Ylide Rearrangements: Duality of Mechanism in the Rearrangement of *N*-Ammonio-amidates

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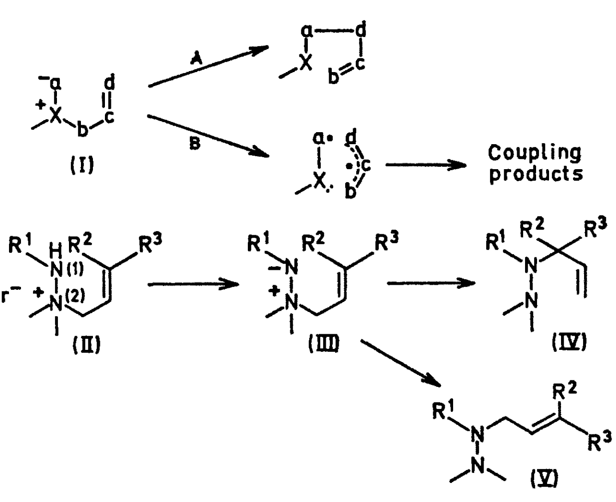
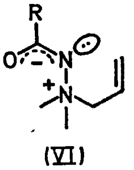
Summary The observation of structural dependence in the mechanism of thermal rearrangement of *N*-ammonio-amidates is reported and explained in terms of charge delocalization in the reactant.

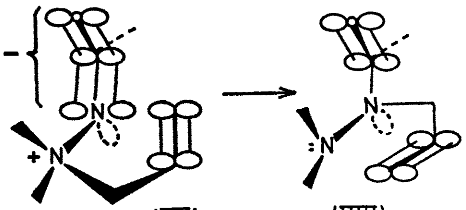
IN an investigation[1,2] of the rearrangements of sulphonium ylides (I; X=S, a=b=c=d=C) we have discovered[3] that there exist two competing mechanistic paths: a concerted suprafacial rearrangement with retention of orbital symmetry (A),[4] and a non-concerted, radical dissociation–recombination process (B). We believe that this specific case is merely one example of a general dual pathway where X = N, O, P *etc.*, and for this reason we have examined a number of related systems. In the earlier work[3] we showed that path A has a lower activation energy and is consequently favoured at low temperatures. This same duality is probably the origin of the well-known temperature dependence in the Stevens–Sommelet–Hauser reaction[5] and also the Wittig rearrangement.[6] We now report a new structural effect which influences the balance of A and B, namely the state of hybridization at the anionic atom a.

Thus the hydrazinium salts (IIa—c)† were deprotonated to the unstable ylides (IIIa—c) which rearranged rapidly ($t_{\frac{1}{2}}$ *ca.* 60 sec.) and quantitatively at 35° to hydrazines (IVa—c). In contrast to this simple concerted reorganization (path A) the ylides (IIId—g) obtained from the acylated salts (IId—g) were relatively stable.[7] One of these compounds (IIg) has recently been reported[8] to rearrange on pyrolysis, but in this one case there were no orienting substituents to differentiate between paths A and B. We have now found that this rearrangement is only induced above 120° ($t_{\frac{1}{2}}$ *ca.* 30 min. at 130°) and that the product structures are (Vd—f). To eliminate the possibility that (IV) could, at high temperature, rearrange to (V), we have synthesized (IVf) and shown that at 170° its rate of rearrangement to (Vf) is approximately one-tenth that of (IIIf) under the same conditions. Thus a prior, concerted rearrangement of (III) to (IV) is *not* involved in the generation of (V). In keeping with our earlier hypothesis[3] *i.e.* that path B involves a radical dissociation–recombination mechanism, we have observed a chemically induced dynamic nuclear polarization (CIDNP emission)[9] of the allylic methylene protons in (Vf) during its generation by pyrolysis of (IIIf) at 180°. A similar observation on an *N*-benzyl *N*-ammonio-amidate has recently been reported.[10] These evidences demonstrate that acylation on nitrogen shifts the mechanism from a ready concerted rearrangement to a homolytic dissociation–recombination pathway, of higher activation energy. An explanation of this effect may be found by consideration of the origin of the driving force involved in the concerted mechanism A. Since the salts (IIa—c) are thermally stable to rearrangement and yet possess, at N-1, a non-bonded electron pair which can satisfy the orbital symmetry requirements[4] of the concerted process, it is evident that a fully developed negative charge is necessary. Rearrangement is thus seen to be driven by a decrease in charge separation in passing to product (IIIa—c). In contrast the stable ylides (IIId—g), ν_{max} 1580 cm^{-1}, although having the requisite orbitals, as (VI), gain extra stabilization from charge delocalization in the amidate anion and it must be this factor which contributes to the higher activation energy of path A and consequent competition from B. It should also be noted that participation of the delocalized amidate orbital, as in (VII), necessarily provides a product (VIII) which is an orthogonal amide. This species is energetically and geometrically equivalent to the conformer of maximum energy in the rotation of amides, which has been estimated by other workers[11] to be some 15—20 kcal./mole above the planar state, and would therefore destabilize the transition state.



	R¹	R²	R³
a	H	H	Me
b	H	Me	Me
c	H	H	Ph
d	Ac	H	Me
e	Ac	Me	Me
f	Ac	H	Ph
g	PhCO	H	H


(VI)


(VII) (VIII)

The phenomenon, in which charge delocalization in the ylide inhibits a concerted rearrangement and permits alternative pathways, is likely to be generally observed and may be of some value in controlling the balance between such reactions.

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† All new compounds have satisfactory analytical and spectroscopic data. All reactions were monitored by n.m.r.

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