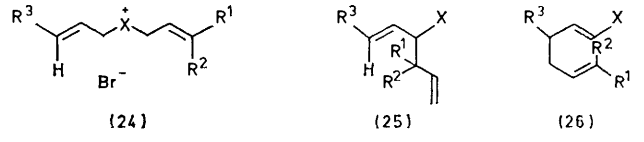
(14) (15) (16)



(17) Ph (18) (19)



(20) (21) (22) (23)



(24) (25) (26)

a ; $R^1 = R^3 = Ph, R^2 = H, X = NMe_2$
b ; $R^1 = R^2 = Me, R^3 = Ph, X = NMe_2$
c ; $R^1 = R^2 = H, R^3 = Ph, X = NMe_2$
d ; $R^1 = R^2 = Me, R^3 = Ph, X = OMe$
e ; $R^1 = R^3 = Ph, R^2 = H, X = SEt$

than for the ether (19; X = OMe). This reaction is of a similar type to the [1,3] rearrangement (16) ⟶ (17) and a concerted [1,3] sigmatropic mechanism has been suggested. It has also been noted [19,32] that in the rearrangement (19) ⟶ (20) the rate of reaction is faster for the compounds (19; X = OMe) and (19; X = Ph) than for the unsubstituted norbornadiene system (19; X = H). Other examples of [1,3] rearrangements accelerated by electron-rich substituents (O$^-$, NR_2, NR$^-$) [13,18,21] and even by a positive charge [20] have also been reported since our work was completed.

The effects of the substituents X at position-9 of the fluorenyl residue upon the rates of the rearrangements (16) ⟶ (17) are explicable either in terms of stabilisation of the fluorenyl radical [33] of a radical-pair intermediate, or in terms of increased configuration interaction [24] as the reaction becomes more polar in character. The question of mechanism therefore remains open but it is worth noting that some stereoselectivity is probably to be expected for orbital symmetry forbidden processes involving weakly interacting radical pair intermediates.[34] This ambiguity regarding substituent effects upon [1,3] rearrangements encouraged us to examine analogous substituent effects in [3,3] sigmatropic rearrangements. These are typical examples of symmetry allowed sigmatropic rearrangements and, at the time this work was carried out, the effect of heteroatom substituents had been studied only for the oxy-Cope rearrangement (21) ⟶ (22). Thus it had been reported [35] that the bicyclo-octenol derivative (23; X = OH) undergoes a [3,3] rearrangement with a rather lower activation energy (E_a 41.8 ± 0.4 kcal mol^{-1}) than the hydrocarbon (23; X = H) (E_a 44.2 ± 1.2 kcal mol^{-1}). The effects of the hydroxy substituent are not very large and it was therefore interesting to note in our earlier study [25] of the [3,2] sigmatropic rearrangement of allylic ammonium ylides that the 3-dimethylaminohexa-1,5-diene (25a) underwent a [3,3] rearrangement at relatively low temperatures (80°) to give the enamine (26a). The accelerating effect of the substituents in the reaction (25a) ⟶ (26a) has been further investigated by a study of the rearrangement rates of a number of related compounds.

The rearrangement (25a) ⟶ (26a) showed good first-order kinetics at 100° and the product (26a) was formed with the *trans*-stereochemistry shown. The precursor (25a) was also a single diastereoisomer, but the stereochemistry of (26a) may be either a consequence of a stereospecific rearrangement of the diene (25a) or merely

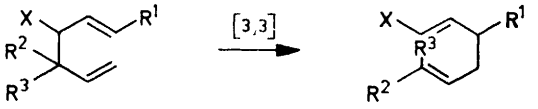
the result of thermal equilibration of diastereoisomeric enamines. The 3-dimethylaminohexa-1,5-dienes (25b and c) were both obtained from the base catalysed [3,2] sigmatropic rearrangement of the ammonium salts (24b and c), respectively. The highly substituted diene (25b) rearranged at 100° to give the *trans*-enamine (26b), but the less substituted diene (25c) required a temperature of 170° before a reasonably rapid Cope rearrangement was observed, giving the *trans*-enamine (26c). Assuming that the 1-phenyl substituent of (25c) has little or no effect on the rate of the rearrangement,[36] it appears that the 3-dimethylamino-substituent has a highly significant effect [$\Delta G_{443}^{\ddagger}$ for (25c) ⟶ (26c) 35.1 kcal mol^{-1}; $\Delta H^{\ddagger}$ for degenerate rearrangement of hexa-1,5-diene [37] 33.5 kcal mol^{-1}, $\Delta G_{443}^{\ddagger}$ 39.6 kcal mol^{-1}]. Similar acceleration of the [3,3] rearrangement of hexa-1,5-dienes results from a 3-phenyl substituent (25a) ⟶ (26a) and 3,3-dimethyl substitution (25b) ⟶ (26b); the accelerating effects of 3-aryl substituents have been noted by others.[36,38] These effects may in part be steric, but they also presumably result from the electron-donating properties of substituents in the 3-position. The effects of the 3-NMe_2 substituent appear to be more marked than those of a 3-OR group. The enamines (26a—c) were characterised by their spectroscopic properties and by hydrolysis to the corresponding aldehydes (27a—c). This conclusion based upon published data [35] was confirmed by the examination of the [3,3] rearrangement of the 3-methoxyhexa-1,5-diene (25d), prepared by base catalysed [3,2] rearrangement of the ether (28) followed by methylation; the free energy of activation for the oxy-Cope rearrangement (25d) ⟶ (26d) is significantly higher ($\Delta G_{469}^{\ddagger}$ 37.2 kcal mol^{-1}) than that for the rearrangement of the corresponding dimethylaminohexa-1,5-diene (25b) ⟶ (26b) ($\Delta G_{373}^{\ddagger}$ 29.7 kcal mol^{-1}). The 3-ethylthiohexa-1,5-diene (25e) also rearranged to give the thioenol ether (26e) with a considerably higher energy of activation ($\Delta G_{443}^{\ddagger}$ 33.0 kcal mol^{-1}) than that for the rearrangement of the analogous dimethylaminohexa-1,5-diene (25a) ⟶ (26a) ($\Delta G_{373}^{\ddagger}$ 27.4 kcal mol^{-1}). We conclude that a 3-dimethylamino substituent is more effective than either a 3-alkoxy or 3-alkylthio substituent in lowering the energy of the transition state for the Cope rearrangement, and this influence appears to be a consequence of its more effective electron-donating properties. Details of the results discussed above are summarised in Table 2. Since the completion of this work a number of papers have appeared in which the effects of substituents upon the rates of Cope [3,3] rearrangements have been noted. In particular, it has been noted [39] that the reaction is dramatically accelerated by an alkoxide substituent at C-3 of the hexa-1,5-diene system and some elegant synthetic procedures [40] have been based upon this observation. The accelerating effects of dialkylamino substituents upon thia-Claisen [41] and dithia-Cope [42] rearrangements have also been recognised.

From the results obtained in this and other work [39–42] it is clear that certain electron donating substituents (4-phenyl, 4,4-dimethyl, and 3-dimethylamino) have important accelerating effects in the Cope [3,3] rearrangement of hexa-1,5-dienes. It is also evident that both 'allowed' concerted [3,3] rearrangements and 'forbidden' and radical pair or concerted [1,3] rearrangements show similar substituent effects. Both [1,3] and [3,3] rearrangements are accelerated by electron donors. It is unlikely that conclusions concerning concertedness or radical pair character in sigmatropic rearrangements can be drawn on the basis of substituent effects. Recent discussion of the mechanism of the Cope rearrangement has been promoted by the suggestion [38] that bond making precedes bond breaking with the consequent involvement of a 1,4-cyclohexylene diradical. The results of studies based upon substituent effects in 2-arylhexa-1,5-dienes [43] and kinetic isotope effects [44] indicate that, in general, the transition state involves synchronous bond breaking and bond making but, depending upon the nature of the substituents, either process may be more advanced than the other. Other papers,[45,46] in which steric effects have been discussed, have considered the reaction in terms of synchronised bond making and breaking and the relationship between the various 'allowed' reaction modes has been examined.[7,45]

A number of other studies, both theoretical [47] and experimental,[34,36,38,48,49] that have been made of substituent effects in [1,3] and [3,3] rearrangements should be noted. The [3,3] rearrangement is also accelerated by electron accepting substituents, and owes its discovery [50] to these effects. In at least one example, the [1,3] re-

TABLE 2

[3,3] Rearrangement of hexa-1,5-diene derivatives



Compound	X	R^1	R^2	R^3	T/°C	$t_{\frac{1}{2}}$/s	k/s^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1}
(25a)	Me_2N	Ph	Ph	H	100	1.09×10^3	6.4×10^{-4}	27.4
(25b)	Me_2N	Ph	Me	Me	100	2.32×10^4	3.0×10^{-5}	29.7
(25c)	Me_2N	Ph	H	H	170	1.52×10^4	4.6×10^{-5}	35.1
(25d)	MeO	Ph	Me	Me	196	1.5×10^4	4.6×10^{-5}	37.2 [a]
(25e)	EtS	Ph	Ph	H	170	1.35×10^3	5.1×10^{-4}	33.0

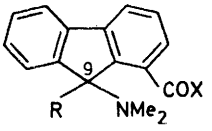
[a] This result is subject to errors since the reaction gave other products in addition to the product of a [3,3] sigmatropic rearrangement.

arrangement has also been shown to be accelerated by an electron-withdrawing substituent on the migrating group.[2] These effects may be and have been discussed in a variety of ways, and in most cases the simple view that the reaction is accelerated by substituents that become conjugated in the transition state is adequate for qualitative predictions. It has also been noted on a number of occasions that sigmatropic rearrangements in charged systems [51] and some extensively conjugated systems [52] may be very significantly enhanced in rate relative to the corresponding hydrocarbon rearrangements.

this bond [*e.g.* (29)] or a rapidly equilibrating set of conformations involving this bond in which the two *N*-methyl groups occupy different time-averaged environments. The process that exchanges the two *N*-methyl groups between the two environments [*e.g.* A and B in (29)] or sets of environments must also involve nitrogen inversion, possibly in a synchronised rotation–inversion process.[53] Table 3 shows appropriate n.m.r. parameters and coalescence data for the amines (11) and (12); the free energy barriers for the rotational process are based upon site exchange rates at the coalescence temperature calculated in the usual way.[54] The n.m.r.

TABLE 3

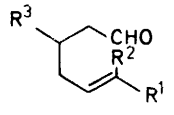
N.m.r. parameters and barriers to rotation about the C(9)–N bond in 9-dimethylaminofluorenes



Compound	R	X	τ_A [a]	τ_B [a]	$\nu_A - \nu_B$ [b]/Hz (±1)	k_c/s^{-1}	T_c [c]/°C ±5	$\Delta G^{\ddagger}$ at T_c/kcal mol^{-1} ±0.3
(8)	$CHPhCH=CH_2$	$OCHMe_2$	7.33	8.31	98	218	−63	9.9
(10)	$CH_2CH=CHPh$	$OCHMe_2$	7.99	8.55	56	124	−80	9.3
(11)	$CHPhCH=CH_2$	NCHMePh	7.17	8.29	112	249	14	13.6
(12)	$CH_2CH=CHPh$	NCHMePh	7.33	8.23	90	200	4	13.3

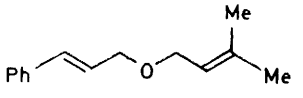
[a] Chemical shifts refer to the two *N*-methyl signals observed at low temperatures. [b] At 100 MHz for solutions in $CDCl_3$ or $CDCl_3$–CS_2. [c] The large signal separation results in a rather larger uncertainty than is usual in the measurement of coalescence temperatures.

Hindered Rotation about the C(9)–N *Bond in the* 9-*Dimethylaminofluorenes* (8) *and* (10)—(12).—The n.m.r. spectra of the amines (11) and (12) at normal probe temperatures (*ca.* 35°) showed very broad singlet signals

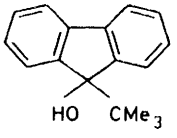


(27)

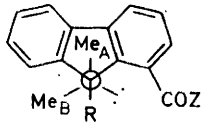
a ; $R^1 = R^3 = Ph$, $R^2 = H$
b ; $R^1 = R^2 = Me$, $R^3 = Ph$
c ; $R^1 = R^2 = H$, $R^3 = Ph$



(28)



(30)



(29)

R = CHPhCH = CH_2 or CH_2CH = CHPh
Z = $OCHMe_2$ or NHCHMePh

for the 9-NMe_2 substituents. These sharpened at higher temperatures and separated into two signals of equal intensity at lower temperatures. We associate this result with hindered rotation about the C(9)–N bond resulting in either a single favoured conformation about

spectra of the amines (8) and (10) show similar temperature dependence over a lower temperature range associated with rather lower energy barriers for the rotational process. This interpretation of the temperature dependence of the n.m.r. spectra of these amines is consistent with the absence of temperature dependence of any signals other than those associated with the 9-NMe_2 group.

The rather higher energy barriers for the amines (11) and (12) in which the substituent at position-1 of the fluorenyl residue is the more bulky amide group suggests that, as expected, the barriers are principally due to non-bonded interactions in the transition states for rotation or rotation–inversion. In view of the complexity of these compounds, it is not possible to analyse the barriers in the usual terms of modern quantitative conformational analysis.[54]

A small rotational barrier has been detected by n.m.r. line-shape techniques in t-butyldimethylamine and it has been noted that in other amines there may be a common transition state for rotation and inversion processes.[53,56] Energy barriers to both rotation and inversion in simple amines are generally low [53,54,56,57] ($\Delta G^{\ddagger}$ *ca.* 6 kcal mol^{-1}) and the high barriers detected in the present study are exceptional for nitrogen linked to sp^3 hybridised carbon. High barriers for C–N rotation are much more commonly encountered in cases involving sp^2 hybridised carbon as in highly substituted tertiary arylamines.[54] The non-equivalence of the two NMe substituents in the 9-dimethylaminofluorenes (29) may be compared with the hindered rotation observed [$\Delta G^{\ddagger}$ 9.4 kcal mol^{-1}; T_c

— 85° (CS_2)] for 9-t-butyl-9-hydroxyfluorene (30).[58] The relation between the free energies of activation for the 9-dimethylaminofluorenes (8) and (10)—(12) (Table 3) and the 9-hydroxyfluorene (30) is acceptable.

EXPERIMENTAL

The general directions are the same as in Part 1.[23]

Allyldimethylfluoren-9-ylammonium Bromide (5a).—Allyl bromide (20 g) and 9-dimethylaminofluorene (16.4 g) in methyl cyanide (50 ml) were stirred at room temperature for 12 h. The resulting solution was poured into dry ether (1 l) and the gummy precipitate crystallised from acetone giving *allyldimethylfluoren-9-ylammonium bromide* (5a) (15.3 g, 59%) as prisms, m.p. 151° (Found: C, 65.5; H, 6.2; N, 4.1; Br, 24.4 $C_{18}H_{20}BrN$ requires C, 65.45; H, 6.1; N, 4.2; Br, 24.25%); τ 2.16—2.93 (m, 8 aromatic H), 3.58 (s, 9-H), 3.87—4.57 (m, $CH{=}CH_2$), 5.80 (d, *J* 7 Hz, $CH_2CH{=}CH_2$), and 6.74 (s, NMe_2).

9-*Allyl*-9-*dimethylaminofluorene* (4a).—Methanolic sodium methoxide (from 2 g sodium in 100 ml methanol) was added to a stirred solution of allyldimethylfluoren-9-ylammonium bromide (9.3 g) in methanol (100 ml) and stirring was continued at room temperature for 15 h. The solution was poured into water (500 ml) and the product extracted into ether; evaporation of the dried ethereal extract gave a residual oil which was distilled. 9-*Allyl*-9-*dimethylaminofluorene* (4a) (7.0 g, 93%) was obtained as the fraction, b.p. 133—135° at 8 mmHg (Found: C, 86.7; H, 8.0; N, 5.5. $C_8H_{19}N$ requires C, 86.7; H, 7.6; N, 5.6%); τ 2.28—2.90 (m, 8 aromatic H), 4.50—5.47 (m, $CH{=}CH_2$), 7.13 (d, *J* 7 Hz, $CH_2CH{=}CH_2$), and 7.83 (s, NMe_2). The *picrate* crystallised from ethanol as broad yellow needles, m.p. 205—208° (Found: C, 60.0; H, 4.5; N, 11.8. $C_{24}H_{22}N_4O_7$ requires C, 60.2; H, 4.7; N, 11.7%).

3,3-*Dimethylallyldimethylfluoren*-9-*ylammonium Bromide* (5b).—*NN*-Dimethyl-3,3-dimethylallylamine [23] (15 g) in dry methyl cyanide (50 ml) was added slowly to a stirred solution of 9-bromofluorene (24.5 g) in dry methyl cyanide (100 ml). The mixture was stirred for 3 h at room temperature and poured into dry ether (1 l). The gummy precipitate was collected and crystallised from acetone giving 3,3-*dimethylallyldimethylfluoren*-9-*ylammonium bromide* (5b) (16.5 g, 46%) as plates, m.p. 142—144° (Found: C, 66.7; H, 6.8; N, 4.0; Br, 22.5. $C_{20}H_{23}BrN$ requires C, 67.0; H, 6.7; N, 3.9; Br, 22.4%); τ 2.08—2.87 (m, 8 aromatic H), 3.40 (s, 9-H), AX_2 system, τ_A 4.53, τ_X 5.76 (J_{AX} 7.5 Hz, $=CH{-}CH_2{-}$), 6.75 (s, NMe_2), 8.13 and 8.22 (s, CMe_2).

9-(1,1-*Dimethylallyl*)-9-*dimethylaminofluorene* (4b).—Methanolic sodium methoxide (from 0.3 g sodium in 50 ml methanol) was added to a stirred solution of 3,3-dimethylallyldimethylfluoren-9-ylammonium bromide (5.0 g) in methanol (50 ml). After 1 h, water (500 ml) was added and the products extracted into ether. Evaporation of the dried ethereal extracts gave a pale yellow oil consisting of two major components which were separated by preparative t.l.c. using silica and benzene. The faster moving band gave 9-(1,1-*dimethylallyl*)-9-*dimethylaminofluorene* (4b) as an oil; τ 2.22—2.86 (m, 8 aromatic H), 3.53 (dd, *J* 10, 18 Hz, $CH{=}CH_2$), 4.78—5.14 (m, $CH{=}CH_2$), 7.73 (s, NMe_2), and 9.02 (s, CMe_2). The *picrate* crystallised from ethanol as yellow plates, m.p. 175—178° (Found: C, 65.1; H, 4.8; N, 9.9. $C_{30}H_{26}N_4O_7$ requires C, 65.0; H, 4.7; N, 10.1%). The slower moving band gave 9-(3,3-*dimethylallyl*)-9-*dimethylaminofluorene* (6b) as an oil (Found: C, 87.0; H, 8.1; N, 5.2. $C_{20}H_{23}N$ requires C, 86.75; H, 8.3; N, 5.0%); τ 2.22—2.86 (m, 8 aromatic H), AX_2 system, τ_A 5.08, τ_X 7.20 (J_{AX} 6 Hz, $CH{=}CH_2$), 7.77 (s, NMe_2), 8.52 and 8.63 (s, CMe_2).

Rearrangement of 9-(1,1-*Dimethylallyl*)-9-*dimethylaminofluorene* (4b). *Formation of* 9-(3,3-*Dimethylallyl*)-9-*dimethylaminofluorene* (6b).—Portions of the amine (4b) (25 mg) were heated in sealed ampoules at 79°, and the products analysed by n.m.r. spectroscopy at various time intervals (see Table 1). The product was identified as the 3,3-*dimethylallyl* derivative (6b) by comparison with an authentic sample.

Cinnamylfluoren-9-*yldimethylammonium Bromide* (5c).—9-Bromofluorene (5.0 g) and *NN*-dimethylcinnamylamine (3.2 g) were stirred in methyl cyanide (25 ml) at room temperature for 12 h. The solution was diluted with ether (500 ml) and the precipitated salt was purified by crystallisation from methyl cyanide–ether giving the *cinnamyl salt* (5c) as prisms (7.5 g, 90%), m.p. 151° (Found: C, 70.4; H, 6.1; N, 3.6; Br, 19.6. $C_{24}H_{24}BrN$ requires C, 70.6; H, 5.9; N, 3.4; Br, 19.7%); τ 2.11—2.82 (m, 13 aromatic H), 3.08—4.10 (m, $PhCH{=}CH$), 3.57 (s, 9-H), 5.58 (d, *J* 7 Hz, $PhCH{=}CHCH_2$), and 6.63 (s, NMe_2).

9-(1-*Phenylallyl*)-9-*dimethylaminofluorene* (4c).—Cinnamylfluoren-9-yldimethylammonium bromide (4.06 g) in dimethyl sulphoxide (20 ml) was added at room temperature to a solution of sodium methoxide prepared from sodium hydride (480 mg), dimethyl sulphoxide (10 ml), and methanol. After 2 h the mixture was diluted with water and extracted with ether (2 × 150 ml). Evaporation of the ethereal extract gave an oil (3 g, 93%) which crystallised from methanol giving 9-(1-*phenylallyl*)-9-*dimethylaminofluorene* (4c) (77%) as prisms, m.p. 114° (Found: C, 88.4; H, 7.2; N, 4.3. $C_{24}H_{23}N$ requires C, 88.3; H, 7.1; N, 4.2%); τ 2.02—3.67 (13 aromatic H and $CH{=}CH_2$), 4.72br (d, *J* 10 Hz, $CH{=}CH_AH_B$), 4.91br (d, *J* 17 Hz, $CH{=}CH_AH_B$), 5.62 (d, *J* 7.5 Hz, $CH_2{=}CHCHPh$), and 7.72 (s, NMe_2). The mother liquors were evaporated and the residue was purified by t.l.c. (silica gel, benzene–ether 1 : 1) giving 9-*cinnamyl*-9-*dimethylaminofluorene* (6c) (16%) as an oil identical with the product obtained by thermal rearrangement of 9-(1-phenylallyl)-9-dimethylaminofluorene (4c).

Rearrangement of 9-(1-*Phenylallyl*)-9-*dimethylaminofluorene* (4c). *Formation of* 9-*Cinnamyl*-9-*dimethylaminofluorene* (6c).—9-(1-Phenylallyl)-9-dimethylaminofluorene (1.0 g) was heated at 170 ° in a sealed ampoule (N_2 atmosphere) for 2 h. The *product* (6c) was obtained as a pale yellow glass (Found: C, 88.45; H, 7.1; N, 4.2. $C_{24}H_{23}N$ requires C, 88.3; H, 7.1; N, 4.2%); τ 1.88—3.02 (m, 13 aromatic H), 3.80 (d, *J* 16 Hz, $PhCH{=}CH$), 4.13 (dt, *J* 16, 7 Hz, $PhCH{=}CHCH_2$), 6.98 (d, *J* 7 Hz, $PhCH{=}CHCH_2$), 7.74 (s, NMe_2.) The *picrate* crystallised from ethanol as yellow plates, m.p. 175—178° (Found: C, 65.1; H, 4.8; N, 9.9. $C_{30}H_{26}N_4O_7$ requires C, 65.0, H, 4.7; N, 10.1%). The kinetics of the rearrangement at 79° in sealed ampoules was followed by n.m.r. analysis of the products at various time intervals (see Table 1).

2-*Benzoyl*-9-*bromofluorene*.—Bromine (11.5 g) in carbon tetrachloride (50 ml) was added dropwise over 90 min to a well stirred solution of 2-benzoylfluorene (18.0 g) [59] and benzoyl peroxide (0.5 g) in carbon tetrachloride (250 ml) heated under reflux. The solution was cooled, washed (10% aqueous $NaHCO_3$ and water), dried, and evaporated. The residual solid crystallised from benzene–light petroleum (b.p. 40—60°) giving 2-*benzoyl*-9-*bromofluorene* (19.5 g, 84%)

as pale yellow needles, m.p. 136—138° (Found: C, 68.85; H, 3.7; Br, 23.1. $C_{20}H_{13}Br$ requires C, 68.8; H, 3.7; Br, 22.9%); $\nu_{max.}$ (KBr) 1 659 cm^{-1}; τ 1.89br (s, 1-H), 2.10—2.88 (m, 11 aromatic H), and 4.08 (s, 9-H).

Cinnamyl-9-(2-benzoylfluorenyl)dimethylammonium Bromide.—2-Benzoyl-9-bromofluorene (3.0 g) was stirred at room temperature overnight with *NN*-dimethylcinnamylamine (1.5 g) in dry methyl cyanide (50 ml). The resulting solution was added to dry ether (500 ml) and the precipitated gummy solid purified by repeated precipitation from chloroform by the addition of ether giving the *salt* as a pale brown gum (3.8 g, 90%) which was suitable for use in the following experiment, τ 2.02—2.78 (m, 17 aromatic H), 3.00 (d, *J* 15 Hz, C*H*=CH), 3.62 (dt, *J* 15, 8 Hz, CH=C*H*), 4.39 (s, 9-H), 5.79 (d, *J* 8 Hz, CH_2CH=CH), and 6.80 (s, NMe_2).

2-Benzoyl-9-dimethylamino-9-(1-phenylallyl)fluorene (7).—The foregoing salt (3.5 g) was stirred for 1 h with ether (100 ml) and aqueous sodium hydroxide (100 ml; 10%). The ether layer was washed with water and the product extracted into hydrochloric acid (3 × 50 ml; 2N). The acidic extract was neutralised (2N aqueous sodium hydroxide) and the product extracted into ether. The ethereal extract was dried and evaporated giving a mixture of both diastereoisomers of *2-benzoyl-9-dimethylamino-9-(1-phenylallyl)fluorene* (7) as a palle yellow gum. Repeated crystallisation from methanol–water gave a single diastereoisomer (500 mg) as pale yellow prisms, m.p. 133—135° (Found: C, 86.2; H, 6.4; N, 3.3. $C_{31}H_{27}NO$ requires C, 86.6; H, 6.3; N, 3.3%); $\nu_{max.}$ (KBr) 1 650 cm^{-1}; τ 1.79 (s, 1-H), 2.03—3.71 (m, 16 aromatic H and C*H*=CH_2), 4.70br (d, *J* 10 Hz, C=C*H*), 4.88br (d, *J* 17 Hz, C=C*H*), 5.53 (d, *J* 8 Hz, C*H*PhCH=CH_2), and 7.70 (s, NMe_2). Attempted resolution by crystallisation of the 3-bromocamphor-8-sulphonate salt and liberation of the base gave a sample, m.p. 139—143°, $[\alpha]^D$ +2.28°.

2-Benzoyl-9-cinnamyl-9-dimethylaminofluorene (9).—2-Benzoyl-9-dimethylamino-9-(1-phenylallyl)fluorene (100 mg) was heated under reflux in benzene for 5 h (N_2 atmosphere) and evaporation of the solvent gave *2-benzoyl-9-cinnamyl-9-dimethylaminofluorene* (9) as a gum (Found: C, 86.4; H, 6.25; N, 3.0. $C_{31}H_{27}NO$ requires C, 86.6; H, 6.3; N, 3.3%); $\nu_{max.}$ 1 654 cm^{-1}; τ 1.99—3.06 (m, 17 aromatic H), ABX_2 system, τ_A 3.97, τ_B 4.06, τ_X 7.01 [J_{AB}, 17.5, J_{BX} 6 Hz, $PhCH_A{=}CH_B{-}C(H_X)_2$], and 7.75 (s, NMe_2).

Isopropyl 9-Hydroxyfluorene-1-carboxylate.— 1-Ethoxycarbonylfluorenone [60] (5.6 g) in warm propan-2-ol (50 ml) was slowly added to a hot solution of aluminium isopropoxide (6.0 g) in propan-2-ol (100 ml). The solution was heated under reflux and the solvent allowed to distil slowly until reduction was complete (no 2,4-dinitrophenylhydrazone reaction from distillate). The resulting solution was poured into dilute hydrochloric acid (550 ml; N) and the product extracted into ether. The ethereal extract was dried and evaporated giving the crude *fluorenol* as a gum (4.3 g, 74%) which crystallised from light petroleum (b.p. 40—60°) as pale yellow plates, m.p. 121—123° (Found: C, 76.1; H, 6.05. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%); $\nu_{max.}$ (KBr) 3 500 and 1 685 cm^{-1}; τ 2.12—2.89 (m, 7 aromatic H), 4.21 (s, 9-H), 4.62br (s, OH), 4.75 (septet, *J* 6 Hz, C*H*Me_2), and 8.68 (d, *J* 6 Hz, CHMe_2).

Isopropyl 9-Bromofluorene-1-carboxylate.—Isopropyl 9-hydroxyfluorene-1-carboxylate (6.5 g) in dry benzene (150 ml) was stirred with phosphorus pentabromide (15.0 g) at room temperature overnight. The mixture was poured onto crushed ice (250 g) and the benzene layer separated, dried, and evaporated giving the crude *bromo-compound* (7.8 g, 97%) as a pale orange oil which was used directly in the next experiment, $\nu_{max.}$ (liquid film) 1 700 cm^{-1}; τ 2.09—2.80 (m, 7 aromatic H), 3.58 (s, 9-H), 4.69 (septet, *J* 6 Hz, C*H*Me_2), 8.53 (d, *J* 6 Hz, CH$Me_A$$Me_B$), and 8.61 (d, *J* 6 Hz, CH$Me_A$$Me_B$).

Cinnamyl-(1-isopropoxycarbonylfluoren-9-yl)dimethylammonium Bromide.—This salt was prepared by the reaction of isopropyl 9-bromofluorene-1-carboxylate (8.1 g) with *NN*-dimethylcinnamylamine (4.5 g) in dry methyl cyanide (75 ml). The *product* (10.3 g, 86%) was purified by repeated precipitation from chloroform solution by the addition of ether (Found: N, 2.8; Br, 16.4. $C_{28}H_{30}BrO_2N$ requires N, 2.8; Br, 16.25%); $\nu_{max.}$ ($CHCl_3$) 1 700 cm^{-1}; τ 2.03—2.98 (m, 12 aromatic H), 3.58br (dt, *J ca.* 15, 7 Hz, =C*H*–CH_2), 3.67 (s, 9-H), 4.83 (septet, *J* 6 Hz, C*H*Me_2), 5.05br (dd, *J ca.* 12, 8 Hz, =CH–C$H_A$$H_B$–), 5.65br (dd, *J ca.* 12, 6 Hz, =CH–C$H_A$$H_B$–), 6.60 (s, NMe_2), 7.19 (s, NMe_2), 8.68 (d, *J* 6 Hz, CH*Me*$_A$$Me_B$), and 8.72 (d, *J* 6 Hz, CHMe_A*Me*$_B$).

Isopropyl 9-Dimethylamino-9-(1-phenylallyl)fluorene-1-carboxylate (8).—The cinnamyl salt (10.0 g) in ether (100 ml) was stirred with aqueous sodium hydroxide (100 ml, 10%) for 2 h. The ethereal layer was washed, dried, and evaporated giving isopropyl 9-dimethylamino-9-(1-phenylallyl)-fluorene-1-carboxylate (8) (7.5 g, 90%) as a pale yellow gum. Crystallisation from methanol gave a single pure diastereoisomer (3.2 g) as prisms, m.p. 115—117° (Found: C, 81.8; H, 7.1; N, 3.4. $C_{28}H_{29}NO_2$ requires C, 82.0; H, 7.1; N, 3.3%); $\nu_{max.}$ (KBr) 1 720 cm^{-1}; τ (220 MHz) 2.22 (m, 2-H), 2.60—3.53 (m, 11 aromatic H and –C*H*=CH_2), 4.53 (d, *J* 8.5 Hz, PhC*H*), 4.66 (septet, *J* 6 Hz, C*H*Me_2), 4.74 (d, *J* 10 Hz, C=CH), 4.83 (d, *J* 17 Hz, C=CH), 7.76 (s, NMe_2), 8.52 (d, *J* 6 Hz, CH*Me*$_A$$Me_B$), and 8.57 (d, *J* 6 Hz, CHMe_A*Me*$_B$).

Isopropyl 9-Cinnamyl-9-dimethylaminofluorene-1-carboxylate (10).—A benzene solution of isopropyl 9-dimethylamino-9-(1-phenylallyl)fluorene-1-carboxylate (400 mg) was heated under reflux for 5 h (N_2 atmosphere). Evaporation of the solvent gave the *cinnamylfluorene* (10) as a clear yellow gum (Found: C, 82.2; H, 7.1; N, 3.3. $C_{28}H_{29}NO_2$ requires C, 82.0; H, 7.1; N, 3.3%); $\nu_{max.}$ (liquid film) 1 720 cm^{-1}; τ 2.33—3.27 (m, 12 aromatic H), 3.98 (d, *J* 16 Hz, PhCH=), 4.69 (dt, *J* 16, 7 Hz, =CHCH_2), *ca.* 4.69 (septet, *J* 6 Hz, C*H*Me_2), 6.23 (dd, *J* 12, 7 Hz, =CH–C$H_A$$H_B$), 6.72 (dd, *J* 12, 7 Hz, =CH–C$H_A$$H_B$), 7.81 (s, NMe_2), 8.58 (d, *J* 6 Hz, CH*Me*$_A$$Me_B$), and 8.64 (d, *J* 6 Hz, CHMe_A*Me*$_B$).

N-(1-Phenylethyl)-9-oxofluorene-1-carboxamide.—A solution of 1-phenylethylamine (6.0 g) in dry benzene (20 ml) was slowly added to a stirred solution of 9-oxofluorene-1-carbonyl chloride (50 g) in dry benzene (50 ml). The mixture was heated under reflux for 3 h, washed successively with 2N-hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and water, dried, and evaporated. The residual gum was purified by chromatography on silica gel (benzene eluant) giving the *amide* as pale yellow needles, m.p. 127° (Found: C, 80.7; H, 5.3; N, 4.3. $C_{22}H_{17}NO_2$ requires C, 80.65; H, 5.2; N, 4.3%); $\nu_{max.}$ (KBr) 3 290, 1 680, and 1 665 cm^{-1}; τ 2.33—2.82 (m, 12 aromatic H), 4.68 (q, *J* 7 Hz, C*H*Me), and 8.28 (d, *J* 7 Hz, CH*Me*).

N-(1-Phenylethyl)-9-hydroxyfluorene-1-carboxamide.— *N*-(1-Phenylethyl)-9-oxofluorene-1-carboxamide (5.0 g) in propan-2-ol (100 ml) was added to a hot solution of aluminium isopropoxide (10.0 g) in propan-2-ol (150 ml), and the mixture heated under reflux for 2 h with slow distillation of the solvent. When the distillate no longer gave a precipitate with 2,4-dinitrophenylhydrazine, the mixture was poured in-

to hydrochloric acid (300 ml; 2N) and the product was extracted into ether. The ethereal extract was dried and evaporated, and crystallisation of the residual gum gave the *fluorenol* (3.1 g, 62%) as needles, m.p. 171—173° (Found: C, 80.2; H, 6.1; N, 4.2. $C_{22}H_{19}NO_2$ requires C, 80.25; H, 5.8; N, 4.25%); $\nu_{max.}$ (KBr) 3 270 and 1 630 cm^{-1}; τ 2.29—2.82 (m, 12 aromatic H), 4.32 (s, 9-H), 4.74br (q, *J* 7 Hz, C*H*Me), and 8.33 (d, *J* 7 Hz, CH*Me*).

N-(1-*Phenylethyl*)-9-*bromofluorene*-1-*carboxamide*.— The foregoing fluorenol (9.0 g) in dry benzene (400 ml) was stirred overnight at room temperature with phosphorus pentabromide (14.0 g). The resulting dark solution was poured onto crushed ice (250 g), washed with water, dried, and evaporated. The residual solid crystallised from methyl cyanide giving the *bromofluorene* (6.3 g, 59%) as needles, m.p. 231—235° (decomp) (Found: C, 67.3; H, 4.9; N, 3.7; Br, 20.7. $C_{22}H_{18}BrNO$ requires C, 67.35; H, 4.6; N, 3.6; Br, 20.4%); $\nu_{max.}$ (KBr) 3 260 and 1 630 cm^{-1}; τ 1.95—2.80 (m, 12 aromatic H), 3.62 (s, 9-H), 4.60br (m, C*H*Me), and 8.27 (d, *J* 7 Hz, CH*Me*).

Cinnamyldimethyl-[1-N-(1-*phenylethyl*)*carbamoyl*-*fluoren*-9-*yl*]*ammonium Bromide* (13).—*N*-(1-Phenylethyl)-9-bromofluorene-1-carboxamide (5.3 g) in dry methyl cyanide (300 ml) was stirred overnight at room temperature with *NN*-dimethylcinnamylamine (2.6 g). The precipitated solid was combined with further material precipitated by the addition of dry ether (11) and was purified by repeated precipitation from chloroform by the addition of ether giving the salt (4.8 g, 64%) as a pale yellow solid which was used without additional purification in the next experiment (Found: Br, 14.8. $C_{33}H_{30}N_2OBr$ requires Br, 14.5%); $\nu_{max.}$ ($CHCl_3$) 3 160 and 1 620 cm^{-1}; τ 2.15—3.0 (m, 17 aromatic H), 3.19 (d, *J* 15 Hz, C*H*=CH), *ca.* 3.86 (m, =C*H*CH_2), 3.88 (s, 9-H), 4.91 (q, *J* 7 Hz, C*H*Me), 6.07br (d, *J* *ca.* 7 Hz, =CHCH_2), 7.32 and 7.41 (s, NMe_AMe_B), and 8.29 (d, *J* 7 Hz, CH*Me*).

9-*Dimethylamino*-9-(1-*phenylallyl*)-N-(1-*phenylethyl*)-*fluorene*-1-*carboxamide* (11).—Methanolic sodium methoxide (from 1.0 g sodium in 50 ml methanol) was slowly added to a stirred solution of the foregoing ammonium salt (13) (2.9 g) in methanol (100 ml). After 1.5 h the solution was poured into water (250 ml) and the product extracted into ether. The ethereal solution was extracted with hydrochloric acid (4 × 50 ml; 2N) and the acidic extract was neutralised (2N-sodium hydroxide), and the product re-extracted into ether. The ether solution was dried and evaporated giving a mixture of diastereoisomers of the *aminofluorene derivative* (11) (2.3 g, 93%) as a pale yellow gum. Repeated crystallisation from methanol–water gave a single pure diastereoisomer (29 mg) as prisms, m.p. 169° (Found: C, 83.9; H, 7.0; N, 5.8. $C_{33}H_{32}N_2O$ requires C, 83.8; H, 6.8; N, 5.9%); $\nu_{max.}$ (KBr) 3 070 and 1 640 cm^{-1}; τ (220 MHz) −2.22 (d, *J* 7 Hz, NH), 2.13 (d, *J* 8 Hz, aromatic H), 2.23 (d, *J* 8 Hz, aromatic H), 2.40 (d, *J* 8 Hz, aromatic H), 2.50—2.83 (m, 8 aromatic H), 2.87 (t, *J* 8 Hz, aromatic H), 3.26 (m, 3 aromatic H), 3.46 (ddd, *J* 17, 10, 10 Hz, C*H*=CH_2), 3.69 (m, 2 aromatic H), 4.51 (q, *J* 7 Hz, C*H*Me), 4.74 (dd, *J* 17, 1.5 Hz, CH=CH_AH_B), 4.86 (dd, *J* 10, 1.5 Hz, CH=CH_AH_B), 5.16 (d, *J* 10 Hz, C*H*Ph), 7.0—7.8 (s, NMe_2), and 8.15 (d, *J* 7 Hz, CH*Me*).

9-*Cinnamyl*-9-*dimethylamino*-N-(1-*phenylethyl*)*fluorene*-1-*carboxamide* (12).—The pure diastereoisomer, m.p. 169°, of 9-dimethylamino-9-(1-phenylallyl)-*N*-(1-phenyethyl)fluorene-1-carboxamide (11) (25 mg) was heated in a sealed tube (N_2 atmosphere) for 5 min at 170° giving the corresponding *cinnamylfluorene* (12) as a pale yellow gum. The product was shown by its n.m.r. spectrum to be a mixture of two diastereoisomers A and B in a ratio of 16 : 3 (Found: C, 83.8; H, 6.7; N, 6.1. $C_{33}H_{32}N_2O$ requires C, 83.8; H, 6.8; N, 5.9%); $\nu_{max.}$ (liquid film) 3 050 and 1 645 cm^{-1}; τ (220 MHz): diastereoisomer A, −2.33 (d, *J* 7 Hz, NH), 1.92 (d, *J* 8 Hz, 2-H), 2.29—2.81 (m, 11 aromatic H), 2.99 (m, 3 aromatic H), 3.22 (m, 2 aromatic H), 4.02 (d, *J* 16 Hz, C*H*=CH), 4.55 (q, *J* 7 Hz, C*H*Me), 4.89 (dt, *J* 16, 7.5 Hz, =C*H*CH_2), 6.47 (dd, *J* 7.5, 13 Hz, =CHCH_AH_B), 6.80 (dd, *J* 5.7, 13 Hz, =CHCH_AH_B), 7.3—8.5 (s, NMe_2), and 8.27 (d, *J* 7 Hz, CHMe); diastereoisomer B (distinct signals only) −2.22 (d, *J* 7 Hz, NH), 4.24 (d, *J* 16 Hz, C*H*=CH), 5.06 (dt, *J* 16,7.5 Hz, =C*H*CH_2), 7.02 (dd, =CHCH_AH_B), 7.18 (dd, =CHCH_AH_B), and 8.37 (d, *J* 7 Hz, CH*Me*).

9-(1-*Phenylallyl*)*fluoren*-9-*ol* (16; X = OH).—Ethereal butyl-lithium (350 ml, 2 molar excess) was added rapidly to a stirred solution of cinnamyl fluoren-9-yl ether [27] (9.3 g) in dry ether (200 ml) at −76° (N_2 atmosphere). After 3 h the deep red solution was allowed to warm to room temperature, water (200 ml) was added, and the ethereal layer was separated, dried, and evaporated. The residue crystallised from n-hexane giving 9-(1-*phenylallyl*)*fluoren*-9-*ol* (16; X = OH) (7.5 g, 81%) as needles, m.p. 84—86° (Found: C, 88.7; H, 5.9. $C_{22}H_{18}O$ requires C, 88.55; H, 6.0%); τ 2.38—3.28 (m, 13 aromatic H), 3.20 (ddd, *J* 9,10,16 Hz, C*H*=CH_2), 4.87 (dd, *J* 1.5, 10 Hz, CH=CH_AH_B), 4.92 (dd, *J* 1.5, 16 Hz, CH=CH_AH_B), 6.08 (d, *J* 9 Hz, C*H*Ph), and 7.56 (s, OH).

Thermolysis of 9-(1-*Phenylallyl*)*fluoren*-9-*ol* (16; X = OH). *Formation of Fluorenone and* trans-1-*Phenylpropene*.—9-(1-Phenylallyl)fluoren-9-ol (250 mg) was heated at 170° (N_2 atmosphere). *trans*-1-Phenylpropene collected in the cooler parts of the reaction vessel, identical in all respects (i.r., n.m.r. spectra) with an authentic sample.[61] The solid residue in the reaction vessel was identified (t.l.c., i.r., n.m.r.) as fluorenone. The experiment was repeated after first shaking a deuteriochloroform solution of the alcohol (250 mg) with deuterium oxide (0.5 ml). The volatile reaction product was identified as *trans*-3-deuterio-1-phenylpropene; $\nu_{max.}$ (liquid film) 3 040, 3 010, 2 945, 2 900, 2 340, and 2 160 cm^{-1}; τ 2.50—3.05 (m, 5 aromatic H), 3.64 (d, *J* 15 Hz, PhC*H*=CH), 3.86 (dt, *J* 15, 6 Hz, =C*H*CH_2D), and 8.21 (dt, J_{HH} 5, J_{HD} 2.5 Hz, $-CH_2D$).

Base Catalysed Rearrangement of 9-(1-*Phenylallyl*)*fluoren*-9-*ol*. *Formation of* 9-*Cinnamylfluoren*-9-*ol* (17; X = OH).—The rearrangement was carried out at room temperature using methanolic sodium methoxide or lithium methoxide at 24°. Purification of the rearrangement products by chromatography on silica gel gave 9-cinnamylfluoren-9-ol [27] as a yellow gum; $\nu_{max.}$ 3 330 cm^{-1}; τ 2.35—3.05 (m, 13 aromatic H), 3.79 (d, *J* 16 Hz, PhC*H*=CH), 3.98 (dt, *J* 16, 6 Hz, =C*H*CH_2), 7.19 (d, *J* 6 Hz, CH_2CH=), and 7.64br (s, OH).

9-*Methoxy*-9-(1-*phenylallyl*)*fluorene* (16; X = OMe).—9-(1-Phenylallyl)fluoren-9-ol (1.0 g) was stirred with methyl iodide (2.0 ml) and sodium hydride (0.25 g) in dimethylformamide for 8 h at room temperature. The mixture was then filtered, the filtrate poured into water (100 ml), and the product extracted into ether. The ethereal extract was dried and evaporated, and the residue crystallised from ether giving the *methyl ether* (16; X = OMe) (0.8 g, 77%) as rods, m.p. 115° (Found: C, 88.1; H, 6.3. $C_{23}H_{20}O$ requires C, 88.3; H, 6.4%); τ 2.35—3.35 (m, 13 aromatic H), 3.68 (ddd, *J* 8.5, 10, 17 Hz, C*H*=CH_2), 5.00br (d, *J* 10 Hz,

$CH{=}CH_AH_B$), 5.13br, (d, *J* 17 Hz, $CH{=}CH_AH_B$), 6.18 (d, *J* 8.5 Hz, *CH*Ph), and 7.29 (s, OMe).

Thermal Rearrangement of 9-*Methoxy*-9-(1-*phenylallyl*)-*fluorene* (16; X = OMe). *Formation of* 9-*Cinnamyl*-9-*methoxyfluorene* (17; X = OMe).—The 9-(1-phenylallyl)-fluorene (16; X = OMe) was heated at 125° (N_2 atmosphere) and samples analysed by n.m.r. spectroscopy at intervals to follow the kinetics of the rearrangement (see Table 1). The product was obtained as a pale yellow oil and consisted of a mixture of starting material and product (Found: *M*, 312. $C_{23}H_{20}O$ requires *M*, 312); τ (signals assignable to 9-cinnamyl-9-methoxyfluorene) 2.31—3.10 (m, 13 aromatic H), 3.62—4.00 (m, PhC*H*=CH), 6.15 (m, PhCH=CH-CH_2), and 7.23 (s, OMe).

Thermal Rearrangement of trans-3-*Dimethylamino*-1,4-*diphenylhexa*-1,5-*diene* (25a). *Formation of* 3,6-*Diphenylhex*-5-*enal* (27a).—Portions (25 mg) of the amine (25a) [23] were heated in ampoules (N_2 atmosphere) at 100° for various lengths of time. The kinetics of the reaction (see Table 2) were followed by n.m.r. analysis of the products. The rearrangement product was identified as trans-1-*dimethylamino*-3,6-*diphenylhexa*-1,5-*diene* (26a); τ 2.6—2.9 (m, 10 aromatic H), 3.64 (d, *J* 16 Hz, 6-H), 3.88 (dt, *J* 16, 6 Hz. 5-H), 4.09br (d, *J* 13.5 Hz, 1-H), 5.61 (dd, *J* 8, 13.5 Hz, 2-H), 6.65 br (q, *J* 8 Hz, 3-H), 7.1—7.7 (m, 4-H_2), and 7.47 (s, NMe_2). The combined products in ether (50 ml) were extracted with hydrochloric acid (3 × 50 ml; 10N) and the ethereal layer dried and evaporated. The residue crystallised from hexane to give 3,6-*diphenylhex*-5-*enal* as prisms, m.p. 76° (Found: C, 86.3; H, 7.2. $C_{18}H_{14}O$ requires C, 86.4; H, 7.2%); $\nu_{max.}$ (KBr) 1 705 cm^{-1}; τ 0.30 (t, *J* 2.5 Hz, 1-H), 2.70br (s, 10 aromatic H), 3.58 (d, *J* 18 Hz, 6-H), 3.91 (dt, *J* 18, 6.5 Hz, 2-H), 6.56br (q, *J* 6.5 Hz, 3-*H*), and 7.1—7.6 (m, 4-H_2). The pyrolysis of the amine (25a) (0.25 g) at 105° for 16 h in a sealed tube gave, after hydrolysis, 3,6-diphenylhex-5-enal, m.p. 78° (180 mg, 81%).

Cinnamyl-(3,3-*dimethylallyl*)*dimethylammonium Bromide* (24b).—*NN*-Dimethyl-3,3-dimethylallylamine (2.3 g) in dry ether was added to a solution of cinnamyl bromide (3.9 g) in dry ether (20 ml). After 12 h at room temperature the precipitated salt was removed by filtration and crystallisation from acetone gave *cinnamyl*-(3,3-*dimethyallyl*)*dimethylammonium bromide* (5.1 g, 80%) as plates, m.p. 131—133° (Found: C, 62.3; H, 7.6; N, 4.5; Br, 25.9. $C_{16}H_{24}BrN$ requires C, 62.0; H, 7.8; N, 4.5; Br, 25.8%); τ 2.4—2.8 (m, 5 aromatic H), 2.84 (d, *J* 16 Hz, PhC*H*=CH), 3.67 (dt, *J* 16, 8 Hz, CH=C*H*CH_2), 4.59br (t, *J ca.* 8 Hz, CH_2-C*H*=CMe_2), 5.45 (d, *J* 8 Hz, *CH*$_2$CH), 5.64 (d, *J* 8 Hz, *CH*$_2$CH), 6.73 (s, NMe_2), and 8.13br (s, =CMe_2).

Base Catalysed Rearrangement of Cinnamyl-(3,3-*dimethylallyl*)*dimethylammonium Bromide* (24b). *Formation of* trans-3-*Dimethylamino*-4,4-*dimethyl*-1-*phenylhexa*-1,5-*diene* (25b) *and* trans-4-*Dimethylamino*-1,1-*dimethyl*-6-*phenylhexa*-1,5-*diene*.—Cinnamyl-(3,3-dimethylallyl)dimethylammonium bromide (3.1 g) in dimethyl sulphoxide (10 ml) was added to a solution of sodium hydride (0.3 g) and methanol (5 ml) in dimethyl sulphoxide (10 ml) at room temperature. After 5 h the solution was diluted with water (250 ml) and extracted with ether. The ethereal solution was extracted with hydrochloric acid (10N; 4 × 50 ml), and the acidic extract neutralised (10N aqueous sodium hydroxide). The liberated base was extracted into ether and the extract dried and evaporated giving an oil which was separated into two components by chromatography on silica gel. The first compound eluted was an oil identified as 3-*dimethylamino*-4,4-*dimethyl*-1-*phenylhexa*-1,5-*diene* (55%) (Found: *M*, 229.1831. $C_{16}H_{23}N$ requires *M*, 229.1830); τ 2.54—2.87 (m, 5 aromatic H), 3.64 (dd, *J* 15.5, 1.5 Hz, 1-H), *ca.* 3.8 (dd, *J* 15.5, 8 Hz, 2-H), 3.96 (dd, *J* 10, 17.5 Hz, 5-H), 5.01 (dd, *J* 10, 2 Hz, 6-H), 5.02 (dd, *J* 17.5, 2 Hz, 6-H), 7.33br (d, *J ca.* 8 Hz, 3-H), 7.76 (s, NMe_2), 8.88 (s, C*Me*), and 9.01 (s, C*Me*). The *picrate* crystallised from ethanol as yellow plates, m.p. 168—170° (Found: C, 57.3; H, 5.8; N, 12.1. $C_{22}H_{26}N_4O_7$ requires C, 57.6; H, 5.7; N, 12.2%).

The second component was obtained as an oil (45%) identified as 4-*dimethylamino*-1,1-*dimethyl*-6-*phenylhexa*-1,5-*diene* (Found: *M*, 229.1833. $C_{16}H_{23}N$ requires *M*, 229.1830); τ 2.61—2.98 (5 aromatic H), 3.63 (d, *J* 16.5 Hz, 6-H), 3.98 (dd, *J* 16.5, 8 Hz, 5-H), 4.93br (t, *J ca.* 7 Hz, 2-H), 7.20 (dt, *J* 5, 8 Hz, 4-H), 7.6—7.9 (m, 3-CH_2), 7.83 (s, NMe_2), 8.41 (s, CMe), and 8.54 (s, CMe). The *picrate* crystallised from ethanol as yellow plates, m.p. 173—175° (Found: C, 57.4; H, 5.9; N, 12.2. $C_{22}H_{26}N_4O_7$ requires C, 57.6; H, 5.7; N, 12.2%).

Thermal Rearrangement of trans-3-*Dimethylamino*-4,4-*dimethyl*-1-*phenylhexa*-1,5-*diene* (25b). *Formation of* 6,6-*Dimethyl*-3-*phenylhex*-5-*enal* (27b).—Portions (25 mg) of 3-dimethylamino-4,4-dimethyl-1-phenylhexa-1,5-diene were heated in ampoules (N_2 atmosphere) at 100° for various lengths of time. The kinetics of the reaction (see Table 2) were followed by n.m.r. analysis of the products. The reaction product was identified as trans-1-*dimethylamino*-6,6-*dimethyl*-3-*phenylhexa*-1,5-*diene* (26b) by its n.m.r. spectrum, τ 2.6—3.9 (m, 5 aromatic H), 3.15 (dd, *J* 13.5, 1 Hz, 1-H), 4.94 (t of septets, *J* 7.5, 1.5 Hz, 5-H), 5.66 (dd, *J* 13.5, 8 Hz, 2-H), 6.83br (q, *J* 7.5 Hz, 3-H), 7.49 (s, NMe_2), 8.37br (s, 6-Me), and 8.48br (s, 6-Me). The combined products in ether (50 ml) were extracted with hydrochloric acid (3 × 25 ml; 10N), and the ethereal solution dried and evaporated giving 6,6-*dimethyl*-3-*phenylhex*-5-*enal* as an oil (Found: *M*, 202.1352. $C_{14}H_{18}O$ requires *M*, 202.1357); $\nu_{max.}$ (liquid film) 1 680 cm^{-1}.

Allylcinnamyldimethylammonium Bromide (24c).—*NN*-Dimethylcinnamylamine (16.1 g) in dry ether (50 ml) was added dropwise to a solution of allyl bromide (14.0 g) in dry ether (150 ml) and the mixture was heated under reflux. After 15 h the precipitate was collected giving *allylcinnamyldimethylammonium bromide* (24c) (20.3 g, 72%) as a hygroscopic solid; τ (D_2O) 2.22—2.58 (m, 5 aromatic H), 2.98 (d, *J* 17 Hz, CH=C*H*Ph), 3.61 (dt, *J* 17, 8 Hz, PhCH=C*H*-CH_2), 3.9—4.3 (m, CH=CH_2), 5.78—6.27 (m, *CH*$_2$CH=CH_2 and CH_2CH=CHPh), and 6.91 (s, $\overset{+}{N}Me_2$).

Base Catalysed Rearrangement of Allylcinnamyldimethylammonium Bromide (24c). *Formation of* trans-3-*Dimethylamino*-1-*phenylhexa*-1,5-*diene* (25c).—A solution of allylcinnamyldimethylammonium bromide (20 g) in dimethyl sulphoxide (100 ml) was added to a solution of sodium hydride (4.25 g) and methanol (20 ml) in dimethyl sulphoxide (50 ml). After 8 h the solution was diluted with water (500 ml) and extracted with ether. The ethereal extract was extracted with hydrochloric acid (3 × 100 ml, 2N), and the combined acidic extracts neutralised (10N-NaOH) and extracted into ether. Evaporation of this extract gave trans-3-*dimethylamino*-1-*phenylhexa*-1,5-*diene* (25c) (10 g, 70%), as an oil; τ 2.53—2.82 (m, 5 aromatic H), 3.54 (d, *J* 16 Hz, 1-H) an oil; τ 2.53—2.82 (m, 5 aromatic H), 3.54 (d, *J* 16 Hz, 1-H), 3.87 (dd, *J* 16, 8 Hz, 2-H), 4.18 (ddt, *J* 7, 10, 17 Hz, 5-H), 4.94br (d, *J* 17 Hz, 6-H), 4.97br (d, *J* 10 Hz, 6-H), 7.03 (dt, *J* 8, 5.5 Hz, 3-H), 7.41—7.81 (m, 4-CH_2), and 7.73 (s,

NMe_2). The *picrate* crystallised from ethanol as fine yellow needles, m.p. 130° (Found: C, 55.9; H, 5.2; N, 12.7. $C_{20}H_{22}N_4O_7$ requires C, 55.8; H, 5.1; N, 13.0%).

Thermal Rearrangement of trans-3-*Dimethylamino*-1-*phenylhexa*-1,5-*diene* (25c). *Formation of* 3-*Phenylhex*-5-*enal* (27c).—Portions (25 mg) of 3-dimethylamino-1-phenylhexa-1,5-diene were heated in sealed ampoules (under N_2) at 170° for various lengths of time, and the kinetics of the reaction (see Table 2) followed by n.m.r. analysis of the products [NMe_2 signals of (25c) and (26c)]. The product mixtures were combined, dissolved in ether (50 ml), and extracted with hydrochloric acid (2 × 50 ml; 10N). The ethereal layer was dried and evaporated to give 3-*phenylhex*-5-*enal* as a pale yellow oil (Found: *M*, 284. $C_{12}H_{14}O$ requires *M*, 284) characterised as the 2,4-*dinitrophenylhydrazone*, m.p. 154—158° (Found: C, 58.55; H, 5.1; N, 15.5. $C_{18}H_{18}N_4O_4,H_2O$, requires C, 58.2; H, 5.4; N, 15.2%).

3-*Methoxy*-4,4-*dimethyl*-1-*phenylhexa*-1,5-*diene* (25d).—Ethereal butyl-lithium (50 ml; 2 mol. equiv.) was added to a stirred solution of cinnamyl 3,3-dimethylallyl ether (5.0 g) and *NNN'N'*-tetramethylethylenediamine (12.0 g, 3 mol. equiv.) in dry ether at —76° (N_2 atmosphere). After 2 h water (200 ml) was added to the blue solution and the product extracted into ether. The ethereal solution was dried and evaporated and the residue purified by column chromatography (silica; benzene) to give 4,4-*dimethyl*-1-*phenylhexa*-1,5-*dien*-3-*ol* as an oil (Found: *M*, 202.1355. $C_{14}H_{18}O$ requires *M*, 202.1357); $\nu_{max.}$ (liquid film) 3 430 cm^{-1}; τ 2.53—2.87 (m, 5 aromatic H), 3.44 (d, *J* 16 Hz, 1-H), 3.78 (dd, *J* 16, 6.5 Hz, 2-H), 4.07 (m, 5-H), 4.89 (dd, *J* 1.5, 10 Hz, 6-H), 4.92 (dd, *J* 1.5, 17 Hz, 6-H), 6.05 (d, *J* 6.5 Hz, 3 H), 7.85br (s, OH), and 8.91 (s, CMe_2). The *methyl ether* was prepared (58% yield) by treating the alcohol (0.8 g) with methyl iodide (2.5 g) and sodium hydride (0.5 g) in dimethylformamide (25 ml) at room temperature for 24 h. The product was purified by t.l.c. (benzene) as an oil (Found: C, 83.0; H, 9.3. $C_{15}H_{20}O$ requires C, 83.3; H, 9.3%); τ 2.5—2.8 (m, 5 aromatic H), 3.45 (d, *J* 16 Hz, 1-H), 3.89 (dd, *J* 16, 8 Hz, 2-H), 3.97 (dd *J* 17 10 Hz, 5-H), 4.93 (dd, *J* 10, 1.5 Hz, 6-H), 4.95 (dd, *J* 17, 1.5 Hz, 6-H), 6.59 (d, *J* 8 Hz, 3-H), 6.65 (s, OMe), 8.87 (s, 4-Me), and 8.91 (s, 4-Me). The rearrangement of this methyl ether at 196° was followed by n.m.r. spectroscopy (see Table 2); the appearance of 6,6-dimethyl-1-methoxy-3-phenylhexa-1,5-diene was monitored by the appearance of the 6-Me signals of the product and the disappearance of the 4-Me signals of the reactant.

Rearrangement of trans-3-*Ethylthio*-1,4-*diphenylhexa*-1,5-*diene* (25e). *Formation of* trans-1-*Ethylthio*-3,6-*diphenylhexa*-1,5-*diene* (26e).—The pure crystalline diastereoisomer [62] of 3-ethylthio-1,4-diphenylhexa-1,5-diene, m.p. 90—92°, was heated at 170° in portions (25 mg) sealed in ampoules (N_2 atmosphere), and the contents analysed by n.m.r. spectroscopy after various time intervals (see Table 2). Column chromatography of the rearrangement products gave trans-1-*ethylthio*-3,6-*diphenylhexa*-1,5-*diene* as a pale yellow oil (Found: *M*, 294.1439; $C_{20}H_{22}S$ requires *M*, 294.1441); τ 2.6—2.9 (m, 10 aromatic H), 3.63 (d, *J* 16 Hz, 6-H), 3.81 (dt, *J* 16, 6.5 Hz, 5-H), 4.04 (d, *J* 15 Hz, 1-H), 4.18 (dd, *J* 15, 6 Hz, 2-H), 6.53 (q, *J ca.* 7 Hz, 3-H), 7.35 (q, *J* 6. 5 Hz, 4-H_2), 7.36 (q, *J* 7.5 Hz, CH_2CH_3), and 8.87 (t, *J* 7.5 Hz, CH_2CH_3).

Cinnamyl 3,3-*Dimethylallyl Ether* (28).—3,3-Dimethylallyl bromide (20.0 g) in dry tetrahydrofuran (50 ml) was slowly added with stirring to a mixture of sodium hydride (3.0 g) and cinnamyl alcohol (13.4 g) in dry tetrahydrofuran (50 ml). After 24 h the mixture was filtered, the filtrate poured into water (250 ml), and the product extracted into ether. The ethereal solution was dried and evaporated and the residual oil distilled to give *cinnamyl* 3,3-*dimethylallyl ether* (12.3 g, 61%) as an oil, b.p. 145—150° at 1.5 mmHg (Found: *M*, 202.1356. $C_{14}H_{18}O$ requires *M*, 202.1357); τ 2.53—2.92 (m, 5 aromatic H), 3.45 (d, *J* 16 Hz, PhC*H*=), 3.75 (dt, *J* 16, 5 Hz, =C*H*CH_2), 4.60br (t, *J* 6.5 Hz, =C*H*CH_2), 5.93 (d, *J* 5 Hz, OCH_2), 6.02br (d, *J* 6.5 Hz, OCH_2), 8.29br (s =CMe), and 8.37br (s, =CMe)

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