The Dehydronorbornyl–Nortricyclyl Radical Equilibrium

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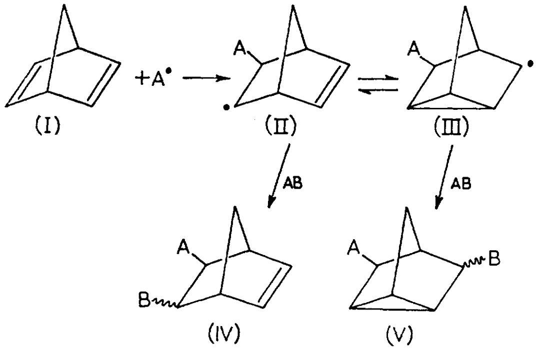
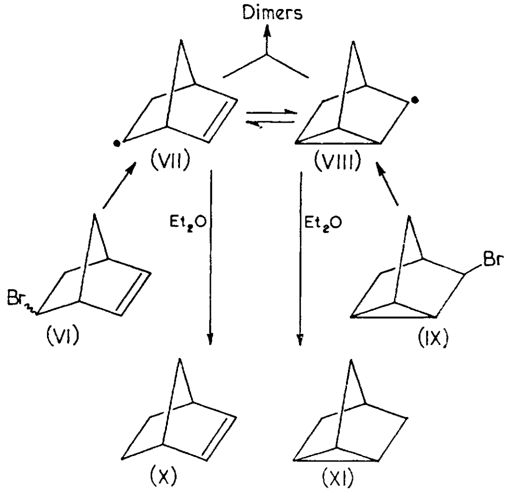
THE free-radical addition of a reagent AB (*e.g.*, thiols,[1,2] polyhalogenomethanes,[2,3] 1-iodoperfluoropropane,[3] aldehydes,[2] benzenesulphonyl halides[4]) to norbornadiene (I) can give a substituted norbornene (IV) and a substituted nortricyclene (V) as products. In many cases, however, the only isolated products have the nortricyclene structure (V).[2,3] The product ratio appears to be governed by the rates of chain transfer with reagent AB of the intermediate radicals (II) and (III) rather than the equilibrium between them. Indeed these addition reactions provide no positive evidence for an equilibrium between the dehydronorbornyl (II) and nortricyclyl (III) radicals, since there is no proof that a nortricyclyl radical (III) can be converted into a dehydronorbornyl radical (II). The results from the addition reactions suggest that any equilibrium is heavily weighted on the side of the nortricyclyl radical (III).



Application to dehydronorbornyl bromide[5] (VI) (a mixture of *endo*- and *exo*-isomers in the ratio 56 : 44) and nortricyclyl bromide[5] (IX) of our recently published procedure[6] for the production of free radicals *via* the cobaltous chloride-catalysed reaction of an organic halide with a Grignard reagent in ether solution has enabled us to study the equilibrium between dehydronorbornyl (VII) and nortricyclyl (VIII) radicals from both sides.



TABLE

Ratio of products formed in the cobaltous chloride-catalysed reaction of MeMgI *with dehydronorbornyl bromide* (VI) *and nortricyclyl bromide* (IX)

Halide	Product ratio %			Norbornene : Nortricyclene
	Norbornene (X)	Nortricyclene (XI)	Dimers*	
(VI)	28·2	66·5	5·3	30 : 70
(IX)	29·2	67·0	3·8	30 : 70

* A mixture of two major and one minor products.

As shown in the Table the major products are norbornene, nortricyclene, and dehydro-dimers, which are formed in approximately the same ratio regardless of the starting halide. This suggests that in these reactions the product ratio is governed largely by a rapidly attained equilibrium between the dehydronorbornyl (VII) and nortricyclyl (VIII) radicals. The radicals are consumed either by dimerization or hydrogen transfer with the solvent ether, processes which are likely to be of comparable rate for both radicals since in the absence of a substituent A, as in (II) or (III), the steric differences between the radicals will be small. At equilibrium we therefore suggest that the proportions of dehydronorbornyl (VII) and nortricyclyl radicals (VIII) present will be similar to those (30:70) of the product norbornene and nortricyclene. The different ratio, 45:55, norbornene:nortricyclene obtained on di-t-butyl peroxide decarbonylation of norborn-5-ene-*endo*-2-carboxyaldehyde[7] may possibly be attributed to the higher temperature (refluxing chlorobenzene) of that reaction compared with our own (refluxing ether).

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