

Radical-coupling Products Derived from Ammonium Ylides. Competing [1,2], [1,3], and [1,4] Anionic Rearrangements

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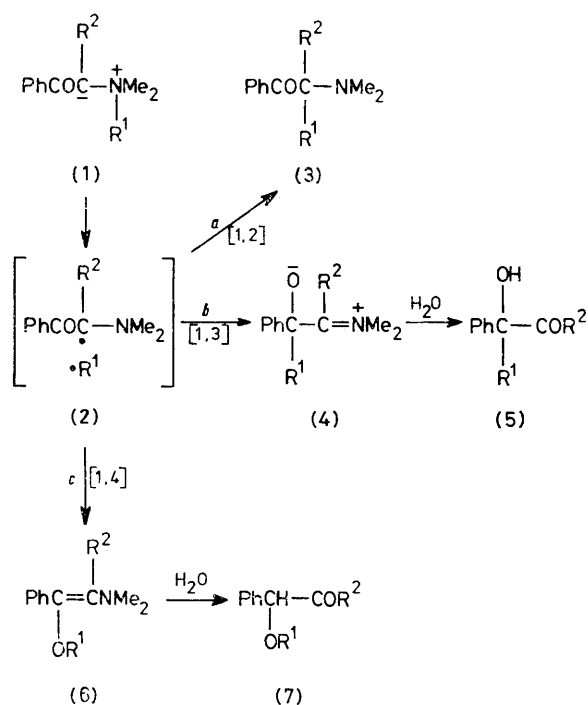
Summary The thermal rearrangements of the ammonium ylides (**1**) give products formally derived from competing [1,2], [1,3], and [1,4] rearrangements; the intramolecularities of these processes are compatible with a radical pair mechanism involving initial homolysis of the ylide (**1**) followed by three possible modes of radical pair recombination (Scheme).

involve homolysis of the ylide (**1**) to give a radical pair (**2**) which recombines to give the product (**3**). The radical pair (**2**) could in principle also recombine to give the product (**4**) of a formal [1,3] rearrangement and the product (**6**) of a formal [1,4] rearrangement (see Scheme). We report an investigation of these possibilities, prompted by the reported² formation of the [1,3] product in the case of the ylide (**8**).

THE Stevens rearrangement of ammonium ylides (**1**) to give the amines (**3**) may formally be regarded as a [1,2] anionic rearrangement although it has been shown¹ to

The salt (**9**) reacted with aqueous sodium hydroxide at 55 °C to give products identified† as the amine (**3a**) (86%), the hydroxy-ketone (**5a**) (6%), and the benzyloxy-ketone (**7a**) (2%). These products can result from the radical

† All new compounds were identified by their spectroscopic properties and molecular formulae were established by analysis or high resolution mass spectrometry.



SCHEME. The three modes of recombination of the radical pair *a*, *b*, and *c* may be intramolecular or intermolecular (see text) and may formally be regarded as [1,2], [1,3], and [1,4] rearrangements respectively.

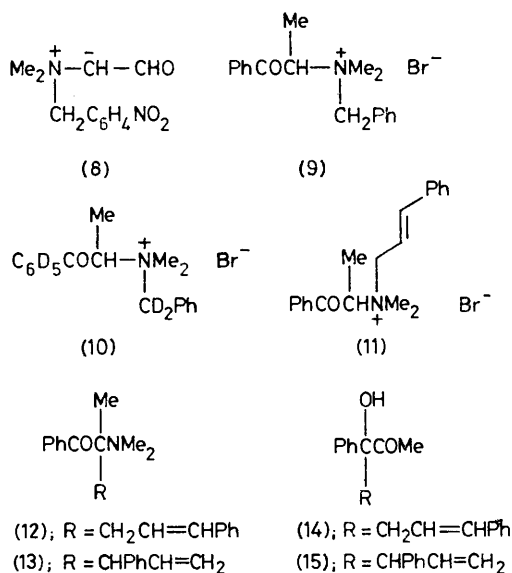
coupling processes *a*, *b*, and *c* (Scheme) followed by hydrolysis of the intermediate products (4a) and (6a). This mechanistic proposal was supported by carrying out the reaction using an equimolar mixture of the salt (9) and the heptadeuterio-derivative (10) to determine¹ the extent to which the coupling processes *a*, *b*, and *c* (Scheme) were intermolecular. The results of this study are summarised in the Table, and they may be compared with our earlier

TABLE. Intermolecularity of [1,2], [1,3], and [1,4] rearrangements of salt (9).

Reaction conditions	Intermolecularity %		
	[1,2] ^b	[1,3] ^c	[1,4] ^d
NaOH in H ₂ O at 55 °C	3	4	1
NaOH in H ₂ O at 95 °C	12	12	4
NaOMe in MeOH at 55 °C	28	28	14

^a Intramolecularity = 4z% and intermolecularity = 100 – 4z% where an equimolar mixture of (9) and (10) gives the following proportions of non-deuteriated and deuteriated products (3a), (5a), or (7a): [²H₀] 50 – z%; [²H₂] z%; [²H₅] z%; [²H₇] 50 – z%. ^b Based upon data for product (3a). ^c Based upon data for product (5a). ^d Based upon data for product (7a).

study¹ of the [1,2] Stevens rearrangement. They are clearly consistent with a radical mechanism for the formation of all three products, as indicated in the Scheme, rather than the alternative possibilities of concerted and ion-pair mechanisms. Both modes of coupling *a* and *b* (Scheme) show similar characteristics, but the [1,4] coupling mode *c* (Scheme) shows significantly greater intramolecularity. This result is in accord with the general ideas, based upon orbital symmetry,³ that the [1,4] coupling mode[†] would involve an electronically different radical pair⁵ from the [1,2] and [1,3] coupling modes *a* and *b*. It is reasonable to suppose that the reported² [1,3] rearrangement of the ylide (8) involves a similar radical mechanism.



The [1,3] sigmatropic rearrangement of ammonium ylides is a fairly general process for ylides of the type (1, R² ≠ H) and a number of examples⁶ have been observed for (1, R² = Me) and (1, R² = Ph). Yields of the [1,3] products are generally low, and they are favoured by an aqueous reaction medium. For ammonium ylides (1) in which R¹ is an allyl unit the number of possible coupling modes is further increased. For example, the ammonium salt (11) with aqueous sodium hydroxide at 0 °C gives the [1,2] product (12) (6%), two diastereomeric [3,2] products (13) (58 and 17.5%), the [1,3] product (14) (2.5%), and two diastereomeric [3,3] products (15) (9.5%).

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† The possibility that the [1,2] product (3) arises from a [1,3] rearrangement of the product (6) can be discounted (ref. 4).

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