Rearrangement of the 7-Azabenzonorbornadienyl Radical Anion

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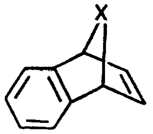
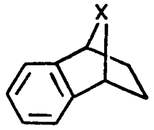
Summary Reaction of 7-azabenzonorbornadienes with potassium in tetrahydrofuran produces radical anions which rearrange to produce either derivatives of pyrrole or of naphthalene.

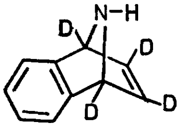
Interest in reactions of the 7-azabenzonorbornadiene system is in evidence.[1] We have found that 7-azabenzonorbornadiene (I) reacts with one equivalent of potassium metal or sodium naphthylide in tetrahydrofuran (THF) to produce 2-phenylpyrrole in 50% yield. Under similar conditions *N*-methyl-7-azabenzonorbornadiene (II) gives a mixture of naphthalene and *N*-methyl-1-naphthylamine, and 7-oxabenzonorbornadiene (III) gives a mixture of naphthalene and 1-naphthol[2] while benzonorbornadiene (IV) fails to react. Treatment of (I)—(III) with potassium in THF at 5° under nitrogen results in disappearance of the metal and the production of deep purple solutions indicative of a solvated free electron. (I) and (II) require 30 min for complete reaction while (III) requires 3 h. If the solvent is changed from THF to n-heptane, a solvent which cannot solvate free electrons, no reaction occurs. The site of the initial electron donation is the 5,6-double bond since the reduced compounds (V)—(VII) do not react with K–THF under these same conditions.



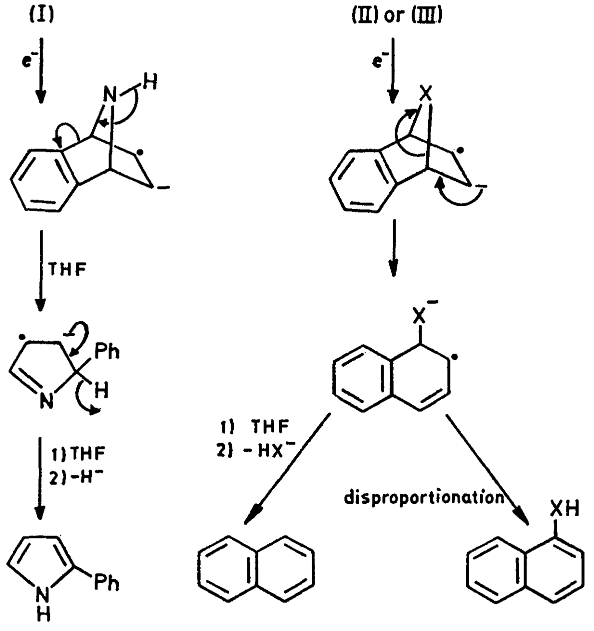
	X
(I)	NH
(II)	NMe
(III)	O
(IV)	CH_2



	X
(V)	NH
(VI)	NMe
(VII)	CH_2



(VIII)



Scheme

The apparent necessity of a hetero-atom at the 7-position for the initial electron donation to occur suggests an intramolecular stabilization of the radical anion by that hetero-atom. Nitrogen is apparently more efficient at stabilizing the radical anion than is oxygen since (I) and (II) were found to react much faster than (III) with potassium. Since (II) gave only naphthalene-type products, it appears that a hydrogen atom must be attached to nitrogen, as in (I), in order to observe pyrrole-type products. This suggests that the N–H bond could be broken during the rearrangement. That this is indeed the case was shown by reacting (I; X = ND) with K–THF, working-up with deuterium oxide, to obtain 2-phenylpyrrole which contained no deuterium as determined by i.r. and n.m.r. analysis. The fate of the bridgehead hydrogen which is lost and the source of the phenyl hydrogen which is gained in the conversion of (I) into 2-phenylpyrrole was determined by treating (VIII) with K–THF. The 2-phenylpyrrole isolated was deuteriated only at the 3-, 4-, and 5-positions of the pyrrole ring as determined by n.m.r. analysis. The source of the hydrogen atoms gained at the phenyl group and at the nitrogen atom of the 2-phenylpyrrole must, therefore, be the solvent. No attempts were made using deuteriated THF to prove this.

We suggest the mechanisms shown in the Scheme to account for all observed products.

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[1] V. Rautenstrauch, *Chem. Comm.*, 1969, 1122; P. Rosso, J. Oberdier, and J. Swenton, *Tetrahedron Letters*, 1971 3947.

[2] A similar reaction with a tetra-t-butylated derivative of (III) has been observed, R. W. Franck, Fordham University, personal communication.