A Probable Aziridine Radical: Mechanism of Addition of Aziridine to Styrenes

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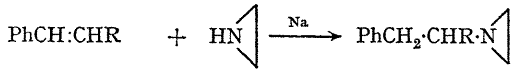
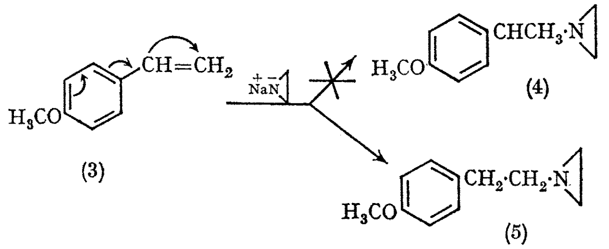
Summary Strong evidence of an aziridine radical in the sodium-catalysed addition of aziridine to styrenes has been obtained.

BESTIAN *et al.*[1] reported that aziridine adds to styrene (1a), in the presence of a catalytic amount of sodium metal, to give *N*-phenethylaziridine (2a) in over 90% yield. Similarly diethylamine,[1] dibutylamine,[2] and propylenimine[3] add to styrene in the presence of sodium metal. The addition of aziridine to styrene was confirmed by Yoshida and Naito[4] and they suggested an ionic reaction mechanism for this reaction.



(1) a, R=H; b, R=CH$_3$ (2) a, R=H; b, R=CH$_3$



By the procedure of Bestian, when β-methylstyrene was allowed to react with aziridine in the presence of a small amount of sodium metal (slices), (1-phenyl-2-propyl)-aziridine† (2b) was isolated in 72% yield; b.p. 90—91°/5 mm.; n.m.r.‡ spectrum 1·02, 1·65 (set of three equal intensity peaks,§ area 4), 1·08 (doublet, 3), 1·37 (multiplet, 1), 2·80 (multiplet, 2), 7·23 (singlet, 5). No isomeric 1-(1-phenylpropyl)aziridine was found, as shown by n.m.r. analysis. It was argued that if the addition of aziridine to styrene proceeded by an ionic mechanism, then reaction with *p*-methoxystyrene (3) should furnish predominantly (4). However the addition of (3) to aziridine yielded *N*-*p*-methoxyphenethylaziridine (5) in 47% yield; b.p. 95—96°/0·4 mm; n.m.r. spectrum 1·01, 1·67 (set of three equal intensity peaks,§ area 4), 2·36 (triplet, 2), 2·77 (triplet, 2), 3·72 (singlet, 3), 6·77 (doublet, 2), 7·09 (doublet, 2). N.m.r. analysis demonstrated the presence of some unreacted (3) and complete absence of (4). Moreover, the aziridine anion (lithium derivative of aziridine) failed to react with an equimolar quantity of β-methylstyrene when the reaction mixture was heated under reflux for 24 hr. in ether,[5] and only starting material was recovered. In the reaction of aziridine with styrenes in the presence of a small amount of

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† Satisfactory analyses were obtained for all new compounds.

‡ All n.m.r. spectra were determined on a Varian A-60 spectrometer in CDCl$_3$. Values are given in p.p.m. relative to Me$_4$Si as an internal standard.

§ The unusual pair of three equal intensity peaks for the aziridine protons must be due to the nonequivalence of the vicinal protons. This is perhaps due to their interaction with the aromatic nucleus which gives rise to a paramagnetic shielding of the protons.

sodium there is an induction period, after which the temperature begins to rise rapidly accompanied by development of deep orange to red coloration. This behaviour appears to support a radical chain mechanism. Thiophenol, thioglycollic acid, and nucleophiles such as bisulphite, *etc.*, add to styrene by a free-radical process to give anti-Markovnikov β-substituted products.[6]

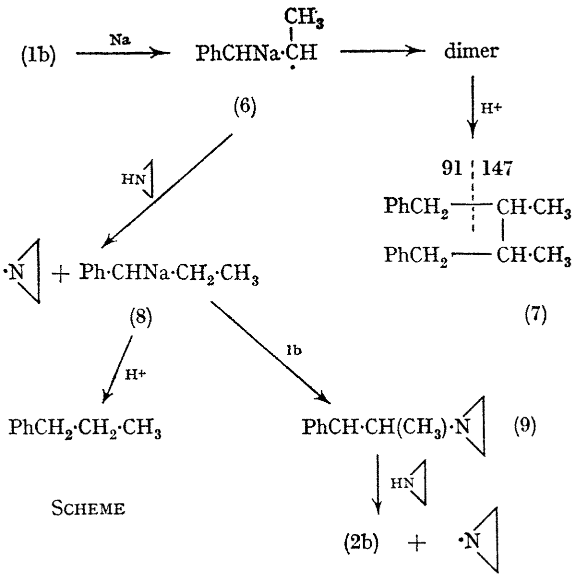
To lend further support to a radical chain mechanism the following experiment was performed. A sample of β-methylstyrene (Aldrich) was purified by preparative g.l.c. The identity and its purity, particularly its freedom from propylbenzene, were demonstrated by g.l.c. and mass spectroscopy. After (1b) had been treated with sodium metal and aziridine, the reaction mixture was worked up and chromatographed under the same conditions. It was found to contain (a) approximately 15% propylbenzene, identified by its retention time under the analysis conditions and by mass spectroscopy, *m/e* 120; (b) 60% (2b), retention time 20 min., mass spectrum (*inter alia*) peaks at *m/e* 161, 91 ($M^+ - 70$), and 70 (base) ($M^+ - 91$) due to the ions $C_6H_5CH_2^+$, 91; and $H_3C\cdot CH:\overset{+}{N}:[CH_2]_2$ 70; and (c) 15% unreacted β-methylstyrene. The mass spectrum of the total reaction mixture showed additional peaks at *m/e* 238 and 147 ($M^+ - 91$) which corresponds to the dimer (7).

We conclude that the reaction proceeds as shown in the Scheme.

It is known that styrene and α-methylstyrene dimerize in the presence of sodium metal *via* intermediates of type (6).[7] The one-electron addition of sodium to styrene occurs exclusively at the α-carbon and is one of the structures postulated by Szwarc[8] in his study of "living polymers" from styrene.

The sodium, therefore, *via* the intermediate (6), acts as an initiator for the generation of an aziridine radical. I further submit that although the formation of the hydrocarbon radical (6) does not in itself prove its intermediacy in the formation of (2b), yet in the light of all the other evidence, the mechanism suggested appears to provide the most satisfactory explanation for the observed results.

I thank Dr. P. Levins for interpretation of spectra.



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