Thermal Rearrangements of Allylic *N*-Ammonio-amidates

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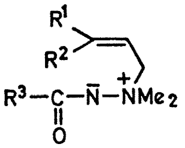
Summary Mechanistic consequences are considered of a CIDNP effect in vicinal migration of an allylic group without inversion during thermolysis of allylic *N*-ammonio-amidates.

Thermal reactions of *N*-ammonio-amidates have recently been well documented; the thermolyses encountered have included the Stevens rearrangement,[1] isocyanate formation,[2] and olefin formation.[3] Recently an example was reported of a thermal isomerisation involving migration of an unsubstituted allyl group, (I) → (IV) and the reaction was considered as proceeding *via* a five-membered transition state.[4]

We have synthesised the unsymmetrically substituted compounds (II) and (III). From thermolyses of (II) and (III) at temperatures of 150° and 130°, respectively we have isolated as the only allylic products 1-acetyl-2,2-dimethyl-1-(3,3-dimethylallyl)hydrazine (V) and 1-acetyl-2,2-dimethyl-1-(3-phenylallyl)hydrazine (VI). This reaction is noteworthy in that within the overall rearrangement no isomerisation of the allylic moiety is observed in either compound.

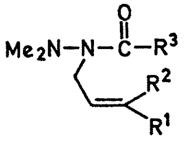
This result is best considered in conjunction with those for thermolysis of allylic amine oxides[5] and the rearrangement of allylic ammonium ylides.[6] In both these cases in which unsymmetrically substituted allylic groups were employed, the primary rearrangement product contained an inverted allyl group, *i.e.*, (VII) → (VIII) and (IX) → (X).



(I) $R^1 = R^2 = H; R^3 = Ph$

(II) $R^1 = R^2 = R^3 = Me$

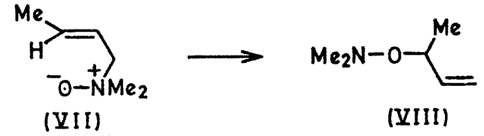
(III) $R^1 = Ph; R^2 = H; R^3 = Me$



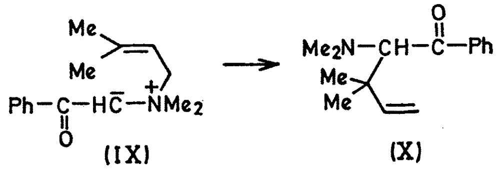
(IV) $R^1 = R^2 = H; R^3 = Ph$

(V) $R^1 = R^2 = R^3 = Me$

(VI) $R^1 = Ph; R^2 = H; R^3 = Me$



(VII) (VIII)



(IX) (X)

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However, in the case of the allylic ammonium ylides the primary rearrangement product was found to undergo an essentially quantitative thermal rearrangement (X) → (XI) at 180° leading to overall lack of rearrangement in the allyl group.

Recently on the basis of results obtained from observations of chemically induced dynamic nuclear polarisation (CIDNP) in the n.m.r. spectrum of products the intervention of radical pair intermediates has been suggested in both the Stevens rearrangement[7] and the thermally promoted allylic rearrangement of (XII).[8] We have examined the rearrangement of (II) in nitrobenzene using n.m.r. spectroscopy with kinetic scanning of the region of the developing allylic methylene doublets of the product (V). Within 20 sec. of insertion into the probe at 180°, a CIDNP effect was visible and at this temperature lasted about 70 sec. (Figure).

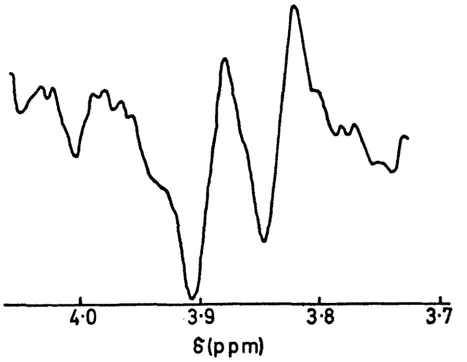
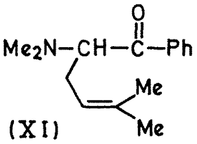
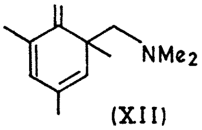


FIGURE. *CIDNP effect observed after* 45 *sec. for allylic methylene protons of the developing product during thermolysis of* (II) → (V). *Spectrum was taken at* 100 *MHz with octamethylcyclotetrasiloxan as lock signal.*

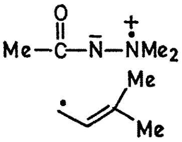
These results are consistent with a mechanism involving homolytic cleavage from (II) yielding a radical-pair intermediate (XIII), which collapses to (V), the more stable allylic isomer. Alternatively, it is possible that prior formation of (XIV) occurs *via* a five-membered transition state with (XIV) rearranging to (V) *via* a homolytic cleavage–recombination pathway. This second scheme has the merit of preserving a common initial mechanistic pattern with allylic amine oxides and ammonium ylides. Thermal rearrangement (XIV) → (V) *via* a radical pair intermediate is then required to proceed at least 40° lower than for (X) → (XI), with a lower transition state for allylic-hydrazino-radical pair formation. Enhanced stability of an allylic-hydrazino-diradical intermediate has recently been suggested to account for the lower temperature required to effect a vinylaziridine to pyrroline rearrangement with respect to that for a vinylcyclopropane rearrangement.[9]



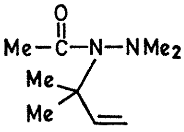
(XI)



(XII)



(XIII)



(XIV)

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