Electron Attachment to *N*-Benzoylaziridines followed by C–N Homolysis of the Aziridine Ring[1]

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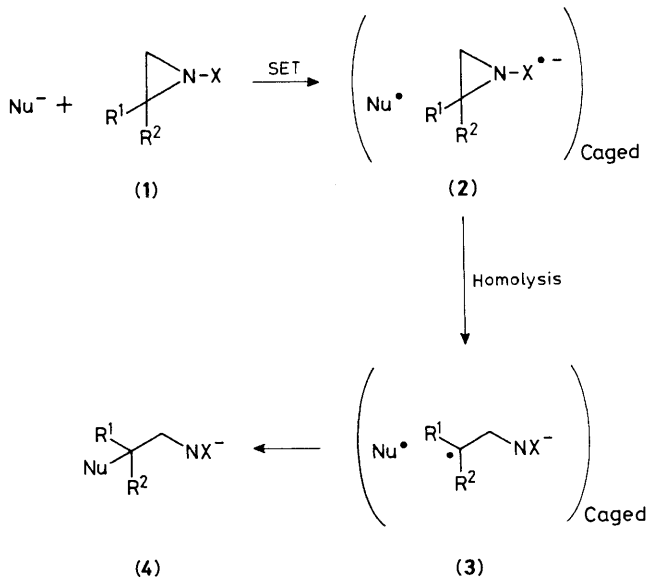
Reactions of *N*-benzoylaziridines with strong electron sources provide direct evidence for the formation of ketyls (**2**) and radicals (**3**), both of which are postulated intermediates in the single electron transfer mechanism of nucleophilic ring opening of activated aziridines.

S_N2-like nucleophilic ring opening of activated aziridines is a well established reaction[2] of considerable synthetic value.[1,3] Recently,[4] a slow single electron transfer (SET) mechanism was proposed to account for the observed change in regiopreference of ring opening of 2,2-dimethylaziridines: strong activation by *N*-sulphonyl groups resulted in S_N2-like normal opening and weak activation by *e.g.* *N*-acyl groups in anomalous opening (Scheme 1, $R^1 = R^2 = Me$, X = 2,4-dinitrophenyl, acyl).

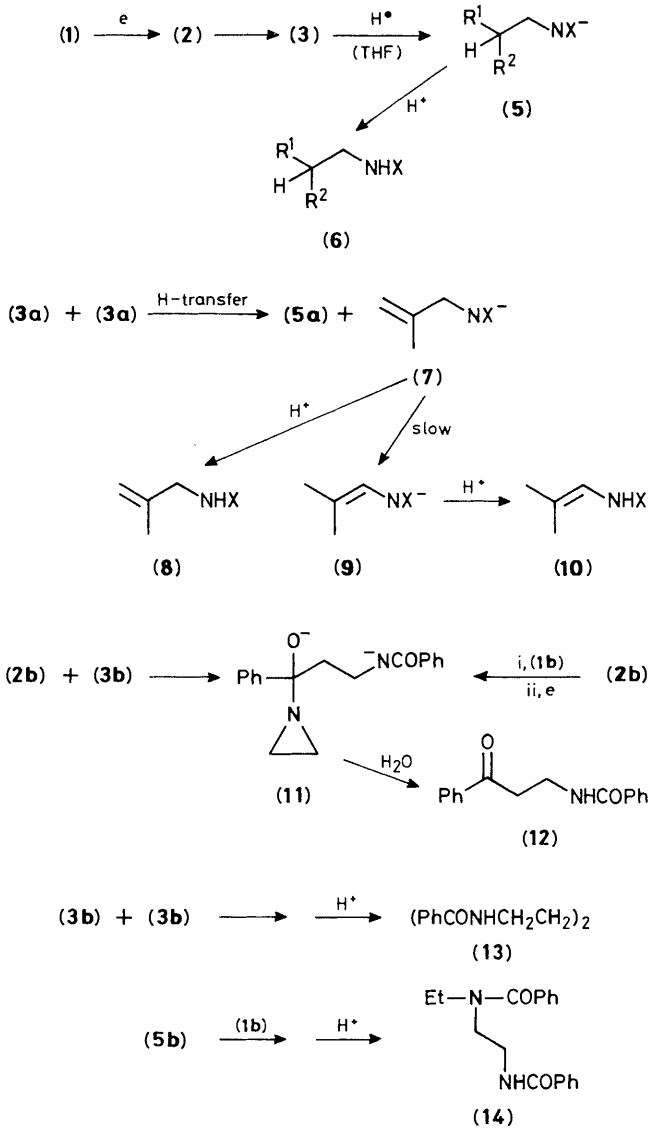
Proof and a better understanding of the postulated mechanism and of the competition between SET and S_N2 has important mechanistic as well as synthetic implications. Corroboration of this competition will provide evidence against the discussed[5] electron transfer mechanism of S_N2. Besides, the postulated mechanism reveals a new concept for introducing tertiary alkyl groups.

Reactions of the *N*-benzoylaziridines (**1a—c**) with metallic sodium or aromatic radical anions in tetrahydrofuran (THF) provide direct evidence for the formation of a ketyl (**2**) and a subsequent ring homolysis forming the radicals (**3**) as shown in Scheme 2 and Table 1. In the absence of a radical Nu·, the radicals (**3a—c**) abstract a hydrogen atom from the solvent yielding the reduction products (**6a—c**) *via* (**5a—c**). The formation of (**6b**) requires the intermediacy of a primary radical (runs 6—8) and shows that the ring homolysis is not confined to the formation of a fairly stable tertiary (runs 1—5) or benzylic (run 9) radical. However, homolysis is slowed down when a primary radical has to be formed. Thus, at −10 °C (run 8) in the reaction with a dissolved electron source which rapidly forms a high concentration of ketyl (**2b**), some ketyl escapes from the solvent cage and reacts with (**1b**) or (**3b**) forming (**11**), the precursor of the isolated (**12**). This isolation of (**12**) is strong evidence for a finite lifetime of ketyl (**2b**).

Even under these conditions (run 8) the lifetime of the primary radical (**3b**) can be expected to be too short for combinations of two of them to occur to a substantial extent.



Scheme 1



♦ X = COPh
♦ **a**; $R^1 = R^2 = Me$
♦ **b**; $R^1 = R^2 = H$
♦ **c**; $R^1 = H, R^2 = Ph$
♦
♦ Scheme 2

Table 1. Reactions[a] of aziridines (**1a—c**) with electron sources in THF.

Run	Aziridine	Electron source[b]	Time	Products[c] (isolated yields, %)					
1	(**1a**)	Na	1 day	(**6a**)	(27)	(**8**)	(4)	(**10**)	(7)
2	(**1a**)	Na	3 days	(**6a**)	(50)	(**8**)	(10)	(**10**)	(12)
3	(**1a**)	Na,disp	3 days	(**6a**)	(42)	(**8**)	(0)	(**10**)	(20)
4	(**1a**)	NaphNa	1 min	(**6a**)	(22)	(**8**)	(4)	(**10**)	(0)
5	(**1a**)	NaphNa[d]	5 days	(**6a**)	(52)	(**8**)	(0)	(**10**)	(28)
6	(**1b**)	Na	2 days	(**6b**)	(52)	(**14**)	(15)		
7	(**1b**)	NaphNa	10 h	(**6b**)	(83)				
8	(**1b**)	ANa[d]	40 h[e]	(**6b**)	(37)	(**12**)	(19)	(**13**)	(0.7)
9	(**1c**)	Na	20 h	(**6c**)	(38)[f]				

[a] Reactions at room temp. with equimolar quantities of electron source and aziridine; 2.5—10 mmol aziridine in 10—150 ml THF under nitrogen. [b] Na = piece of sodium; Na, disp = dispersion of sodium in paraffin; NaphNa = sodium naphthalenide; ANa = sodium anthracenide. [c] All compounds (**6**)—(**14**) gave satisfactory analyses and spectra (i.r., ^{1}H n.m.r.). The melting points of the known compounds (**6a**),[6] (**6b**),[7] (**6c**),[8] and (**13**)[9] agreed with the literature values; (**13**) was additionally identified by comparison with an authentic sample. Spectral and other details will be published in a full paper (to follow). [d] 100% excess. [e] Reaction was started at −10 °C and probably went to completion at this temperature. [f] Isolation of 41% benzoic acid indicates the amount of unreacted aziridine (**1c**).

So, we isolated only a very small quantity of the dimer (**13**) which must have formed *via* radical (**3b**).

On the other hand, the lifetime of the tertiary radical (**3a**) is sufficient to make the disproportionation of (**3a**) the main reaction (runs 1—3, 5), *i.e.* a reaction that requires collisions of two radicals (**3a**). The primary product of this disproportionation is (**7**) and not (**9**) as shown by the time dependence of product distribution (runs 1—5) and in accordance with sterical and statistical expectations. The transformation of (**7**) into (**9**) could be verified by stirring (**8**) with sodium and sodium hydride in THF: after four days at room temperature only (**10**), some benzamide, and no (**8**) were detected. The benzamide was formed by hydrolysis during work-up. This isomerization of a simple allylamide indicates a probable general transformation of an allylamide or allylamine into a saturated carbonyl compound with the same carbon skeleton.

If both SET is slow, *i.e.* with a piece of sodium, and S_N2 ring opening is fast, *i.e.* in the absence of steric hindrance, then part of (**5**) may react with unreacted (**1**) as is shown by the formation of (**14**) in run 6.

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