Evidence for the Intermediacy of Discrete Classical Carbanions in the Rearrangements of the 5-Norbornenyl and Benzonorbornenyl systems

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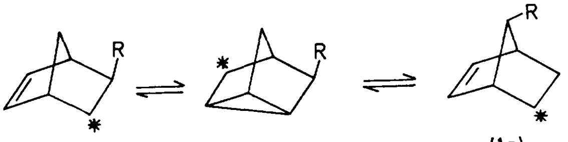
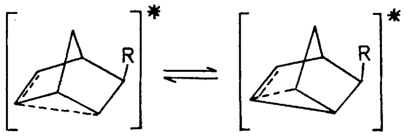
Summary The carbanions in the title series were generated *via* the Birch reduction of norbornadiene and benzonorbornadiene and on the basis of both product and labelling studies evidence is presented which favours the intermediacy of classical carbanions.

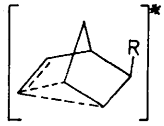
The dichotomy of classical *vs.* nonclassical intermediates in the interconversions of the 5-norbornenyl and 3-nortricyclyl systems, (**1**) ⇌ (**2**) *via* cationic and radical pathways has received widespread attention. The cationic pathway is best described in terms of the interconverting asymmetrical nonclassical homoallylic species, (**3a**) ⇌ (**3b**) (* = +), and which might also involve the nortricyclyl ion (**2**; * = +),[1a,2] whereas the radical pathway almost certainly involves the classical species, (**1**) ⇌ (**2**) (* = ·).[1b,3] The results of a recent investigation by Stille and Sannes[4] on the corresponding carbanionic mechanism were consistent either with the equilibrating charge localised species, (**1**) ⇌ (**2**) (* = —), or with a *single* symmetrical (C_s symmetry) charge delocalised (nonclassical) carbanion, (**4**; * = —).† The conditions of the experiment[4] precluded low-temperature studies of the reaction which could, in principle, distinguish between these alternatives.

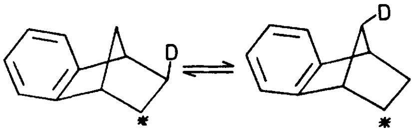
We have studied the carbanionic reactions of the 5-norbornenyl and the benzonorbornenyl systems at −33 °C, *via* the sodium–liquid ammonia reduction of norbornadiene[5] and benzonorbornadiene, and we present evidence which strongly implicates the presence of the classical carbanions, (**1**) ⇌ (**2**), and (**5**; * = —) respectively.

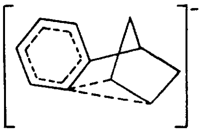
The reduction of norbornadiene in the presence of a proton source (Na, liq. NH_3, −33 °C, tetrahydrofuran as cosolvent, Bu^tOH as proton source) resulted in the forma-


(1) (2) (1a)


(3a) (3b)


(4)


(5) (5a)


(6)

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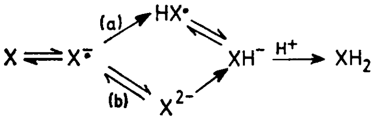
† Specifically, Stille and Sannes[4] generated the deuterium-labelled carbanion from the corresponding precursor of (**1**; R = D) at 60 °C. They isolated, in addition to nortricyclene (57%), equal quantities of the norbornenes (**1**) and (**1a**; R = D, * = H). This result is consistent with either a degenerate rearrangement involving the rapidly equilibrating species, (**1**) ⇌ (**2**), or with the single species (**4**).

tion of nortricyclene and norbornadiene in the ratio of 1 : 19.‡§ When the proton source was omitted, norbornadiene still underwent reduction (albeit slowly) but the nortricyclene-norbornene ratio was *ca.* 1 : 200.

The commonly accepted mechanisms of the metal–ammonia reductions of a substrate X, with and without a proton source,[6] are outlined in the Scheme. In the presence of a proton source more powerful than the ammonia, the radical anion $X^{\bar{\cdot}}$ is converted into the radical HX· [path (a), Scheme], otherwise conversion into the dianion X_2^- occurs [path (b), Scheme]. However, both mechanisms involve the anionic species XH^- as the penultimate intermediate. A necessary condition for the presence of a *single* carbanionic species, irrespective of its classical or nonclassical nature, is that the product ratio be independent of the genesis of that carbanion. Since our findings are not in accordance with this condition we are forced to postulate the existence of at least two discrete carbanions. The larger proportion of nortricyclene formed *via* the proton source pathway [path (a)] is reasonable when one considers that the intermediate norbornenyl radical HX· is known to undergo partial rearrangement to the nortricyclyl radical, even at −58 °C.[1b,3b]¶



SCHEME. (a) Presence of proton source. (b) Absence of proton source.

The second piece of evidence is our observation that the deuterium scrambling of the type observed by Stille and Sannes[4]† is due to a slow rearrangement of the norbornenyl carbanion, (**1**) ⇌ (**1a**) (R=D) rather than to the sole presence of (**4**; R=D). Reduction of norbornadiene in $NaND_3$ (CH_3OD deuteron source, tetrahydrofuran cosolvent, −35°) led to the formation of the following products (yields):§ *exo,cis*-[5,6-$^2H_2$]norbornene (93%) (**1**; R=D, * = *exo*-D), [3,5-$^2H_2$]nortricyclene (4·7%) (**2**; R=D, * = D), and a product which is presumably [7-*anti*-5-*exo*-$^2H_2$]norbornene (2·3%) (**1a**; R=D, * = *exo*-D). ^1H N.m.r. spectroscopy allowed the stereochemical assignments of (**1**)[7a] and (**2**).[7b] Evidence for the presence of (**1a**; R=D, * = *exo*-D) is less direct as its low incidence precluded ^1H n.m.r. analysis. However the ratio** of the mass spectral peaks at *m/e* 66 and 67 of the norbornene fraction revealed the presence (2·3%) of a product with only one of its deuterium atoms located in the ethano-bridge.

Clearly our results rule out the presence of substantial quantities of the nonclassical species (**4**; * = —). The simplest scheme which is consistent with all the data involves the exclusive presence of the classical species (**1**) and (**2**) (* = —) whose rate of interconversion is slow at −33 °C yet rapid at 60 °C.[4]

This conclusion is consistent with the optimised geometrical features, charge distribution and atomic bond indices of the 5-norbornenyl anion obtained by INDO MO SCF calculations. In particular, the C(3)–C(5) atomic bond index is only 0·03 and the excess charges on C(2) and C(3) are merely 0·024 and 0·011 respectively. Clearly the extent of homoallylic charge delocalisation in the anion is minimal.

Finally, insight into the nature of the benzonorbornenyl anion (**5** ⇌ **5a** *vs.* **6**; * = —) was obtained from the results of the reduction of benzonorbornadiene in ND_3 (CH_3OD, Na, tetrahydrofuran, −35 °C). Quantitative formation of [$^2H_2$]benzonorbornene occurred and the ^1H n.m.r. and mass spectral analysis** revealed the presence of the 2,3-*exo,cis*-$^2H_2$ product, (**5**; * = *exo*-D), (97·5%), and a $^2H_2$-scrambled product (*ca.* 2·5%) which is probably (**5a**; * = *exo*-D). This result is inconsistent with the exclusive presence of an intermediate of C_s symmetry (*i.e.* **6**) and we prefer the mechanistic description of two slowly interconverting classical ions, (**5**) ⇌ (**5a**) (* = —).

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‡ Ortiz de Montellano *et al.* apparently failed to detect the presence of any nortricyclene (ref. 5).

§ All products were isolated by pentane extraction and g.l.c. (6 ft column, 30% SE 30 on DCMS-treated chromosorb W). Product identification was by ^1H n.m.r. (Varian, HA100, $CHCl_3$ lock) and mass spectrometry (Varian Mat III GC/MS system operating at 22 eV). Product ratios were estimated by g.l.c.

¶ INDO MO SCF calculations indicate that the geometry of the dianion, X^{2-}, resembles that of norbornadiene (M. N. Paddon-Row, unpublished data). Therefore protonation would be expected to form almost exclusively the norbornenyl anion (**1**) *via* pathway (b) (Scheme).

** The mass spectral fragmentation of norbornene and benzonorbornene is known to occur without hydrogen migration: T. Goto, A. Tatematsu, Y. Hata, R. Muneyuji, H. Tanida, and K. Tori, *Tetrahedron*, 1966, **22**, 2213.

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