Base Catalysed Rearrangements involving Ylide Intermediates. Part 18.[1] Competing [1,2], [1,3], and [1,4] Rearrangements of Ammonium Ylides

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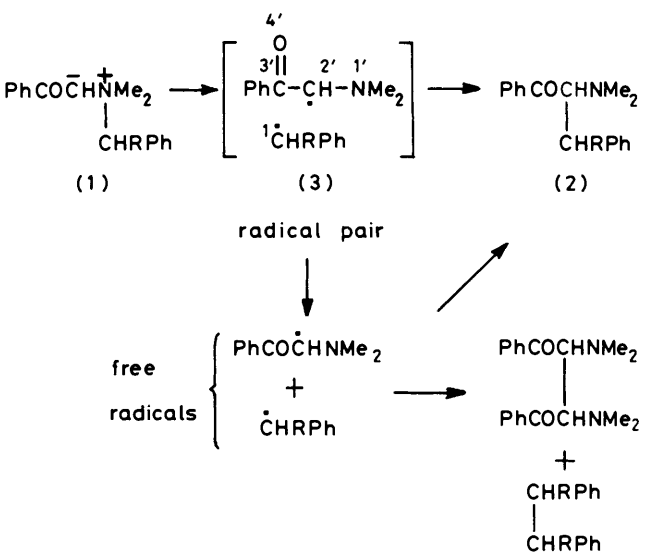
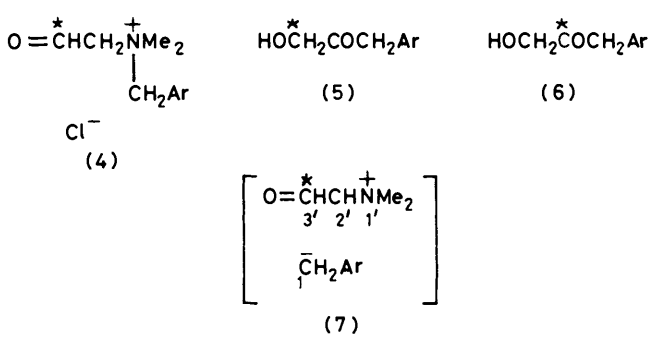
The [1,2] rearrangements of acyl stabilised ammonium ylides are, in several cases, accompanied by competing [1,3] rearrangements and in one case by a [1,4] rearrangement. For examples involving migrating benzyl or phenylethyl groups the mechanism of these rearrangements has been studied. Thus the competing [1,2], [1,3], and [1,4] rearrangements of the ylide (12) are largely intramolecular, but the intermolecularity is as high as 28% for the [1,2] and [1,3] rearrangements and 14% for the [1,4] rearrangement in methanol at 55 °C. The competing [1,2] and [1,3] rearrangements of the optically active ylide (29a) give products with predominant retention of the configuration of the migrating phenylethyl group, but the intramolecular stereoselectivity of the [1,2] rearrangement is significantly greater than that of the [1,3] rearrangement. These results are consistent with a radical pair pathway for all three modes of rearrangement. Suitably substituted acyl stabilised allylammonium ylides (55) rearrange by competing [1,2], [1,3], [3,2], and [3,3] processes.

The [1,2] Stevens rearrangement of acyl-stabilised ammonium ylides (1) ⟶ (2) has been shown [2] to involve an intermediate radical pair (3) on the basis of studies of reaction products, intramolecularity, and stereoselectivity in rearrangements involving a chiral migrating group. This mechanism, summarised in Scheme 1, involved both intramolecular and intermolecular radical coupling to an extent that depends upon reaction conditions, but the rearrangement product (2) from 1,2′-coupling † is virtually the only detectable product of intramolecular radical coupling. In view of the history of the Stevens rearrangement [3] this regioselective radical coupling did not seem to be unusual, but there are reports of cases in which analogous radical pairs couple by modes additional to the 1,2′-mode. For example, the ^{14}C-labelled ammonium salt (4) was reported [4] to undergo a base catalysed rearrangement to give the hydroxyketones (5) and (6). This result was rationalised in the terms of 1,2′- and 1,3′-coupling of an ion-pair intermediate (7) followed by hydrolysis and rearrangement of the products. Although this proposal could be modified to involve a radical pair mechanism in the light of more recent evidence [2,5] concerning the mechanism of ylide rearrangements, it is difficult to account for the isotopic labelling in the product (6) without invoking 1,3′-coupling. Furthermore, it has been shown [6] in earlier papers of this series that 2-oxidoanilinium ylides (8; R = benzyl or allyl) rearrange in a number of cases by a [1,4] sigmatropic rearrangement to give the ethers (9) in addition to the product(s) of other rearrangement modes. This [1,4] rearrangement has been shown [6] to involve a contribution from 1,4′-coupling in a radical pair intermediate and related 1,4′-coupling occurs [7-10] in a number of cases of Stevens [1,2] rearrangements which involve allylic systems. However, the [1,4] rearrangement, although a symmetry allowed process [11] with geometrically reasonable *s,r* geometry, has not been observed generally as a competing process that accompanies the [1,2] rearrangement of acyl-stabilised ammonium ylides (1) ⟶ (2).

It was anticipated that alternative modes of rearrangement of the ylides (1) would become relatively more favourable if 1,2′-coupling of the radical pair (3) were inhibited by substitution at C-2′ of the acyldimethylaminomethyl component. The ammonium salt (10) was therefore prepared [12] by the reaction of 2-dimethylamino-1-phenylpropan-1-one with benzyl bromide. Base catalysed rearrangement of the salt (10)

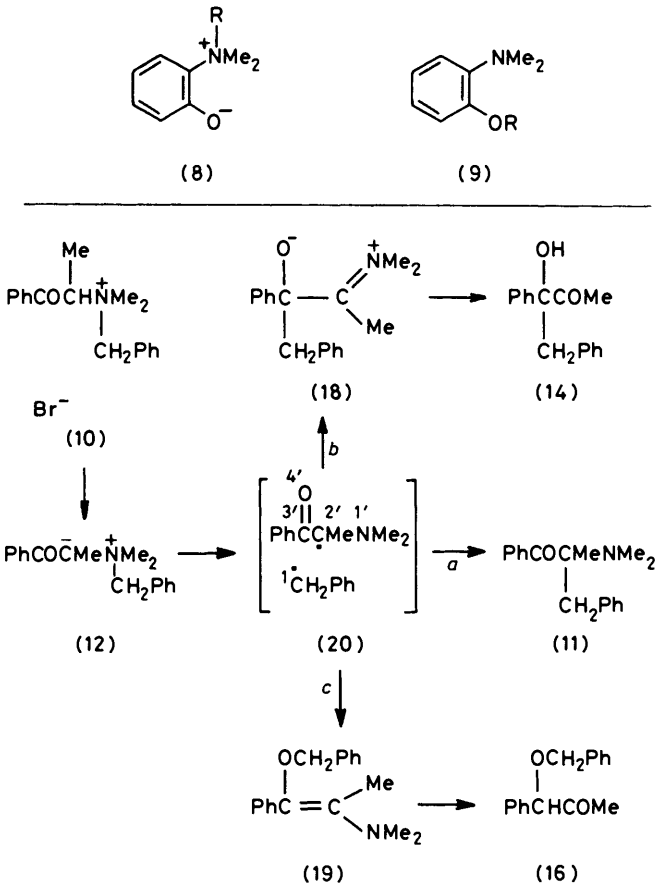


Scheme 1. Radical coupling processes associated with the Stevens [1,2] rearrangement (R = H or Me)



In (4)—(7): Ar = *p*-$C_6H_4NO_2$ and *C represents a ^{14}C labelled carbon atom

† The descriptions 1,2′-coupling *etc.*, are based upon the numbering in the radical pair (3) or analogous radical or ion pairs. In general *m,n*′-coupling gives the product corresponding to a sigmatropic rearrangement of order [*m,n*]. The use in this paper of the description [*m,n*] rearrangement is not intended to have mechanistic implications.



Scheme 2. Base catalysed rearrangement of salt (10)

in aqueous sodium hydroxide at 55 °C gave three reaction products. The major product was basic and it was readily identified (molecular formula, n.m.r., and i.r. spectra, methiodide derivative) as the expected aminoketone (11), formed by [1,2] rearrangement of the ylide (12). This identification was supported by reduction of the aminoketone (11) with zinc and acetic acid to give the ketone (13). Two neutral products were obtained in addition to the aminoketone (11). The first of these, $C_{16}H_{16}O_2$, formed in 6% yield was identified as the hydroxyketone (14) (i.r. and n.m.r. spectra); the position of the carbonyl group was confirmed by reduction with sodium borohydride to give two diastereoisomeric diols (15) which each contained a $CH(OH)CH_3$ grouping (AX_3 system in the n.m.r. spectrum). The second neutral product, $C_{16}H_{16}O_2$, was formed in 2% yield and was identified as the benzyloxyketone (16) ($\nu_{max.}$ 1 720 cm^{-1}; AB system in the n.m.r. spectrum assignable to OCH_AH_BPh); this identification was confirmed by reduction with sodium borohydride to give the two diastereoisomeric alcohols (17) which each contained a $>CHCH(OH)Me$ grouping (ABX_3 system in n.m.r. spectrum). These two neutral products are readily accounted for as hydrolysis products of the betaine (18) and the benzyloxyenamine (19) formed, respectively, by 1,3′- and 1,4′-coupling of the radical pair (20) (Scheme 2, pathways *b* and *c*). The derivation of the hydroxyketone (14) by hydrolysis and rearrangement of the aminoketone (11) was considered unlikely and was ruled out when it was shown that the aminoketone (11) was recovered in quantitative yield after being heated under reflux in aqueous sodium hydroxide (*cf.* ref. 4).

In view of this possible derivation of all three products (11), (14), and (16) by the radical coupling processes *a*, *b*, and *c*

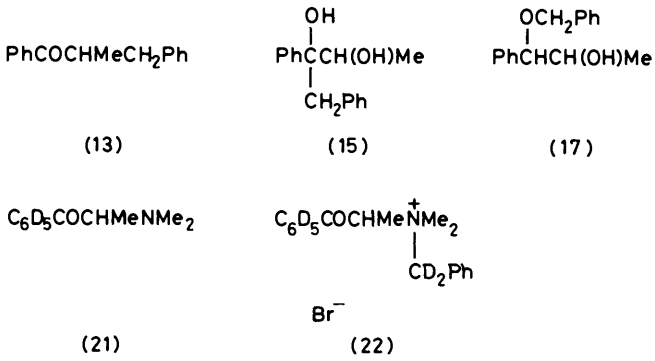


Table 1. Intramolecularity of the [1,2], [1,3], and [1,4] rearrangements of *N*-benzyl-*N*-(1-benzoylethyl)-*N*,*N*-dimethylammonium bromide (10) under various reaction conditions.

Reaction conditions			Intramolecularity (%) [a] (±2)		
Solvent	Base	Temp. (°C)	[1,2] [b]	[1,3] [b]	[1,4] [b]
H_2O	NaOH	55	97	96	99
H_2O	NaOH	95	88	88	96
MeOH	NaOMe	55	72	72	86

[a] $4z$% Intermolecularity gives z%[$^2H_2$], z%[$^2H_5$], $(50 - z)$%[$^2H_0$], and $(50 - z)$%[$^2H_7$] products. Intramolecularity = $(100 - 4z)$%. [b] The [1,2] rearrangement leads to product (11), the [1,3] rearrangement to product (14), and the [1,4] rearrangement to product (16) (Scheme 2).

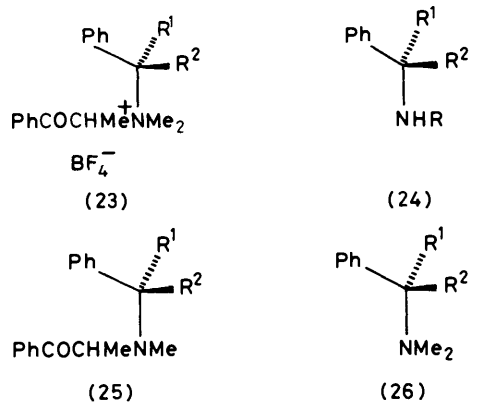
shown in Scheme 2, it was of interest to examine the relative intermolecularities of these three processes since they apparently involve different coupling modes of a single radical pair. The [$^2H_5$]amine (21) was prepared from anhydrous dimethylamine and 2-bromo-1-[$^2H_5$]phenylpropan-1-one; reaction of the [$^2H_5$]amine (21) with [$\alpha\alpha$-$^2H_2$]benzyl bromide gave the [$^2H_7$]salt (22). The base catalysed rearrangement of a 1 : 1 mixture of the [$^2H_0$]salt (10) and the [$^2H_7$]salt (22) gave the rearrangement products (11), (14), and (16) which were examined for their isotopic composition ([$^2H_0$], [$^2H_2$], [$^2H_5$], and [$^2H_7$]) by mass spectrometry. This information was used to provide quantitative information on the percentage intramolecularity and intermolecularity for the formation of each product from the ylide (12) using the following relationships [2]:

$$\% \text{ Intermolecularity} = 2 \times (\% \text{ crossover products, } [^2H_2] + [^2H_5])$$

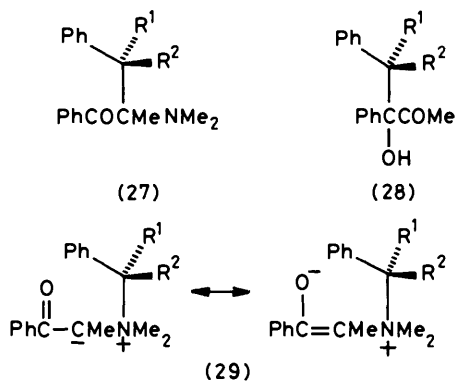
$$\% \text{ Intramolecularity} = 100 - \% \text{ Intermolecularity}$$

The results of this investigation are summarised in Table 1. As expected, and as found in our earlier investigation [2] of the Stevens [1,2] rearrangement, the intermolecularities of all three modes of coupling are increased by higher reaction temperatures or by changing the solvent from water to methanol. This is typical behaviour for radical coupling processes and provides evidence that all three products arise from the radical pair (20). However, the 1,2′- and 1,3′-coupling modes are significantly less intramolecular than the 1,4′-coupling mode. The reason for this difference is not clear, but we note that 1,4′-coupling would be allowed as a concerted,*

* For a discussion of the term 'concerted' see Part 1 (ref. 13) and ref. 14.



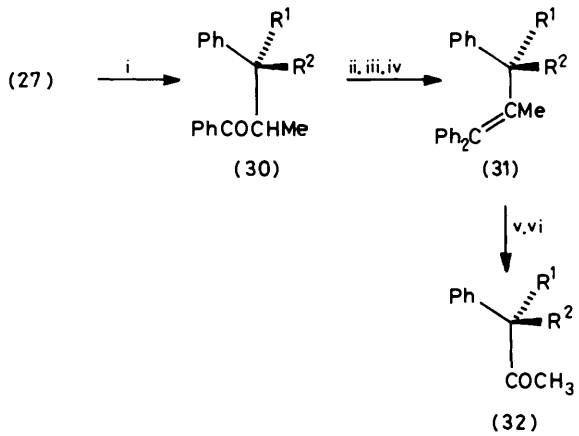
In (23)—(26): a, R^1 = H, R^2 = Me; b, R^1 = Me, R^2 = H



In (27)—(29): a, R^1 = H, R^2 = Me; b, R^1 = Me, R^2 = H

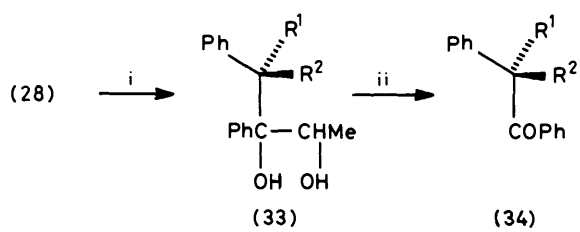
pericyclic (and therefore intramolecular) process; unfortunately the low yield of the product (16) (Table 8) precludes a more thorough examination of the intramolecularity of the [1,4] rearrangement (12) ⟶ (19).

The loss of the stereochemical configuration of a chiral migrating group was applied successfully as a second probe for a radical coupling mechanism in our investigation of the Stevens [1,2] rearrangement.[2] The application of this method to the competing [1,2], [1,3], and [1,4] rearrangements of the ylide (12) required the synthesis of an optically active quaternary salt with a chiral centre at the migrating carbon substituent. The salt (23a),* having an (*R*)-phenylethyl substituent was selected for this study. (*R*)-1-Phenylethylamine (24a; R = H) was formylated (formic acid–acetic anhydride) and the formamide (24a; R = CHO) was reduced with lithium aluminium hydride to give the *N*-methylamine (24a; R = Me). Alkylation of the (*R*)-amine (24a; R = Me) with 2-bromo-1-phenylpropan-1-one gave the tertiary amine (25a) as a mixture of diastereoisomers, both having the (*R*)-configuration at C-1 of the phenylethyl substituent. The mixture of diastereoisomeric quaternary salts (23a), obtained by methylating the tertiary amine (25a) with trimethyloxonium fluoroborate, crystallised from ethanol to give a single diastereoisomer, m.p. 146—147 °C, $[\alpha]_D$ +108°. The enantiomeric excess of this salt (23a), at C-1 of the phenylethyl group, was checked by reduction with



In (30)—(32): a, R^1 = H, R^2 = Me; b, R^1 = Me, R^2 = H

Scheme 3. Determination of absolute configuration and the enantiomeric excess of the rearrangement product (27). *Reagents*: i, Zn/CH_3CO_2H; ii, PhMgBr; iii, $SOCl_2$, C_5H_5N; iv, HCl ;v, O_3; vi, H_2/Pd–$CaCO_3$



In (33) and (34): a, R^1 = H, R^2 = Me; b, R^1 = Me, R^2 = H

Scheme 4. Determination of absolute configuration and optical purity of the rearrangement product (28). *Reagents*: i, $NaBH_4/EtOH$; ii, $NaIO_4/EtOH$–H_2O

zinc and acetic acid which gave the (*R*)-(+)-amine (26a), $[\alpha]_D$ +68° (100% e.e.) on the basis of our earlier work.[2] The (*R*,*S*)-ammonium salt (23) was prepared by a similar procedure from the (*R*,*S*)-amine (24; R = Me).

Base catalysed rearrangement of the (*R*,*S*)-salt (23) gave the aminoketone (27), derivable by [1,2] rearrangement of the ylide (29) and the hydroxyketone (28), derivable by [1,3] rearrangement, but unfortunately a further product from [1,4] rearrangement of (29) could not be detected in the reaction products. The enantiomeric excesses of the products (27) and (28), derived by base catalysed rearrangement of the optically active salt (23a) (100% e.e.) were established by the degradation sequences outlined in Schemes 3 and 4. The aminoketone (27) was reduced (zinc–acetic acid) to the ketone (30) which was converted by a modified Barbier–Wieland degradation into the olefin (31) and 3-phenylbutan-2-one (32). The absolute configuration and specific rotation of the ketone (32) have been established [15] {$[\alpha]_D$ +368° (c 2.96 in benzene) for the (*S*)-ketone} and racemisation is unlikely during the degradation procedure outlined in Scheme 3. The optical rotations of the ketone (32) obtained from the product (27) of the rearrangement (23a) ⟶ (27), conducted under a variety of conditions, are recorded in Table 6. The results establish that the [1,2] rearrangement product has the configuration shown in (27a) and that it is formed with the stereoselectivity summarised in Table 2. The good correlation between the optical rotations of the ketone (32) and the olefin (31) (Table 6) confirms that racemisation does not occur during the ozonolysis and reduction steps (31) ⟶ (32). The hydroxyketone

* Throughout this paper formulae analogous to (23) will be used for (*R*,*S*)-, (*R*)- and (*S*)-isomers of chiral compounds. The use of the unqualified description (23), *etc.*, will refer to the (*R*,*S*)-compounds and (23a), *etc.*, will refer to an excess of the enantiomer indicated by the substituents R^1 and R^2.

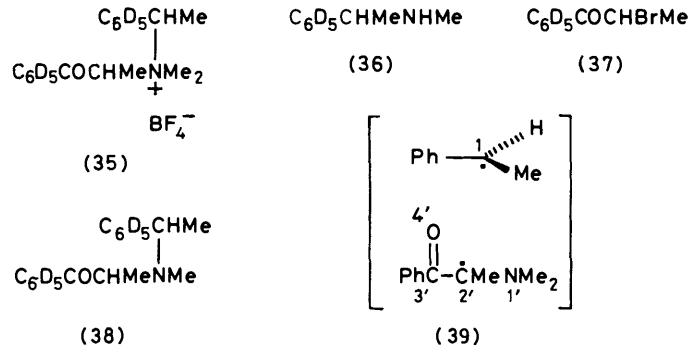


Table 2. Stereoselectivity and intramolecularity of [1,2] and [1,3] rearrangements of (+)-*N*,*N*-dimethyl-*N*-[(*R*)-1-phenylethyl]-*N*-(1-benzoyl ethyl)ammonium tetrafluoroborate (23a) under various reaction conditions

Reaction conditions				[1,2] Rearrangement			[1,3] Rearrangement		
Solvent	Base	Temp. (°C)	Solvent viscosity (cP)	Stereoselectivity [a] (±2%)	Intramolecularity [b] (%)	Intramolecular stereoselectivity [d] (%)	Stereoselectivity [a] (±2%)	Intramolecularity [b] (%)	Intramolecular stereoselectivity [d] (%)
H_2O	NaOH	55	0.5	85	— [c]	— [c]	55	— [c]	— [c]
H_2O–MeOH	NaOMe	55	0.8	68	84	81	47	83	57
MeOH	NaOMe	40	0.5	48	63	76	38	67	57
MeOH	NaOMe	60	0.3	42	59	71	37	66	56

[a] Stereoselectivity based upon specific rotations of products (32a) and (34a) and literature values of absolute rotations given in Table 6. [b] For a 1 : 1 mixture of the [$^2H_0$]salt (23) and the [$^2H_{10}$]salt (35) for 4z% intermolecularity the isotopic composition of the product is [$^2H_5$] 2z%, [$^2H_0$] (50 − z%), and [$^2H_{10}$] (50 − z%). Intramolecularity = (100 − 4z)%. The isotopic compositions of the products are summarised in Table 7. [c] Due to incomplete solubility of the salts (23) and (35) the intermolecularity could not be determined under these reaction conditions. [d] Intramolecular stereoselectivity = (stereoselectivity)/(intramolecularity) × 100%.

(28) was reduced to the diol (33) which was oxidised by sodium metaperiodate to give α-methyldeoxybenzoin (34). The absolute configuration and specific rotation of the ketone (34) have been established [16] {$[\alpha]_D$ +252° (c 1.4 in ethanol) for the (*S*)-ketone}, and the optical rotations of the ketone (34), obtained from the product (28) of the rearrangement (23a) ⟶ (28), summarised in Table 6 correspond to the stereoselectivities for the rearrangement summarised in Table 2. The possibility of racemisation during the formation of the ketone (34) from the diol (33) was ruled out when it was shown that the optically active ketone (34) did not undergo detectable racemisation in the presence of sodium metaperiodate under the conditions used for the interconversion (33) ⟶ (34).

The intramolecularities of the [1,2] and [1,3] rearrangements of the ylide (29) were examined to determine the extent to which the intramolecular reactions were stereoselective, since the intermolecular components of these rearrangements necessarily result in loss of configuration of the migrating phenylethyl group. The [$^2H_{10}$]salt (35) was prepared by the reaction of *N*-methyl-1-[$^2H_5$]phenylethylamine (36) with 2-bromo-1-[$^2H_5$]phenylpropan-1-one (37) to give the [$^2H_{10}$]-tertiary amine (38) which was methylated with trimethyloxonium tetrafluoroborate to give the salt (35). The base catalysed rearrangement of a 1 : 1 mixture of the [$^2H_0$]salt (23) and the [$^2H_{10}$]salt (35) gave the rearrangement products (27) and (28) which were analysed for their isotopic composition ([$^2H_0$], [$^2H_5$], and [$^2H_{10}$]) by mass spectrometry (Table 7). This information was used to determine the percentage intramolecularity and percentage intermolecularity for the formation of each product from the salts (23) and (35) using [2] the relationships:

% Intermolecularity = 2 × (% crossover products, [$^2H_5$])

% Intramolecularity = 100% − % intermolecularity

The results of this investigation are summarised in Table 2, which also includes the derived stereoselectivities for the intramolecular [1,2] and [1,3] rearrangements under various reaction conditions. The intramolecularities for the [1,2] and the [1,3] rearrangements are evidently similar for each particular set of reaction conditions, but the intramolecular stereoselectivity of the [1,2] rearrangement is significantly greater than that for the [1,3] rearrangement. This is consistent with the limited translational motion required within the radical pair (39) for intramolecular 1,2′-coupling as compared with the greater translational motion, and correspondingly greater opportunity for rotational motion and loss of configuration, required for 1,3′-coupling. It is also of interest to compare the ratios * k_c/k_{r+t} and k_c/k_d with those obtained during our earlier investigation [2] of the related [1,2] rearrangement (1; R = Me) ⟶ (2; R = Me). These ratios are summarised in Table 3. We note that their values are of the same order of magnitude for all three reactions, consistent with our belief that all three processes involve similar radical pair intermediates.

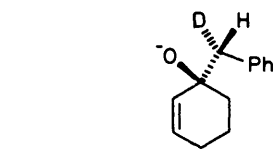
The [1,3] rearrangement (29) ⟶ (28) may formally be regarded as a retro-analogue of an alkoxide accelerated [1,3] rearrangement [see mesomeric forms of the ylide (29)] and it has recently been noted [18] that such a rearrangement [19] might be expected to proceed with an increased tendency for a non-allowed *s*,*r* pathway due to the greater stabilisation of the transition state for a ' forbidden ' reaction as compared with an allowed reaction. The rearrangement (40) ⟶ (41)

* These ratios are calculated as described in our earlier paper; [2] the rate constants k_c, k_d, and k_{r+t} refer to radical pair recombination, diffusion from the radical pair to give free radicals, and rotation and tumbling processes leading to loss of the stereochemical configuration of the radical pair (*cf.* ref. 17).

Table 3. Values of k_c/k_{r+t} and k_c/k_d for [1,2] and [1,3] rearrangements of ylide (29) and [1,2] rearrangement of ylide (1; R = Me) [a]

Reaction conditions				Ylide (29)				Ylide (1; R = Me)	
				[1,2]		[1,3]		[1,2]	
Solvent	Base	Temp. (°C)	Solvent viscosity (cP)	k_c/k_{r+t}	k_c/k_d	k_c/k_{r+t}	k_c/k_d	k_c/k_{r+t}	k_c/k_d
H_2O–MeOH	NaOMe	55	0.8	7.5	2.6	2.7	2.4	—	—
MeOH	NaOMe	40	0.5	6.3	0.96	2.7	1.0	4.7	2.5
MeOH	NaOMe	60	0.3	4.9	0.73	2.5	0.97	—	1.7

[a] Data for ylide (1; R = Me) taken from ref. 2.



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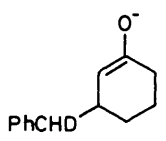

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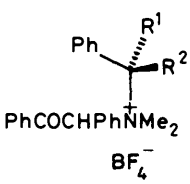

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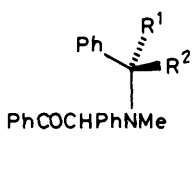

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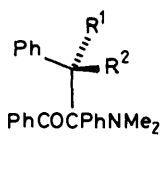

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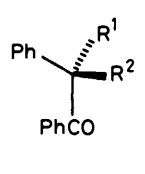

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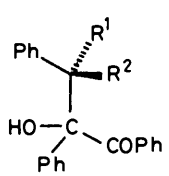

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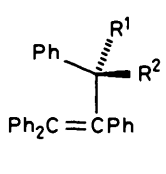

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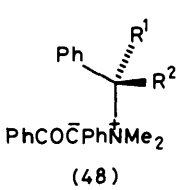


(48)

In (42)—(48): a, R^1 = H, R^2 = Me: b, R^1 = Me, R^2 = H

apparently supports this view,[18] but we note that the observed degrees of intramolecularity and intramolecular stereoselectivity for this reaction (in HMPA at 22 °C) are of the same order as those reported in Table 3. As pointed out by the authors,[18] a fragmentation and recombination mechanism is an alternative explanation for these results.

The overall stereoselectivity of the [1,2] rearrangement (29) ⟶ (27) (Table 2) is comparable with that observed [2] for the [1,2] rearrangement (1; R = Me) ⟶ (2; R = Me) under similar reaction conditions in spite of the expected inhibition of the required radical pair recombination by the methyl substituent at C-2′ in (39). The effect of C-2′ substitution upon stereoselectivity was further investigated by an examination of the [1,2] rearrangement of the ylide derived from the phenyl-substituted salt (42). The (±)-salt (42) was synthesised by methylation of a single diastereoisomer of the tertiary amine (43) with trimethyloxonium tetrafluoroborate. The base catalysed rearrangement of the (±)-salt (42) gave the aminoketone (44) as a 1 : 1 mixture of two diastereoisomers, a small quantity of α-methylbenzyl alcohol and small amounts of two other neutral products tentatively identified as two diastereoisomers of the hydroxyketone (46).

Table 4. Overall stereoselectivity of the [1,2] rearrangement of (+)-*N*,*N*-dimethyl-*N*-[(*R*)-1-phenylethyl]-*N*-(α-phenylphenacyl)-ammonium tetrafluoroborate (42a).

Reaction conditions			Specific rotations of products		Stereoselectivity [a]
Solvent	Base	Temp. (°C)	(47a)	(45a)	(%)
H_2O	NaOH	50	−248	−81.3	32
MeOH	NaOMe	60	−38.5	−12.6	5

[a] Based upon absolute rotation for (*S*)-α-methyldeoxybenzoin (45b), $[\alpha]_D$ +252° (*c* 1.4 in EtOH) (ref. 16).

The aminoketone (44) could be degraded, by a similar sequence of reduction and modified Barbier-Wieland degradation to that used for the aminoketone (27), to give α-methyldeoxybenzoin (45).

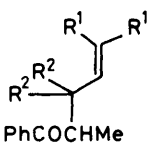
The [1,2] rearrangement of the optically active salt (42a), derived from (*R*)-(+)-*N*-methyl-1-phenylethylamine (24a; R = Me), gave the optically active aminoketone (43). The enantiomeric excess of the salt (42a) {$[\alpha]_D$ +180.5° (*c* 2.4 in $CHCl_3$)} (100% e.e.) was established by reduction (zinc–acetic acid) to give (*R*)-(+)-*N*,*N*-dimethyl-1-phenylethylamine (26a) {$[\alpha]_D$ +68.1° (*c* 2.795 in $CHCl_3$)} (100% e.e.). The enantiomeric excess of the aminoketone (43) was established by degradation to give (*R*)-(−)-α-methyldeoxybenzoin (45a) having the specific rotations recorded in Table 4, which were consistent with the measured specific rotations of the olefin (47a), obtained as an intermediate in the degradation. The overall stereoselectivity for the [1,2] rearrangement (48a) ⟶ (43) could be derived from the measured rotations of the product α-methyldeoxybenzoin and the known specific rotation [16] of (*S*)-(+)-α-methyldeoxybenzoin (45b) {$[\alpha]_D$ +252°} (100% e.e.). The results of this study, using two different sets of conditions for the rearrangement, are summarised in Table 4. The stereoselectivity of the [1,2] rearrangement is very low in methanol and even in water at 50 °C the product (43) is formed with only 32% retention of configuration of the migrating phenylethyl group. This result is a further illustration of the rather variable stereoselectivities of radical pair processes and their dependence upon reaction conditions and substitution pattern.

The recognition of the [1,3] rearrangement of acyl-stabilised ammonium ylides as a process that may accompany the [1,2] rearrangement, particularly when the reaction is carried out in aqueous solvents, suggested that our earlier investigation [13,20,21] of the rearrangement reactions of allylic ammonium ylides should be extended. In particular, it was of interest to determine whether the predominance of [3,2] over [1,2] rearrangement of these allylic systems is accompanied by a similar predominance of [3,3] over [1,3] rearrangement.

Table 5. Products from rearrangements of acyl stabilised allylammonium ylides (55) under various reaction conditions

	Reaction conditions			Reaction products (%)			
Salt (49)	Solvent	Base	Temp. (°C)	[3,2] (50)	[1,2] (51)	[3,3] (52)	[1,3] (53)
(49a)	H_2O	NaOH	55	70 [a]		20 [a]	
(49a)	MeOH	NaOMe	55	62 [a]		12 [a]	
(49a)	DMSO	NaH	55	88 [a]		3 [a]	
(49b)	H_2O	NaOH	0	75.5 [b]	6	9.5 [b]	2.5
(49b)	MeOH	NaOMe	0	82 [b]	10	*c*	*c*
(49b)	MeOH	NaOMe	55	67.5 [b]	22.5	—	3
(49c)	H_2O	NaOH	55	28	55	—	5

[a] In this case (50a) ≡ (51a) and (52a) ≡ (53a). [b] As a mixture of diastereoisomers. [c] <2% Of neutral products obtained under these conditions.

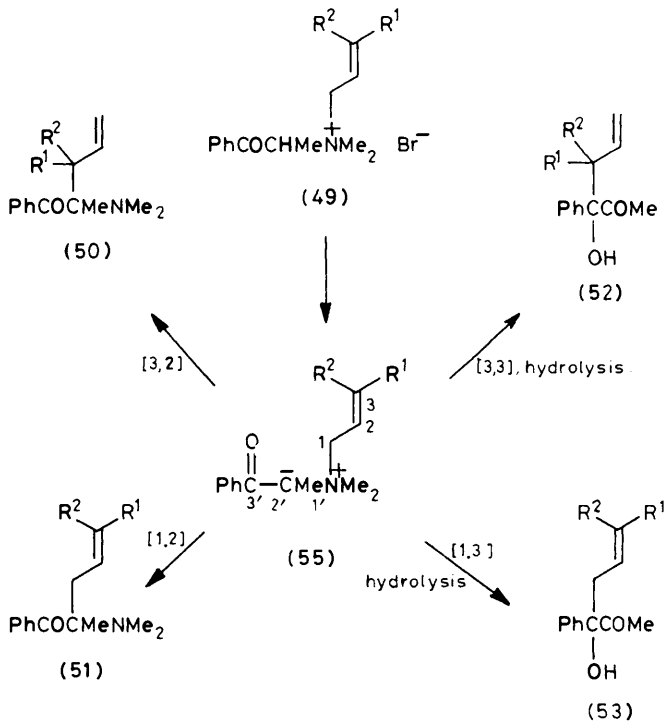


(54)

a, R^1 = Me, R^2 = H
b, R^1 = H R^2 = Me

The quaternary salts (49) were prepared by the reaction of 2-dimethylamino-1-phenylpropan-1-one with the appropriate allyl bromide. Base catalysed rearrangement of the salt (49a), under the conditions summarised in Table 5, gave a basic product, identified as the aminoketone (50a), and a neutral product, identified as the hydroxyketone (52a) in yields that depended upon the reaction conditions. The salt (49b) also gave basic and neutral products. The three basic products were identified (n.m.r. spectroscopy) as the two diastereoisomers of the aminoketone (50b) and the constitutional isomer (51b). The neutral products were separated to give the two diastereoisomers of the hydroxyketone (52b) and the isomeric hydroxyketone (53b). Other neutral products were formed, but they could not be purified sufficiently to permit identification. The base catalysed rearrangement of the salt (49c), using aqueous sodium hydroxide, had been studied in our earlier work [20] and a mixture of the two isomeric aminoketones (50c) and (51c) had been isolated. The structures of these two products were confirmed by reduction (zinc–acetic acid) to give a separable mixture of the ketones (54a) and (54b) which were both fully characterised. A neutral product was also isolated which was identified (molecular formula and spectroscopic properties) as the hydroxyketone (53c). The derivation of these products (50)—(54) by [1,2], [3,2], [1,3], and [3,3] sigmatropic rearrangements of the ylides (55), derived from the salts (49), is summarised in Scheme 5 and the yields of the products under different reaction conditions are summarised in Table 5.

The rearrangements of the ylides (55) (Table 5) show the expected mixture of allowed [3,2] and [3,3] and non-allowed [1,2] and [1,3] rearrangements, although some of these rearrangement modes may be undetectable under certain reaction conditions. We conclude from the work described in this paper and earlier papers in this series that the base catalysed rearrangements of ammonium salts show an interesting variation that depends upon the structure of the salt and the rearrangement conditions. The extension of this work to pentadienylammonium salts and a summary of observed reaction modes will be presented in the next paper in this series.[22]



Scheme 5. In (49)—(53) and (55): a, R^1 = R^2 = H; b, R^1 = Ph, R^2 = H; c, R^1 = R^2 = Me

Experimental

For general directions see Part 1.[13] ^{1}H N.m.r. chemical shifts are given in p.p.m. (δ) relative to tetramethylsilane as an internal reference.

1-[$^2H_5$]*Phenylpropan*-1-*one*.—Propionyl chloride (11.01 g) was added over 15 min to a suspension of anhydrous aluminium chloride (19.80 g) in carbon disulphide (20 ml) pre-treated with 1 drop of D_2O. The suspension was heated under reflux for 5—10 min and a solution of [$^2H_6$]benzene (10.0 g, >99 atom %D) in carbon disulphide (10 ml) was added dropwise with stirring. The mixture was heated under reflux for 6 h, poured into stirred ice–water (150 ml), and the product extracted into dichloromethane. The extract was dried and concentrated and the residue distilled to give 1-[$^2H_5$]phenylpropan-1-one (14.5 g, 88%), b.p. 103 °C at 23 mmHg (Found: C, 77.6; H,* 7.4. $C_9H_5D_5O$ requires C, 77.7; H,* 7.2%); $\nu_{max.}$ (liquid film)

* For this and other deuteriated compounds the value for H refers to the combined D and H content estimated as H.

1 685 cm^{-1}; δ, A_2X_3 system, δ_A 2.96, δ_X 1.19 [J_{AX} 8 Hz, $C(H_A)_2C(H_X)_3$], the spectrum showed no detectable signals for aryl H indicating >99 atom %D in the phenyl group.

2-*Bromo*-1-[$^2H_5$]*phenylpropan*-1-*one*.—Anhydrous aluminium chloride (0.2 g) was added to a cold (0 °C), stirred solution of 1-[$^2H_5$]phenylpropan-1-one (14.40 g) in dry ether (25 ml) followed by bromine (16.60 g) over a period of 15 min. Ether (50 ml) was added and the solution poured into water. The ether layer was washed with water, dried, and concentrated and the residue distilled to give 2-bromo-1-[$^2H_5$]phenylpropan-1-one (20 g, 89%), b.p. 134—138 °C at 12 mmHg; δ, AX_3 system, δ_A 5.32, δ_X 1.88 [J_{AX} 7 Hz, $COCH_ABrC(H_X)_3$]; the spectrum showed no detectable signals for aryl H.

2-*Dimethylamino*-1-[$^2H_5$]*phenylpropan*-1-*one* (21).—A solution of 2-bromo-1-[$^2H_5$]phenylpropan-1-one (15.0 g) in ether (100 ml) was added dropwise to anhydrous dimethylamine (10.0 g) at 0 °C. The solution was stirred at 0 °C for 3 h and at room temperature for 8 h and then poured into water. The ether layer was separated, dried, and concentrated and the residue distilled to give 2-dimethylamino-1-[$^2H_5$]phenylpropan-1-one (21) (10.0 g, 80%), b.p. 90—93 °C at 0.5 mmHg. The n.m.r. spectrum of the product showed no detectable signals for aryl H.

(R,S)- *and* (R)-(+)-N-*Methyl*-1-*phenylethylamine* (24; R = Me).—(*R,S*)-1-Phenylethylamine (72.7 g) was added dropwise to a stirred mixture of formic acid (34.4 ml) and acetic anhydride (81.6 ml) at such a rate that the temperature did not exceed 40 °C. After a further 30 min ether (240 ml) was added and the solution stirred at room temperature overnight. The reaction mixture was diluted with ether and the solution washed with water, aqueous $NaHCO_3$ (saturated), and aqueous HCl (5%), dried and concentrated to give the formyl derivative (24; R = CHO) (75.6 g, 84%) as an oil. A solution of this product (65.4 g) in tetrahydrofuran (200 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (36.0 g) in tetrahydrofuran (300 ml) at a rate sufficient to maintain a gentle reflux. The mixture was heated under reflux for a further 5 h, stirred at room temperature overnight, and excess of hydride destroyed by the addition of water. The ether solution was separated by filtration, dried, and concentrated. The residual oil was distilled to give the (*R,S*)-amine (24; R = Me) (46.8 g, 80%), b.p. 79—80 °C at 16 mmHg (lit.,[23] b.p. 74 °C at 14 mmHg), $\nu_{max.}$ 3 300 cm^{-1}; δ 7.29 (s, 5 aryl H), AX_3 system, δ_A 3.60, δ_X 1.33 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 2.28 (s, NMe), and 1.33 (s, NH). Using a similar procedure (*R*)-(+)-1-phenylethylamine (24a; R = H) (72.7 g) (α_D^{20} +39°, neat; 99% e.e.) gave the (*R*)-(+)-formyl derivative (24a; R = CHO) (72.5 g, 81%) with b.p. 128 °C at 0.07 mmHg; $[\alpha]_D$ +171.5° (*c* 6.07 in $CHCl_3$) and (*R*)-(+)-*N*-methyl-1-phenylethylamine (24a; R = Me) (81%) with b.p. 74—76 °C at 11 mmHg (lit.,[23] b.p. 74 °C at 14 mmHg); $[\alpha]_D$ +78.3° (*c* 2.18 in $CHCl_3$) {lit. $[\alpha]_D^{22}$ +62.7° (*c* 4 in EtOH)[24], α_D^{22} +75.8° (neat)[25], $[\alpha]_D$ +70.8° (*c* 1.92 in $CHCl_3$)[23]}.

(R,S)-N-*Methyl*-1-[$^2H_5$]*phenylethylamine* (26).—A mixture of [$^2H_5$]acetophenone (11.5 g),[2] formic acid (90%, 11.76 g), and methylformamide (16.28 g) was heated in an autoclave for 16 h at 190 °C. The product was distributed between ether and aqueous HCl (10%), the aqueous layer was washed with ether, concentrated to a small volume, made basic (Na_2CO_3), and extracted with ether. The extract was dried and evaporated and the residual oil distilled to give the [$^2H_5$]amine (26) (4.50 g, 35%) as a liquid, b.p. 85—90 °C at 20 mmHg. The n.m.r. spectrum of the product showed no detectable signals for aryl H.

N-*Methyl*-N-[(R,S)-1-*phenylethyl*]-N-(1-*benzoylethyl*)*amine* (25).—2-Bromo-1-phenylpropan-1-one (21.30 g) was added dropwise to a stirred suspension of potassium carbonate (13.80 g) in methyl cyanide (50 ml) containing (*R,S*)-*N*-methyl-1-phenylethylamine (24; R = Me) (13.50 g) at room temperature. The mixture was stirred for 5 h and then poured into water; the ether layer was separated, concentrated, and the residue dissolved in aqueous HCl (200 ml; 10%). The acid solution was washed with ether, made basic (Na_2CO_3), and extracted with ether. The extract was dried and evaporated to give the (*R,S*)-amine (25) (24.50 g, 92%) as a mixture of diastereoisomers *A* and *B* (3 : 2 ratio), b.p. 145—150 °C at 0.02 mmHg (Found: C, 80.6; H, 8.1; N, 5.3. $C_{18}H_{21}NO$ requires C, 80.9; H, 7.9; N, 5.3%); $\nu_{max.}$ 1 680 cm^{-1}; δ diastereoisomer *A*, 8.04 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.60—7.20 (m, 8 aryl H), AX_3 system, δ_A 4.19, δ_X 1.45 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], AX_3 system, δ_A 3.69, δ_X 1.20 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 2.00 (s, NMe); diastereoisomer *B*, δ 7.79 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.60—7.20 (m, 8 aryl H), AX_3 system, δ_A 4.54, δ_X 1.31 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], AX_3 system, δ_X 3.75, δ_A 1.20 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 2.19 (s, NMe_2).

(+)-N-*Methyl*-N-[(R)-1-*phenylethyl*]-N-(1-*benzoylethyl*)-*amine* (25a).—This was prepared in a similar manner from (*R,S*)-2-bromo-1-phenylpropan-1-one (21.30 g) and (*R*)-(+)-*N*-methyl-1-phenylethylamine (24a; R = Me) (13.50 g) as a mixture of diastereoisomers (25a) (24.0 g, 90%), b.p. 140—150 °C at 0.03 mmHg; $[\alpha]_D$ +7.01° (*c* 3.182 in $CHCl_3$).

N-*Methyl*-N-(1-[$^2H_5$]*phenylethyl*)-N-(1-[$^2H_5$]*benzoylethyl*)-*amine* (38).—This was prepared in a similar manner from 2-bromo-1-[$^2H_5$]phenylpropan-1-one (37) (8.56 g) and *N*-methyl-1-[$^2H_5$]phenylethylamine (36) (4.50 g) as a mixture of diastereoisomers (38) (7.50 g, 89%), b.p. 145—152 °C at 0.02 mmHg; the n.m.r. spectrum of the product showed no signals assignable to aryl-H.

N,N-*Dimethyl*-N-[(R,S)-1-*phenylethyl*]-N-(1-*benzoylethyl*)-*ammonium Tetrafluoroborate* (23).—A solution of the (*R,S*)-amine (25) (26.70 g) in nitromethane (40 ml) was added during 15 min to a stirred solution of trimethyloxonium tetrafluoroborate (14.79 g) in nitromethane (60 ml) at room temperature. The solution was kept for 3 h at room temperature, evaporated to dryness, and the residual solid washed with ether and recrystallised from isopropyl alcohol to give the (*R,S*)-salt (23) (17.0 g, 46%) as a single diastereoisomer, m.p. 142—146 °C (Found: C, 61.8; H, 6.8; N, 3.7. $C_{19}H_{24}BF_4NO$ requires C, 61.8; H, 6.5; N, 3.8%); $\nu_{max.}$ 1 692 cm^{-1}; δ (CD_3OD) 7.80—7.20 (m, 10 aryl H), AX_3 system, δ_A 5.20, δ_X 1.88 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], AX_3 system, δ_A 5.00, δ_X 1.64 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.48 (s, $\overset{+}{N}Me$), and 3.26 (s, $\overset{+}{N}Me$).

(+)-N,N-*Dimethyl*-N-[(R)-1-*phenylethyl*]-N-(1-*benzoylethyl*)*ammonium Tetrafluoroborate* (23a).—This was prepared by a similar method from the (*R*)-amine (25a) (26.70 g) and trimethyloxonium tetrafluoroborate (14.79 g). The product (15.50 g, 42%) was obtained as a single diastereoisomer, m.p. 146—147 °C after crystallisation from ethanol; $[\alpha]_D$ +108.5° (*c* 1.125 in $CHCl_3$); n.m.r. spectrum identical with that of the (±)-salt (23).

N,N-*Dimethyl*-N-(1-[$^2H_5$]*phenylethyl*)-N-(1-[$^2H_5$]*benzoylethyl*)*ammonium Tetrafluoroborate* (35).—This was prepared by a similar method from the [$^2H_{10}$]amine (38) (7.00 g) and trimethyloxonium tetrafluoroborate (3.70 g). The [$^2H_{10}$]salt (35) (4.50 g, 47%) had m.p. 145—147 °C after crystallisation from isopropyl alcohol; the n.m.r. spectrum showed no signals

assignable to aryl H, but was otherwise identical with that of the (±)-salt (23).

Reduction of (+)-N,N-*Dimethyl*-N-[(R)-1-*phenylethyl*]-N-(1-*benzoylethyl*)*ammonium Tetrafluoroborate* (23a): *Formation of* (R)-(+)-N,N-*Dimethyl*-1-*phenylethylamine* (26a).—Zinc dust (1.50 g) was added portionwise during 20 min to a stirred solution of the (+)-salt (23a) (3.69 g, $[\alpha]_D$ +108.5°) in acetic acid (30 ml) at 80—85 °C. The mixture was cooled, aqueous HCl (40 ml; 10%) added, and unchanged zinc removed by filtration. The filtrate was washed with ether, made basic (Na_2CO_3), and extracted with dichloromethane. The extracts were dried and concentrated and the residual oil distilled to give the (*R*)-(+)-amine (26a) (0.95 g, 64%), b.p. 78—90 °C at 12 mmHg; $[\alpha]_D$ +68.0° (*c* 2.8 in $CHCl_3$) [lit.,[2] α_D^{22} +65.8° (neat)] (100% e.e.); n.m.r. spectrum identical with that of an authentic sample.

Base Catalysed Rearrangement of (R,S)-N,N-*Dimethyl*-N-(1-*phenylethyl*)-N-(1-*benzoylethyl*)*ammonium Tetrafluoroborate* (23): *Formation of* 2-*Dimethylamino*-2-*methyl*-1,3-*diphenylbutan*-1-*one* (*Diastereoisomers* A *and* B) (27) *and* 3-*Hydroxy*-3,4-*diphenylpentan*-2-*one* (*Diastereoisomers* A *and* B) (28).—Warm (55 °C) aqueous sodium hydroxide (10 ml; 10%) was added to a stirred solution of the (*R,S*)-salt (23) (8.30 g) in methanol (50 ml) at 55 °C and the temperature of the reaction mixture was maintained at 55° C (±2 °C) for a further 30 min. The mixture was cooled, diluted with ether (300 ml), and washed with water. The ether layer was concentrated and the residual viscous oil partitioned between aqueous HCl (100 ml; 10%) and ether. The aqueous layer was made basic (Na_2CO_3) and extracted with ether to give 2-*dimethylamino*-2-*methyl*-1,3-*diphenylbutan*-1-*one* (27) (4.90 g, 77%) as a mixture of diastereoisomers *A* and *B* (5 : 6 ratio), b.p. 145—150 °C at 0.01 mmHg (Found: C, 80.9; H, 8.4; N, 5.0. $C_{19}H_{23}NO$ requires C, 81.1; H, 8.2; N, 5.0%); $\nu_{max.}$ 1 678 cm^{-1}; diastereoisomer *A*: δ 7.40—7.00 (m, 10 aryl H), AX_3 system, δ_A 3.74, δ_X 1.34 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 2.44 (s, NMe_2), and 1.29 (s, CMe); diastereoisomer *B*: δ 8.34 (dd, *J* 8, 2 Hz, 2′-*H* and 6′-*H* of PhCO), 7.50—7.00 (m, 8 aryl H), AX_3 system, δ_A 3.44, δ_X 1.18 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.21 (s, NMe_2), and 1.22 (s, CMe). The ether layer was evaporated to dryness and the residue (1.10 g) separated by t.l.c. (ether–light petroleum, 3 : 10) to give two products.

(a) 3-*Hydroxy*-3,4-*diphenylpentan*-2-*one* (28; diastereoisomer *A*). This was obtained as crystals, m.p. 67—69 °C (200 mg, 3.5%) after crystallisation from light petroleum (Found: C, 80.1; H, 7.2. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%); $\nu_{max.}$ 3 450, 1 705, and 1 600 cm^{-1}; δ 7.52—7.00 (m, 10 aryl H), 4.33br (s, OH), AX_3 system, δ_A 3.89, δ_X 1.27 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 2.24 (s, $COCH_3$).

(b) 3-*Hydroxy*-3,4-*diphenylpentan*-2-*one* (28; diastereoisomer *B*). This was obtained as crystals, m.p. 127—128 °C (600 mg, 10.5%) after crystallisation from light petroleum (Found: C, 80.1; H, 7.1. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%); $\nu_{max.}$ 3 440, 1 710, 1 600, and 1 582 cm^{-1}; δ 7.75—7.17 (m, 10 aryl H, 4.48 (s, OH), AX_3 system, δ_A 3.90, δ_X 1.25 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 1.99 (s, $COCH_3$).

2-*Methyl*-1,3-*diphenylbutan*-1-*one* (30).—A solution of the amine (27) (4.8 g) in acetic acid (30 ml) at 90 °C was treated portionwise with zinc dust (2.2 g) during a period of 15 min. The cooled mixture was diluted with aqueous HCl (30 ml; 10%), unchanged zinc removed by filtration, and the filtrate extracted with ether. The ether solution was washed (water and saturated aqueous $NaHCO_3$), dried, and evaporated. The residual oil was distilled to give 2-*methyl*-1,3-*diphenylbutan*-1-*one* (30) (3.90 g, 96%), b.p. 130—140 °C at 0.05 mmHg (Found: C, 85.8; H, 7.6. $C_{17}H_{18}O$ requires C, 85.6; H, 7.6%); $\nu_{max.}$ 1 680 cm^{-1}; δ 8.10—7.00 (m, 10 aryl H), 3.84—3.49 (m, $CHCHCH_3$), 3.35—3.00 (m, $CHCHCH_3$), 1.18 (d, *J* 7 Hz, $CHCH_3$), and 0.92 (d, *J* 7 Hz, $CHCH_3$).

Degradation of 2-*Methyl*-1,3-*diphenylbutan*-1-*one* (30): *Formation of* 3-*Phenylbutan*-2-*one* (32).—A solution of the ketone (30) (3.64 g) in ether (15 ml) was added during 20 min to a stirred ethereal solution of phenylmagnesium bromide [prepared from bromobenzene (3.93 g) and magnesium (0.61 g) in ether (25 ml)]. The mixture was heated under reflux for 6 h, hydrolysed by the addition of ice-saturated aqueous NH_4Cl, and the organic layer separated and combined with ether extracts of the aqueous layer. The combined ether solutions were dried and evaporated. The residual oil was dissolved in pyridine (40 ml) and treated with thionyl chloride (10 ml) at 0 °C; the mixture was kept at 0 °C for 1 h and 40 °C for 2 h, poured into aqueous HCl–ice and the product extracted with ether and benzene. The combined extracts were dried and evaporated and the residual oil purified by t.l.c. (light petroleum) to give 2-methyl-1,1,3-triphenylbut-2-ene (31) (3.5 g, 77%), b.p. 160—170 °C at 0.02 mmHg (Found: C, 92.75; H, 7.6. $C_{22}H_{32}$ requires C, 92.6; H, 7.4%); δ 7.40—7.05 (m, 15 aryl H), AX_3 system, δ_A 4.01, δ_X 1.42 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 1.47 (s, C=CMe). Ozonised oxygen was passed through a solution of the hydrocarbon (31) (1.99 g) in ethyl acetate (30 ml) at −20 °C until absorption of ozone was complete. The solution was hydrogenated at −10 °C at atmospheric pressure using a palladium–calcium carbonate catalyst (100 mg, 5%). The catalyst was removed by filtration, the filtrate evaporated, and the residual oil purified by t.l.c. (light petroleum–ether, 100 : 15) to give 3-phenylbutan-2-one contaminated with acetophenone. Further purification by g.l.c. (7% OV17 on 60/80 Chromosorb G.AW.DMCS at 120 °C) gave pure 3-phenylbutan-2-one (32) (450 mg, 45%), b.p. 105 °C at 12 mmHg (lit.,[15] b.p. 102.5—103.5 °C at 15 mmHg); $\nu_{max.}$ 1 712 cm^{-1}; δ 7.38—7.10 (m, 5 aryl H), AX_3 system, δ_A 3.72, δ_X 1.46 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 2.01 (s, $COCH_3$).

Degradation of 3-*Hydroxy*-3,4-*diphenylpentan*-2-*one* (28): *Formation of* α-*Methyldeoxybenzoin* (34).—Sodium borohydride (1.7 g) was added portionwise to a stirred solution of the hydroxyketone (28) (700 mg) in ethanol (25 ml) at room temperature. After 12 h, water (15 ml) was added and the product extracted into ether. The extract was dried and evaporated to give the crude diol (33) (710 mg) which was dissolved in ethanol (5 ml) and treated with aqueous sodium metaperiodate (10 ml; 0.54M). The mixture was stirred for 6 h, filtered, and residue washed with ether. The combined filtrate and ether solution were dried and evaporated and the residue purified by t.l.c. (light petroleum–ether, 100 : 10) to give, after distillation, α-methyldeoxybenzoin (34) (400 mg, 69%), b.p. 125—135 °C at 0.05 mmHg (lit.,[26] m.p. 41—44 °C); $\nu_{max.}$ 1 685 cm^{-1}; δ 8.93 (dd, *J* 2, 7.5 Hz, 2-*H* and 6-H of COPh), 7.60—7.10 (m, 8 aryl H), and AX_3 system, δ_A 4.65, δ_X 1.51 [J_{AX} 7 Hz, $CH_AC(H_X)_3$].

Base Catalysed Rearrangement of (+)-N,N-*Dimethyl*-N-[(R)-1-*phenylethyl*]-N-(1-*benzoylethyl*)*ammonium Tetrafluoroborate* (23a): *Stereoselectivity of Product Formation under Various Reaction Conditions.*—(a) *Rearrangement.* The rearrangements were conducted under the conditions summarised in Table 6. In each case a solution of the appropriate base (2 mol equiv.) in the stated solvent (5 ml) was added to a stirred solution of the (*R*)-salt (23a) (5.0 g, $[\alpha]_D$ +108.5°) (100% e.e.) in the same solvent (30 ml). Both solutions were initially adjusted to the stated temperature which was maintained (±2 °C) during the addition and the subsequent

Table 6. Specifiic rotations of products from the rearrangement of (*R*)-(+)-*N*,*N*-dimethyl-*N*-[(*R*)-1-phenylethyl]-*N*-(1-benzoylethyl)ammonium tetrafluoroborate (23a) under various reaction conditions

Conditions			Yield of products (%)						Specific rotations of products ($[\alpha]_D$/°)		
					Degradation products						
Base	Solvent	Temp. °C	[1,2] (27a)	[1,3] (28a)	(30a)	(31a)	(32a)	(34a)	(31a)	(32a)	(34a)
NaOH	H_2O	55	74	18	94 [a]	79 [b]	65	73 [c]	+42 [d]	−313 [e]	−138 [f]
NaOMe	H_2O–MeOH	55	75	18	96	65	68	72	+32	−249	−119
NaOMe	MeOH	40	86	3	92	75	56	78	+27	−178	−96
NaOMe	MeOH	60	85	3	94	69	70	75	+23	−154	−95

[a] B.p. 130—140 °C, 0.05mmHg or 125—135 °C, 0.02 mmHg. [b] B.p. 175—180 °C, 0.05 mmHg or 170—180 °C, 0.02 mmHg. [c] B.p. 125—134 °C, 0.05 mmHg or 125—130 °C, 0.02 mmHg. [d] *c* 2.245 in $CHCl_3$. [e] *c* 0.92, 1.38, or 1.34 in C_6H_6, $[\alpha]_D$ +368° (*c* 2.96 in C_6H_6) for 100% e.e. (*S*)-enantiomer (ref. 15). [f] *c* 3.25, 3.20 in EtOH, $[\alpha]_D$ +252° (*c* 1.4 in EtOH) for 100% e.e. (*S*)-enantiomer (ref. 16).

Table 7. Isotopic compositions of rearrangement products of a 1 : 1 mixture of *N*,*N*-dimethyl-*N*-(1-phenylethyl)-*N*-(1-benzoylethyl)-ammonium tetrafluoroborate (23) and *N*,*N*-dimethyl-*N*-(1-[$^2H_5$]phenylethyl)-*N*-(1-[$^2H_5$]benzoylethyl)ammonium tetrafluoroborate (35) under various reaction conditions

Reaction conditions			Isotopic composition of products (%)						Yields (%)	
			[1,2] [a]			[1,3] [b]				
Base	Solvent	Temp. (°C)	[$^2H_0$]	[$^2H_5$]	[$^2H_{10}$]	[$^2H_0$]	[$^2H_5$]	[$^2H_{10}$]	[1,2]	[1,3]
NaOMe	H_2O–MeOH	55	47	8	45	45	9	46	73	14
NaOMe	MeOH	40	42	19	39	39	16	45	85	2
NaOMe	MeOH	60	40	20	39	40	17	43	86	2

[a] Based upon heights of M^+, $(M + 5)^+$, and $(M + 10)^+$ peaks. [b] Based upon heights of $(M - COCH_3)^+$, $(M + 5 - COCH_3)^+$, and $(M + 10 - COCH_3)^+$ peaks.

reaction period. At the completion of the reaction the mixture was concentrated to half its volume, diluted with ether (150 ml), and washed with water. The organic layer was evaporated and the residue partitioned between aqueous HCl (100 ml; 5%) and ether. The reaction products were isolated as described for the products from the (±)-salt (23) and degraded as summarised below.

(b) *Degradation of* (3R)-2-*dimethylamino*-2-*methyl*-1,3-*diphenylbutan*-1-*one* (27a). The mixture of optically active dimethylaminoketones (27a; diastereoisomers *A* and *B*) (3.0 g) was reduced with zinc dust (1.50 g) in acetic acid (30 ml) as for the (±)-ketone (27) to give crude (3*R*)-2-methyl-1,3-diphenylbutan-1-one (30a) (2.4 g, 94%) as an oil. The (*R*)-ketone (30a) (2.4 g) was degraded by the Barbier-Wieland procedure as described for the (±)-ketone (30) to give (*R*)-(−)-3-phenylbutan-2-one (32a) after purification by g.l.c. The yields, b.p.s, and specific rotations of this product are given in Table 6.

(c) *Degradation of* (4R)-3-*hydroxy*-3,4-*diphenylpentan*-2-*one* (28a). A mixture of the optically active ketones (28a; diastereoisomers A and B) (100 mg) was reduced with sodium borohydride and the resulting diol oxidised with sodium metaperiodate to give (*R*)-(−)-α-methyldeoxybenzoin (34a) after purification by t.l.c. The yields, b.p.s, and optical rotations of this product are recorded in Table 6.

Base Catalysed Rearrangement of N,N-*Dimethyl*-N-(1-*phenylethyl*)-N-(1-*benzoylethyl*)*ammonium Tetrafluoroborate* (23): *Determination of Intramolecularity under Various Reaction Conditions*.—(a) *Rearrangement*. The rearrangements were conducted under the conditions summarised in Table 7. In each case a solution of the appropriate base (2 mol equiv.) in the stated solvent (3 ml) was added to a stirred solution of a 1 : 1 mixture (1.97 g) of the [$^2H_0$]salt (23) and the [$^2H_{10}$]salt (35) in the same solvent (30 ml). Both solutions were initially adjusted to the stated temperature which was maintained (±2 °C) during the addition and the subsequent reaction period. Products were isolated as for the products from the (*R*,*S*)-salt (23) and the (*R*)-salt (23a) and their isotopic compositions examined as described below.

(b) *Isotopic compositions of rearrangement products*. The dimethylaminoketone (27) was reduced (zinc–acetic acid) to give 2-methyl-1,3-diphenylbutan-1-one (30). The isotopic compositions of both products were determined by mass spectrometry using the peak heights (averaged over several spectra) of the M^+, $(M + 5)^+$, and $(M + 10)^+$ ions. The isotopic composition of the hydroxyketone (28) was determined by mass spectrometry using the peak heights (averaged over several spectra) of the $(M - COCH_3)^+$, $(M + 5 - COCH_3)^+$, and $(M + 10 - COCH_3)^+$ ions since this product did not give a molecular ion. The results of this investigation are summarised in Table 7.

(R,S)-N-*Methyl*-N-(1-*phenylethyl*)-N-(α-*phenylphenacyl*)-*amine* (43).—This was prepared from α-bromodeoxybenzoin (27.5 g), (*R*,*S*)-*N*-methyl-1-phenylethylamine (24; R = Me) (13.50 g), and potassium carbonate (14.0 g) in methyl cyanide (120 ml) at room temperature for 12 h. The product was extracted into ether after concentration of the reaction mixture and the addition of water (100 ml). Purification as a base and crystallisation from ethanol gave the (*R*,*S*)-amine (43) as yellow crystals, m.p. 112—113 °C (Found: C, 83.8; H, 7.2; N, 4.15. $C_{23}H_{23}NO$ requires C, 83.9; H, 7.0; N, 4.25%); $\nu_{max.}$ 1 685 cm^{-1}; δ 7.83 (dd, *J* 2, 8 Hz, 2′-H and 6′-H of COPh), 7.50—7.15 (m, 13 aryl H), 5.42 (s, C*H*Ph), AX_3 system, δ_A 5.96, δ_X 1.35 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 2.26 (s, NMe). The n.m.r. spectrum was consistent with this product being a single diastereoisomer.

(+)-N-*Methyl*-N-[(R)-1-*phenylethyl*]-N-(α-*phenylphenacyl*)-*amine* (43a).—This was prepared in a similar manner from (*R*,*S*)-α-bromodeoxybenzoin (27.5 g) and (*R*)-(+)-*N*-methyl-1-phenylethylamine (24a; R = Me) (13.5 g, $[\alpha]_D$ +78.3°) as

yellow crystals (15.0 g, 46%), m.p. 112—113 °C; $[\alpha]_D$ +188.6° (*c* 3.17 in $CHCl_3$).

(±)-N,N-*Dimethyl*-N-(1-*phenylethyl*)-N-(α-*phenylphenacyl*)*ammonium Tetrafluoroborate* (42).—This was prepared from the (±)-amine (43) (6.58 g) and trimethyloxonium tetrafluoroborate (2.96 g) in nitromethane (130 ml) at room temperature for 6 h. The product crystallised from ethanol to give the (±)-salt (42) (5.0 g, 58%), m.p. 175—176 °C (Found: C, 67.1; H, 6.2; N, 3.0. $C_{24}H_{26}BF_4NO$ requires C, 66.8; H, 6.1; N, 32.5%); $\nu_{max.}$ 1 680 cm^{-1}; δ ($CDCl_3$ + CD_3OD) 8.10 (dd, *J* 2, 8 Hz), 7.84—7.32 (m, 13 aryl H), 6.73 (s, C*H*Ph), AX_3 system, δ_A 5.33, δ_X 1.89 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.14 (s, $\overset{+}{N}Me$), and 2.95 (s, $\overset{+}{N}Me$).

(+)-N,N-*Dimethyl*-N-[(R)-1-*phenylethyl*]-N-(α-*phenylphenacyl*)*ammonium Tetrafluoroborate* (42a).—This was prepared by a similar method from the (*R*)-(+)-amine (43a) (6.58 g, $[\alpha]_D$ +188.6°) and trimethyloxonium tetrafluoroborate (2.96 g). The product was obtained as crystals (4.80 g, 56%), m.p. 175—176 °C after crystallisation from ethanol; $[\alpha]_D$ +180.5° (*c* 2.4 in $CHCl_3$). Reduction of this salt (zinc–acetic acid) gave (*R*)-(+)-*N*,*N*-dimethyl-1-phenylethylamine (26a) b.p. 75—95 °C at 12 mmHg; $[\alpha]_D$ +68.1° (*c* 2.795 in $CHCl_3$) (100% e.e.); n.m.r. spectrum identical with that of an authentic sample.

Base Catalysed Rearrangement of (±)-N,N-*Dimethyl*-N-(1-*phenylethyl*)-N-(α-*phenylphenacyl*)*ammonium Tetrafluoroborate* (42): *Formation of* 2-*Dimethylamino*-1,2,3-*triphenylbutan*-1-*one* (*Diastereoisomers* A *and* B) (44).—Warm (60 °C) methanolic sodium methoxide (10 ml; 10%) was added to a stirred solution of the (±)-salt (42) (4.31 g) in methanol (150 ml) at 60 °C. After a further 30 min at 60 °C (±2 °C) the solution was cooled, concentrated to half its volume, and diluted with ether (200 ml). The ether layer was evaporated and the residue partitioned between ether and aqueous HCl (30 ml; 10%). The aqueous layer was made basic (Na_2CO_3) and extracted with ether; evaporation of the ether gave the aminoketone (44) (3.0 g, 87%) which consisted of a 1 : 1 mixture of diastereoisomers which could be separated by t.l.c. (light petroleum–ether, 100 : 20). *Diastereoisomer* A was obtained as yellow crystals, m.p. 99—101 °C after crystallisation from light petroleum (Found: *m*/*z* 238. $C_{24}H_{25}NO - C_6H_5CO$ requires *m*/*z* 238); $\nu_{max.}$ 1 645 cm^{-1}; δ 7.60 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of PhCO), 7.45—6.55 (m, 13 aryl H), AX_3 system, δ_A 4.22, δ_X 1.11 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 2.32 (s, NMe_2). *Diastereoisomer* B was obtained as yellow crystals, m.p. 75—78 °C after crystallisation from light petroleum (Found: C, 83.9; H, 7.5; N, 3.9. $C_{24}H_{25}NO$ requires C, 83.9; H, 7.7; N, 4.1%); $\nu_{max.}$ 1 645 cm^{-1}; δ 7.50—6.55 (m, 15 aryl H), AX_3 system, δ_A 4.37, δ_X 1.12 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 2.39 (s, NMe_2). Purification of the neutral reaction products (150 mg) by t.l.c. gave α-methylbenzyl alcohol (50 mg), b.p. 120—125 °C at 0.02 mmHg, identical (n.m.r. spectrum) with an authentic sample and two products tentatively identified as two diastereoisomers of 2-hydroxy-1,2,3-triphenylbutan-1-one (46). Diastereoisomer *A* (15 mg) (Found: *m*/*z* 211. $C_{22}H_{20}O_2 - C_6H_5CO$ requires *m*/*z*, 211); δ 8.05—7.10 (m, 15 aryl H), 5.50 (s, OH), and AX_3 system, δ_A 4.46, δ_X 1.49 [J_{AX} 7 Hz, $CH_AC(H_X)_3$]. Diastereoisomer *B* (17 mg) (Found: *m*/*z*, 211. $C_{22}H_{20}O_2 - C_6H_5CO$ requires *m*/*z* 211); δ 7.93 (dd, *J* 7, 2 Hz, 2-H and 6-H of COPh), 5.43 (s, OH), and AX_3 system, δ_A 4.55, δ_X 1.49 [J_{AX} 7 Hz, $CH_AC(H_X)_3$].

Degradation of 2-*Dimethylamino*-1,2,3-*triphenylbutan*-1-*one* (44): *Formation of* α-*Methyldeoxybenzoin*.—Zinc dust (4.0 g) was added portionwise during 15 min to a stirred solution of the aminoketone (44) (1.90 g) in acetic acid (20 ml) at 80—90 °C. The mixture was cooled, diluted with aqueous HCl (10 ml; 5%), and extracted with ether. The extracts were washed (water and saturated aqueous $NaHCO_3$), dried, and evaporated to dryness. The residual solid crystallised from methanol to give 1,2,3-triphenylbutan-1-one (1.20 g, 72%), m.p. 186—188 °C (Found: C, 87.7; H, 6.8. $C_{22}H_{20}O$ requires C, 88.0; H, 6.7%); $\nu_{max.}$ 1 680 cm^{-1}; δ 7.74 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.50—6.98 (m, 13 aryl H), and ABX_3 system, δ_A 4.80, δ_B 3.71, δ_X 1.05 [J_{AB} 11, J_{BX} 7 Hz, $CH_ACH_BC(H_X)_3$]. This ketone (1.80 g) in ether (25 ml) was added to a stirred solution of phenylmagnesium bromide [prepared from bromobenzene (1.96 g) and magnesium (0.31 g) in ether (15 ml)]. The mixture was heated under reflux for 24 h, hydrolysed by the addition of ice–saturated aqueous NH_4Cl, and the organic layer separated, dried, and evaporated. The residual oil was dissolved in pyridine (20 ml) and treated with thionyl chloride (at 0 °C); the mixture was warmed to 40—45 °C and after 3 h cooled, poured into ice–aqueous HCl and extracted with ether and benzene. The extracts were washed (water and saturated aqueous $NaHCO_3$), dried, and evaporated and the residue purified by t.l.c. (light petroleum) to give 1,1,2,3-*tetraphenylbut*-1-*ene* (47) (500 mg, 23%) as a low m.p. solid, b.p. 205—208 °C at 0.02 mmHg (Found: C, 93.3; H, 6.7. $C_{18}H_{24}$ requires C, 93.3; H, 6.7%); δ 7.65—6.50 (m, 20 aryl H), and AX_3 system, δ_A 4.37, δ_X 1.29 [J_{AX} 7 Hz, $CH_AC(H_X)_3$]. The olefin (47) (450 mg) in ethyl acetate (20 ml) was treated with ozone at −5 °C. The reaction products were reduced (H_2 at 1 atm, Pd–$CaCO_3$) and purified by t.l.c. (light petroleum–ether, 100 : 10) to give α-methyldeoxybenzoin (45), b.p. 120—130 °C at 0.05 mmHg (50 mg, 19%), identical (n.m.r. spectrum) with an authentic sample.

Base Catalysed Rearrangement of (+)-N,N-*Dimethyl*-N-[(R)-1-*phenylethyl*]-N-(α-*phenylphenacyl*)*ammonium Tetrafluoroborate* (42a): *Stereoselectivity of Product Formation*.—(a) *Rearrangement*. The rearrangements were conducted using (i) aqueous sodium hydroxide (10%) at 50 °C and (ii) methanolic sodium hydroxide (2M) at 60 °C. In each case the base (2 mol equiv.) was added to a stirred solution of the (*R*)-salt (42a) (3.5 g; $[\alpha]_D$ +180.5°) (100% e.e.) and the reaction allowed to proceed for 12 h and 45 min respectively. The product (43a) was isolated in the usual manner as a mixture of diastereoisomers which were degraded by the Barbier-Wieland procedure to give α-methyldeoxybenzoin (45a) as a liquid, b.p. 120—123 °C.

(b) *Stereoselectivity*. This was based upon the measured specific rotations of the α-methyldeoxybenzoin (45a) {(i) $[\alpha]_D$ −81.33° and (ii) $[\alpha]_D$ −12.6° (*c* 0.635 in EtOH)}, and the olefin (47a) {(i) $[\alpha]_D$ −248.2° and (ii) $[\alpha]_D$ −38.4°} {lit.,[16] for (*S*)-α-methyldeoxybenzoin $[\alpha]_D$ +252°}.

Preparation of Ammonium Salts (49; a—c), (10), *and* (22).—The salts were prepared by the reaction of equimolar quantities of the appropriate bromide and 2-dimethylamino-1-phenylpropan-1-one or 2-dimethylamino-1-[$^2H_5$]phenylpropan-1-one in methyl cyanide at room temperature for 12 h. The crude salts were recrystallised from ethanol–ether.

N-*Allyl*-N-(1-*benzoylethyl*)-N,N-*dimethylammonium bromide* (49a). This (84% yield) had m.p. 150—151 °C (Found: C, 56.1; H, 6.7; Br, 26.8; N, 5.0. $C_{14}H_{20}BrNO$ requires C, 56.4; H, 6.7; Br, 26.85; N, 4.7%); $\nu_{max.}$ 1 685 cm^{-1}; δ 8.32 (dd, *J* 8, 2 Hz, 2′-*H* and 6′-*H* of COPh), 7.70—7.30 (m, 3 aryl H), AX_3 system, δ_A 6.29, δ_X 1.76 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], $AMNX_2$ system, δ_A 6.20, δ_M 5.67, δ_N 5.62, δ_X 4.60 [J_{AM} 18, J_{AN} 10, J_{AX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_A{=}CH_MH_N$], 3.60 (s, $\overset{+}{N}Me$), and 3.53 (s, $\overset{+}{N}Me$).

N-(1-Benzoylethyl)-N-cinnamyl-N,N-dimethylammonium bromide (49b). This (87% yield) had m.p. 149—151 °C (Found: C, 64.0; H, 6.6; Br, 21.5; N, 3.8. $C_{20}H_{24}BrNO$ requires C, 64.2; H, 6.4; Br, 21.4; N, 3.7%); $\nu_{max.}$ 1 690, 1 650 cm^{-1}; δ (CD_3OD) 8.08 (d, *J* 8 Hz, 2′-H and 6′-H of COPh), 7.60—7.10 (m, 8 aryl H), ABX_2 system, δ_A 6.72, δ_B 6.44, δ_X 4.44 [J_{AB} 15, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_A$], AX_3 system, δ_A 5.59, δ_X 1.71 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], and 3.46 (s, NMe_2).

N-(1-Benzoylethyl)-N,N-dimethyl-N-(3,3-dimethylallyl)-ammonium bromide (49c). This (79% yield) had m.p. 131—132 °C (lit.,[20] m.p. 127 °C); δ (CD_3OD) 8.11 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.80—7.45 (m, 3 aryl H), AX_3 system, δ_A 5.60, δ_X 1.69 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], ABXY system, δ_A 5.48, δ_X 4.38, δ_Y 4.07 (J_{AX} 10, J_{AY} 6, J_{XY} 13 Hz, $\overset{+}{N}CH_XH_Y$-CH_A), 3.39 (s, $\overset{+}{N}Me$), 3.34 (s, $\overset{+}{N}Me$), 1.65 (s, $C{=}CMe$), and 1.52 (s, $C{=}CMe$).

N-Benzyl-N-(1-benzoylethyl)-N,N-dimethylammonium bromide (10). This (89% yield) had m.p. 182—183 °C (Found: C, 62.0; H, 6.3; Br, 22.9; N, 3.95. $C_{18}H_{22}BrNO$ requires C, 62.1; H, 6.3; Br, 23.0; N, 4.0%); $\nu_{max.}$ 1 690 cm^{-1}; δ (CD_3OD) 8.12 (dd, *J* 8 Hz, 2′-H and 6′-H of COPh), 7.80—7.40 (m, 8 aryl H), AX_3 system, δ_A 5.62, δ_X 1.80 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], AB system, δ_A 5.00, δ_B 4.82 (J_{AB} 12 Hz, $\overset{+}{N}CH_AH_B$), 3.33 (s, $\overset{+}{N}Me$), and 3.29 (s, $\overset{+}{N}Me$).

N-([α,α-$^2H_2$]Benzyl)-N-(1-[$^2H_5$]benzoylethyl)-N,N-dimethylammonium bromide (22). This (90% yield) had m.p. 183—184 °C (Found: C, 60.6; H, 6.4; Br, 22.3; N, 4.2. $C_{18}H_{15}D_7BrNO$ requires C, 60.8; H, 6.2; Br, 22.5; N, 3.9%); $\nu_{max.}$ 1 685 cm^{-1}; δ 7.80—7.40 (m, 5 aryl H), AX_3 system, δ_A 6.73, δ_X 1.82 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 3.44 (s, $\overset{+}{N}Me$), and 3.36 (s, $\overset{+}{N}Me$).

Base Catalysed Rearrangement of N-Allyl-N-(1-benzoylethyl)-N,N-dimethylammonium Bromide (49a): *Formation of 2-Benzoyl-2-dimethylaminopent-4-ene* [(50a) ≡ (51a)] *and 3-Hydroxy-3-phenylhex-5-en-2-one* [(52a) ≡ (53a)].—Warm (55 °C) aqueous sodium hydroxide (8 ml; 10%) was added to a stirred solution of the salt (49a) (2.98 g) in water (10 ml) at 55 °C. After 30 min at 55 °C the reaction mixture was cooled and extracted with ether. The extract was evaporated and the residue partitioned between aqueous HCl (50 ml; 10%) and ether. The aqueous layer was made basic (Na_2CO_3) and extracted with ether; the extract was dried and evaporated to give the *aminoketone* [(50a) ≡ (51a)] (1.5 g, 70%), b.p. 105—110 °C at 0.05 mmHg (Found: C, 77.4; H, 8.8; N, 6.6. $C_{14}H_{19}NO$ requires C, 77.4; H, 8.8; N, 6.45%); $\nu_{max.}$ 1 680 cm^{-1}; δ 8.44 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of PhCO), 7.52—7.22 (m, 3 aryl H), AMNXY system, δ_A 5.55, δ_M 4.90, δ_N 4.82, δ_X 2.76, δ_Y 2.49 (J_{AM} 10, J_{AN} 18, J_{AX} 6, J_{AY} 8, J_{XY} 13 Hz, $CH_XH_YCH_A{=}CH_MH_N$), 2.27 (s, NMe_2), and 1.19 (s, CMe). The ether-soluble reaction product was isolated after evaporation of the solvent as an oil, b.p. 120—122 °C at 0.1 mmHg identified as the *hydroxyketone* [(52a) ≡ (53a)] (0.45 g, 20%) (Found: C, 75.45; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.75; H, 7.4%); $\nu_{max.}$ 3 460, 1 715, 1 642, and 1 600 cm^{-1}; δ 7.56—7.23 (m, 5 aryl H), $AMNX_2$ system, δ_A 5.76, δ_M 5.18, δ_N 5.16, δ_X 2.94 [J_{AM} 17, J_{AN} 10, J_{AX} 7 Hz; $C(H_X)_2CH_A{=}CH_MH_N$], 4.21 (s, OH), and 2.05 (s, $COCH_3$). The rearrangement was also carried out in methanol (NaOMe) and dimethyl sulphoxide (NaH) at 55 °C to give products in the yields recorded in Table 5.

Base Catalysed Rearrangement of N-(1-Benzoylethyl)-N-cinnamyl-N,N-dimethylammonium Bromide (49b): *Formation of 2-benzoyl-2-dimethylamino-5-phenylpent-4-ene* (51b), *2-Benzoyl-2-dimethylamino-3-phenylpent-4-ene* (50b; *Diastereoisomers* A *and* B), *3-Hydroxy-3,6-diphenylhex-5-en-2-one* (53b), *and 3-Hydroxy-3,4-diphenylhex-5-en-2-one* (52b; *Diastereoisomers* A *and* B).—A solution of the salt (49b) (3.74 g) in water (50 ml) at 0 °C was treated with aqueous sodium hydroxide (8 ml; 10%) at 0 °C and the temperature of the reaction mixture maintained at 0 °C for 18 h. The mixture was allowed to warm to room temperature and extracted with ether; the ether extract was concentrated and the residue partitioned between aqueous HCl (50 ml; 10%) and ether in the usual way. The aqueous layer was made basic (Na_2CO_3) and extracted with ether; the extract was dried and evaporated and the residue separated by t.l.c. (light petroleum–ether, 4 : 1) to give three aminoketones. (a) *2-Benzoyl-2-dimethylamino-5-phenylpent-4-ene* (51b) (176 mg, 6%) had b.p. 225—230 °C at 0.01 mmHg (Found: C, 81.7; H, 8.1; N, 4.7. $C_{20}H_{23}NO$ requires C, 81.9; H, 7.85; N, 4.8%); $\nu_{max.}$ 1 680 cm^{-1}; δ 8.42 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.58—7.14 (m, 8 aryl H), ABXY system, δ_A 6.14, δ_B 5.92, δ_X 2.88, δ_Y 2.54 (J_{AB} 15, J_{BX} 6, J_{BY} 8, J_{XY} 13 Hz, $CH_A{=}CH_BCH_XH_Y$), 2.31 (s, NMe_2), and 1.24 (s, CMe). The *methiodide* had m.p. 156—157 °C (Found: C, 57.7; H, 6.0; I, 29.1; N, 3.2. $C_{21}H_{26}INO$ requires C, 57.9; H, 6.0; I, 29.2; N, 3.2%); $\nu_{max.}$ 1 680 cm^{-1}; δ 7.70—7.35 (m, 5 aryl H), 7.20 (s, 5 aryl H), ABXY system, δ_A 6.65, δ_B 5.82, δ_X 3.35, δ_Y 3.17 (J_{AB} 15, J_{BX} 7, J_{BY} 7, J_{XY} 13 Hz, $CH_A{=}CH_BCH_XH_Y$), 3.72 (s, $\overset{+}{N}Me_3$), and 2.17 (s, CMe). (b) *2-Benzoyl-2-dimethylamino-3-phenylpent-4-ene* (50b; Diastereoisomer *A*) (1.70 g, 58%); $\nu_{max.}$ 1 680 cm^{-1}; δ 7.56 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.33—7.08 (m, 3 aryl H), 7.08 (s, 5 aryl H), AMNX system, δ_A 6.38, δ_M 5.15, δ_N 5.13, δ_X 4.32 (J_{AM} 10, J_{AN} 18, J_{AX} 10 Hz, $CH_XCH_A{=}CH_M$-H_N), 2.43 (s, NMe_2), and 1.43 (s, CMe). (c) *2-Benzoyl-2-dimethylamino-3-phenylpent-4-ene* (50b; Diastereoisomer *B*) (0.50 g, 17%); $\nu_{max.}$ 1 673 cm^{-1}; δ 8.28 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.52—7.10 (m, 8 aryl H), AMNX system, δ_A 6.20, δ_M 4.94, δ_N 4.82, δ_X 4.07 (J_{AM} 10, J_{AN} 17, J_{AX} 8.5 Hz, $CH_XCH_A{=}CH_MH_N$), 2.24 (s, NMe_2), and 1.28 (s, CMe). The ether-soluble reaction products were separated by t.l.c. (light petroleum–ether, 4 : 1) to give two components. (a) *3-Hydroxy-3,6-diphenylhex-5-en-2-one* (53b) (67 mg, 2.5%) crystallised from light petroleum to give crystals, m.p. 89—90 °C (Found: C, 81.1; H, 6.9. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%); $\nu_{max.}$ 3 460 and 1 712 cm^{-1}; δ 7.55—7.12 (m, 10 aryl H), ABX_2 system, δ_A 6.54, δ_B 6.10, δ_X 3.09 [J_{AB} 15, J_{BX} 7 Hz, $CH_A{=}CH_BC(H_X)_2$], 4.21br (s, OH), and 2.09 (s, $COCH_3$). (b) *3-Hydroxy-3,4-diphenylhex-5-en-2-one* (52b; Diastereoisomers *A* and *B*) was obtained as a semi-solid mixture of the two diastereoisomers (250 mg, 9%) (Found: C, 81.1; H, 6.9. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%); $\nu_{max.}$ 3 430 and 1 705 cm^{-1}; δ (major diastereoisomer only) δ 7.76 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of Ph), 7.62—7.24 (m, 8 aryl H), AMNX system, δ_A 6.10, δ_M 4.99, δ_N 4.97, δ_X 4.61 (J_{AM} 10, J_{AN} 18, J_{AX} 7 Hz, $CH_XCH_A{=}CH_MH_N$), and 2.01 (s, $COCH_3$). The mixture of diastereoisomers showed signals assignable to two other isomeric compounds and CMe signals (δ 1.39 and 1.69) suggested that these were the two diastereoisomers of 2-benzoyl-2-hydroxy-3-phenylpent-4-ene. The rearrangement was also carried out in methanol (NaOMe) at 0 °C and 55 °C to give products in the yields recorded in Table 5.

Base Catalysed Rearrangement of N-(1-Benzoylethyl)-N,N-dimethyl-N-(3,3-dimethylallyl)ammonium Bromide (49c): *Formation of 2-Benzoyl-2-dimethylamino-5-methylhex-4-ene* (51c), *2-Benzoyl-2-dimethylamino-3,3-dimethylpent-4-ene* (50c), and *3-Hydroxy-6-methyl-3-phenylhept-5-en-2-one* (53c) (cf. *Ref.* 20).—Warm (55 °C) aqueous sodium hydroxide (15 ml; 10%) was added to a stirred solution of the salt (49c) (5.0 g) in

water (15 ml) at 55 °C. The reaction mixture was maintained at 55 °C for 1 h, cooled, and extracted with ether. The ether was evaporated and the residue partitioned between aqueous HCl (40 ml; 10%) and ether in the usual way. The aqueous layer was made basic (Na_2CO_3) and extracted with ether; the extract was dried and evaporated to give a mixture of the aminoketones (51c) and (50c) in a 2 : 1 ratio (3.1 g, 83%) which could not be separated. The mixture (1.0 g) was heated under reflux in xylene (3 ml) for 6 h and the solvent evaporated; the residual oil was purified by t.l.c. (light petroleum–ether, 100 : 20) to give the aminoketone (51c) (850 mg, 85%) as an oil, b.p. 120—125 °C at 0.1 mmHg; $\nu_{max.}$ 1 690 cm^{-1}; δ 8.39 (dd, *J* 2, 8 Hz, 2′-H and 6′-H of COPh), 7.44—7.21 (m, 3 aryl H), AXY system, δ_A 4.79, δ_X 2.56, δ_Y 2.40 (J_{AX} 7, J_{AY} 7, J_{XY} *ca.* 14 Hz, $CH_XH_YCH_A{=}C$), 2.26 (s, NMe_2), 1.52 (s, CMe), 1.24 (s, CMe), and 1.14 (s, CMe). The mixture of aminoketones gave additional signals assignable to the aminoketone (50c) δ 8.31 (dd, *J* 2, 8 Hz, 2′-H and 6′-H of COPh), 7.44—7.21 (m, 3 aryl H), AXY system, δ_A 6.16, δ_X 4.85, δ_Y 4.84 (J_{AX} 10, J_{AY} 17 Hz, $CH_A{=}CH_XH_Y$), 2.32 (s, NMe_2), 1.24 (s, CMe), 1.03 (s, CMe), and 0.99 (s, CMe). The aminoketones were further characterised by reduction (zinc–acetic acid) to give a mixture of the ketones (54a) and (54b) (92% yield) which was separated by g.l.c. (7% OV17 on 60/80 Chromosorb G.AW.-DMCS at 190 °C). 2-*Benzoyl*-5-*methylhex*-4-*ene* (54a) (65% yield) had b.p. 140—142 °C at 0.1 mmHg (Found: C, 82.8; H, 9.1. $C_{14}H_{18}O$ requires C, 83.1; H, 8.9%); $\nu_{max.}$ 1 680 cm^{-1}; δ 7.86 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.46—7.04 (m, 3 aryl H), $ABMNX_3$ system, δ_A 5.04, δ_B 3.36, δ_M 1.38, δ_N 1.06, δ_X 1.12 [J_{AM}, J_{AN}, J_{BM}, J_{BN}, J_{BX} all 7, J_{MN} 14 Hz, $C{=}CH_ACH_MH_N$-$CH_BC(H_X)_3$], 1.63 (s, CMe), and 1.56 (s, CMe). 2-*Benzoyl*-3,3-*dimethylpent*-4-*ene* (54b) (32% yield) had b.p. 130—135 °C at 0.02 mmHg (Found: C, 83.1; H, 9.1. $C_{14}H_{18}O$ requires C, 83.1; H, 8.9%); $\nu_{max.}$ 1 678 cm^{-1}; δ 7.85 (dd, *J* 2, 8 Hz, 2′-H and 6′-H of COPh), 7.50—7.26 (m, 3 aryl H), AXY system, δ_A 5.86, δ_X 4.90, δ_Y 4.88 (J_{AX} 18, J_{AY} 10 Hz, $CH_A{=}CH_XH_Y$), AX_3 system, δ_A 3.39, δ_X 1.07 [J_{AX} 7 Hz, $CH_AC(H_X)_3$], 1.05 (s, CMe), and 1.00 (s, CMe). The ether-soluble rearrangement product was purified by t.l.c. (light petroleum–ether, 100 : 20) to give the *hydroxyketone* (53c) (200 mg, 5%), b.p. 150—160 °C at 0.05 mmHg (Found: C, 76.9; H, 8.4. $C_{14}H_{18}O_2$ requires C, 77.1; H, 8.3%); $\nu_{max.}$ (liquid film) 3 460 and 1 710 cm^{-1}; δ 7.60—7.20 (m, 5 aryl H), AXY system, δ_A 5.04, δ_X 2.97, δ_Y 2.80 (J_{AX} 7, J_{AY} 7, J_{XY} *ca.* 14 Hz, $C{=}CH_ACH_XH_Y$), 4.12 (s, OH), 2.03 (s, $COCH_3$), and 1.67 (s, $C{=}CMe_2$).

Base Catalysed Rearrangement of N-*Benzyl*-N-(1-*benzoylethyl*)-N,N-*dimethylammonium Bromide* (10): *Formation of* 2-*Benzoyl*-2-*dimethylamino*-3-*phenylpropane* (11), 2-*Hydroxy*-1,2-*diphenylbutan*-3-*one* (14), *and* 1-*Benzyloxy*-1-*phenylpropan*-2-*one* (16). Warm (55 °C) aqueous sodium hydroxide (8 ml; 10%) was added to a stirred solution of the salt (10) (3.48 g) in water (20 ml) at 55 °C. The reaction mixture was kept at 55 °C for 30 min, cooled, and extracted with ether. The extract was evaporated and the residue partitioned in the usual way between aqueous HCl (50 ml; 10%) and ether. The aqueous layer was made basic (Na_2CO_3) and extracted with ether; the extract was dried and evaporated to give a residual oil identified as the aminoketone (11) (2.30 g, 86%), δ 8.43 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.57—6.80 (m, 8 aryl H), AB system, δ_A 3.44, δ_B 2.93 (J_{AB} 14 Hz, CH_AH_B), 2.33 (s, NMe_2), and 1.15 (s, CMe). The *methiodide* had m.p. 189—190 °C (Found: C, 55.6; H, 5.9; I, 31.2; N, 3.5. $C_{19}H_{24}INO$ requires C, 55.7; H, 5.9; I, 31.05; N, 3.4%); $\nu_{max.}$ (Nujol) 1 685 cm^{-1}; δ (CD_3OD) 7.50—7.07 (m, 10 aryl H), AB system, δ_A 3.87, δ_B *ca.* 3.5 (J_{AB} 12 Hz, CH_AH_B), 3.49 (s, $\overset{+}{N}Me_3$), and 1.91 (s, CMe). The ether-soluble rearrangement products were separated by t.l.c. (light petroleum–ether, 100 : 15) to give two products.

Table 8. Products from the base catalysed rearrangement of *N*-benzyl-*N*-(1-benzoylethyl)-*N*,*N*-dimethylammonium bromide (10) under various reaction conditions

Reaction conditions			Product yields (%) [a]		
Solvent	Base	Temp. (°C)	[1,2]	[1,3]	[1,4]
H_2O	NaOH	55	86	6	2
MeOH	NaOMe	55	43	6	1
DMSO	NaH	55	91	3	<1

[a] The [1,2] rearrangement leads to product (11), the [1,3] rearrangement to product (14), and the [1,4] rearrangement to product (16) (Scheme 2).

(a) 2-*Hydroxy*-1,2-*diphenylbutan*-3-*one* (14) (145 mg, 6%) crystallised from light petroleum to give a sample, m.p. 71—72 °C (Found: C, 80.2; H, 6.7. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%); $\nu_{max.}$ 3 570, 3 470, and 1 716 cm^{-1}; δ 7.63—7.00 (m, 10 aryl H), 3.83 (s, OH), AB system, δ_A 3.62, δ_B 3.35 (J_{AB} 14 Hz, CH_AH_B), and 2.08 (s, $COCH_3$).

(b) 1-*Benzyloxy*-1-*phenylpropan*-2-*one* (16) (54 mg, 2%) was obtained as a semi-solid, b.p. 175—180 °C at 0.05 mmHg (Found: C, 79.8; H, 6.8. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%); $\nu_{max.}$ (liquid film) 1 720 cm^{-1}; δ 7.59—7.19 (m, 10 aryl H), 4.80 (s, CH), AB system, δ_A 4.59, δ_B 4.48 (J_{AB} 11 Hz, OCH_AH_B), and 2.13 (s, $COCH_3$). The rearrangement was also carried out in methanol (NaOMe), and dimethyl sulphoxide (NaH) at 55 °C to give products in the yields recorded in Table 8.

Reduction of 2-*Benzoyl*-2-*dimethylamino*-3-*phenylpropane* (11): *Formation of* 2-*Benzoyl*-3-*phenylpropane* (13).—The aminoketone (11) (1.33 g) in acetic acid (15 ml) was reduced with zinc dust (800 mg) in the usual way (100 °C, 75 min). The neutral reaction product was identified as the ketone (13) (1.00 g, 90%), b.p. 160—170 °C at 0.05 mmHg (Found: C, 85.9; H, 7.4. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%); $\nu_{max.}$ 1 682 cm^{-1}; δ 7.89 (dd, *J* 8, 2 Hz, 2′-H and 6′-H of COPh), 7.60—7.10 (m, 8 aryl H), and $AMNX_3$ system, δ_A 3.73, δ_M 3.13, δ_N 2.66, δ_X 1.16 [J_{AM} 6, J_{AN} 8, J_{AX} 7, J_{MN} 14 Hz, $CH_MH_NCH_AC(H_X)_3$].

Reduction of 2-*Hydroxy*-1,2-*diphenylbutan*-3-*one* (14): *Formation of* 2,3-*Dihydroxy*-1,2-*diphenylbutanone* (15; *Diastereoisomers* A *and* B).—The hydroxyketone (14) (100 mg) in ethanol (5 ml) was treated with sodium borohydride (64 mg). After 12 h at room temperature the product was isolated to give the two diastereoisomeric diols (15) (90 mg) in a 1 : 3 : 5 ratio. The pure diastereoisomers were obtained by t.l.c. (light petroleum–ether, 100 : 40).

(a) *Diastereoisomer* A was obtained as an oil (Found: M^+, 242. $C_{16}H_{18}O_2$ requires *M*, 242), $\nu_{max.}$ 3 565 and 3 460 cm^{-1}; δ 7.32—6.78 (m, 10 aryl H), AX_3 system, δ_A 4.07, δ_X 0.94 [J_{AX} 6 Hz, $CH_AC(H_X)_3$], AB system, δ_A 3.35, δ_B 3.23 (J_{AB} 14 Hz, CH_AH_B), and 2.16br (s, 2 × OH).

(b) *Diastereoisomer* B crystallised from light petroleum to give a sample m.p. 73—74 °C (Found: C, 79.4; H, 7.6%; M^+, 242. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.4%; *M*, 242); $\nu_{max.}$ 3 570 and 3 460 cm^{-1}; δ 7.50—6.45 (m, 10 aryl H), AX_3 system, δ_A 3.98, δ_X 1.18 [J_{AX} 6 Hz, $CH_AC(H_X)_3$], 3.18 (s, CH_2), 2.27br (s, OH), and 1.93br (s, OH).

Reduction of 1-*Benzyloxy*-1-*phenylpropan*-2-*one* (16): *Formation of* 1-*Benzyloxy*-2-*hydroxy*-1-*phenylpropane* (17; *Diastereoisomers* A *and* B).—The benzyloxyketone (16) (100 mg) in ethanol (3 ml) was reduced with sodium borohydride

(65 mg). After 12 h at room temperature the product was isolated to give the two diastereoisomeric alcohols (17) (95 mg) in a 1 : 2.2 ratio. The two diastereoisomers were separated by t.l.c. (light petroleum–ether, 100 : 40).

(a) Diastereoisomer *A* was obtained as an oil (Found: M^+, 242. $C_{16}H_{18}O_2$ requires *M*, 242); $\nu_{max.}$ 3 580 and 3 460 cm^{-1}; δ 7.31 (s, 5 aryl H), 7.27 (s, 5 aryl H), AB system, δ_A 4.52, δ_B 4.29 (J_{AB} 12 Hz, OCH_AH_B), ABX_3 system, δ_A 4.25, δ_B 3.94, δ_X 1.10 [J_{AB} and J_{BX} 6 Hz, $OCH_ACH_BC(H_X)_3$], and 2.19br (s, OH).

(b) Diastereoisomer *B* was obtained as an oil (Found: M^+, 242. $C_{16}H_{18}O_2$ requires *M*, 242); $\nu_{max.}$ 3 570 cm^{-1}; δ 7.33 (s, 5 aryl H), 7.28 (s, 5 aryl H), AB system, δ_A 4.45, δ_B 4.26, (J_{AB} 11 Hz, OCH_AH_B), ABX_3 system, δ_A 4.08, δ_B 3.94, δ_X 1.95 [J_{AB} 8, J_{BX} 6 Hz, $OCH_ACH_BC(H_X)_3$], and 3.10br (s, OH).

Base Catalysed Rearrangement of N-*Benzyl*-N-(1-*benzoylethyl*)-N,N-*dimethylammonium Bromide* (10): *Determination of Intramolecularity under Various Reaction Conditions.*—(a) *Rearrangement.* The rearrangements were conducted under the conditions summarised in Table 1. In each case a solution of the appropriate base (2 mol equiv.) in the stated solvent was added to a stirred solution of a 1 : 1 mixture (1.98 g) of the [$^2H_0$]salt (10) and the [$^2H_7$]salt (22) in the same solvent (5 ml). Both solutions were maintained at the stated temperature (±2 °C) during the addition and the subsequent reaction period. The products (11), (14), and (16) were isolated as described for the rearrangement of the [$^2H_0$]salt (10) and their isotopic compositions determined as below.

(b) *Isotopic compositions of rearrangement products.* The dimethylaminoketone (11) was reduced (zinc–acetic acid) to the ketone (13). The isotopic compositions of both products were determined by mass spectrometry using the peak heights (averaged over several spectra) of the M^+, $(M + 2)^+$, $(M + 5)^+$, and $(M + 7)^+$ ions. The isotopic compositions of the hydroxyketone (14) and the benzyloxyketone (16) were determined by mass spectrometry using the peak heights (averaged over several spectra) of the $(M - COCH_3)^+$, $(M + 2 - COCH_3)^+$, $(M + 5 - COCH_3)^+$, and $(M + 7 - COCH_3)^+$ ions since these products did not give strong peaks from the molecular ions.

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