Evidence for Hydrogen Abstraction by Classical Radicals in the Norbornenyl-Nortricyclen System*

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ABSTRACT Studies of product compositions and deuterium-label rearrangements at various concentrations of tri-n-butyltin hydride in the reductions of exo- and endo-5-bromonorbornene and 2-bromonortricyclene to mixtures of norbornene and nortricyclene lead to three main conclusions: (i) at least two radical intermediates contribute to product formation; (ii) each intermediate yields predominantly (80% or more) one product; and (iii) nortricyclene is predominantly derived from a symmetrical intermediate. This constitutes strong evidence for hydrogen abstraction by classical (i.e., single-product) norbornenyl and nortricyclen radicals. It is argued that the norbornenyl-nortricyclen system is exceptionally well suited for the generation of a nonclassical (dual-product) radical; hence, the existence of a nonclassical radical in any other system is rather unlikely.

Many rate-enhancement and product-composition studies have implicated nonclassical carbonium ions as reaction intermediates (1). In contrast, no definite evidence has been reported for a nonclassical radical, that is, a σ radical in which the unpaired electron is sufficiently delocalized so that reaction can occur at more than one center or with the stereospecificity characteristic of some nonclassical cations†. Thus, only small rate enhancements have been reported in reactions in which free-radicals are formed (2), and formation of products from classical radical intermediates can account for the results of extensive studies of product composition (3). Indeed, in most cases, the exclusive intermediary of a single localized radical can be ruled out (3). Nevertheless, no available evidence excludes product formation partly from a nonclassical radical. For example, Kuivila’s work on the norbornenyl-nortricyclen system (3a) clearly shows the presence of at least two radical intermediates, but does not reveal their precise nature.

We report here evidence from product-composition and isotopic-labeling studies that the radical intermediates in the norbornenyl-nortricyclen system are, in fact, the classical (i.e., single-product) norbornenyl and nortricyclen radicals (Fig. 1). This is a significant finding, because the norbornenyl-nortricyclen system seems exceptionally well suited for the generation of a nonclassical radical. In this case, (a) a strong driving force for formation of a nonclassical ion is exhibited in carbon-ion reactions (4), (b) the geometrical requirement for effective homolysis participation is built in (5), and (c) the classical radicals may be expected to have closely similar geometries and energies‡. For these reasons, the conclusion that the radicals in this system are classical indicates that the existence of nonclassical radicals in other systems is rather unlikely.

Radical reduction (6) of endo-5-bromonorbornene (endo-I), exo-5-bromonorbornene (exo-I), and 2-bromonortricyclene (II) by tri-n-butyltin hydride in toluene produces norbornene (V) and nortricyclene (VI) as the only major hydrocarbon products (3a), in 90–100% yield, either thermally (0 to 25°C) or photolytically (−10 to 22°C)§. Some results for photolytically initiated reductions at −10°C are shown in Fig. 2.

With both endo-I and II, the relative amount of the unreacted hydrocarbon increases linearly with tin hydride concentration. At least two product-forming intermediates are required to account for this result; for simplicity and economy, the classical norbornenyl (III) and nortricyclen radicals (IV) (Fig. 1) are attractive candidates.

The steady-state hypothesis (7) with the mechanism of Fig. 1 yields for the ratio of V to VI from reduction of exo- or endo-I:

$$\frac{[V]}{[VI]} = \frac{k_3}{k_5 + (k_k/k_d)[BuSnH]} = A + B[BuSnH]. \quad (1)$$

For reduction of II, this ratio is given by

$$\frac{[V]}{[VI]} = \frac{1/A + B/A[BuSnH]}{[1/A + B/A[BuSnH]]^{-1}}, \quad (2)$$

and this should be predictable from product ratios observed with I. The line to the open squares in Fig. 2 has been calculated from Eq. 2, by the use of the values $A = 1.26$ and $B = 0.12$ M$^{-1}$ from the results for endo-I. Although there is a systematic deviation, the anticipated reciprocal inter-

† Thus, the free energies of norbornene and nortricyclene differ by only 1 kcal/mol at 100°C [Schleyer, P. v. R., J. Amer. Chem. Soc., 80, 1700 (1958)], and in each case conversion to the radical requires the breaking of a secondary C–H bond.

§ Samples were degassed and, for the photolytic reaction, were irradiated with a Hanovia 450-W high-pressure mercury lamp for the minimal periods necessary for essentially complete reaction of the bromide.

‡ The systematic error (mostly in the predicted intercept) may arise from competing photo-initiated hydrostannation of norbornene. The intercept relationship seems to be more closely obeyed in thermal reactions.

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† The distribution of the unpaired electron may be the best measure of nonclassical character. However, we use here an operational definition based on reactivity. A stereospecificity argument for a nonclassical radical, Warkentin, J., and E. San-

relationship of slopes and intercepts is reasonably well satisfied. Similar results have been obtained at other temperatures, in thermally initiated reductions, and with the exo-bromide.

If \( k_s/k_a = k_b/k_i \), the mechanism shown in Fig. 3 also conforms to Eqs. 1 and 2 but with different definitions of \( A \) and \( B \). To differentiate these possibilities, we studied the reduction of deuterium-labeled bromonorbornene (VII). Experimental ratios of rearranged (XII) and unarranged (XI) norbornene-d3 are shown in Fig. 2 and the classical-radical mechanism is elaborated in Fig. 4. The pairs of carbon atoms, interchanged when norbornenyl-d3 radicals VIII and X are interconverted, are indistinguishable (apart from the deuterium label) in the nortricyclad3 radical IX. Because IX is the precursor of XIII, the efficiency of the trapping of VIII to X is directly related to that of VIII relative to IX (or III relative to IV) in the classical-radical mechanism. A mechanism in which XIII is to any extent derived from an asymmetrical intermediate predicts less formation of XII for a given concentration of tin hydride, and, in the limiting case (Fig. 3), no XII at all.

For classical radicals, the ratio XI to XII is given by:

\[
[XI]/[XII] = \frac{(k_a^u k_1^v k_2^r)/(k_a^u k_1^v k_2^r)} + [2k_a^u k_1^v k_2^r]/(k_a^u k_1^v k_2^r) + [k_a^u k_1^v k_2^r]/(k_1^v k_2^r)} + (2k_a^u k_1^v k_2^r)/[BuSnH] + 2B^2/A[BuSnH].
\] (3)

If secondary deuterium isotope effects are neglected, Eq. 3 reduces to the form

\[
\] (4)

The experimental ratios actually correspond to about 25% more XII than is predicted by Eq. 4 with \( A = 1.26 \) and \( B = 0.12 \) M\(^{-1}\) (the dashed line in Fig. 2). This difference is consistent with expected isotope effects on the equilibrium
between VIII and X. Thus, rearranged radical X should be favored over VIII at \(-10^\circ C\) by 15-20% because the trigonal \(\alpha\)-deuterated carbon in VIII is tetrahedral in X (8), and by an additional 5-10% because the CD\(_3\) group is adjacent to the radical center in VIII (9), or 20-30% overall**.

For nonzero hydride concentrations, the product ratios calculated from Eq. 3 depend slightly on the manner in which the isotope effect is partitioned among the individual reaction steps. The specification \(k^u = 1.10 \, k_1, k^t = 0.95 \, k_1, k^u = 0.90 \, k_2, k^t = 1.05 \, k_2\) yields the solid line in Fig. 2. Clearly, the classical-radical mechanism accounts for the data and the nonclassical-radical mechanism of Fig. 3 does not.

Alternative mechanisms in which (i) the "norbornyl!" radical is nonclassical and gives nortricyclene and norbornene in a ratio of \(\alpha\), or (ii) the "nortricyclyl" radical is nonclassical and gives norbornene and nortricyclene in a ratio of \(\beta\) cannot be excluded. However, we can show that \(\alpha\) and \(\beta\) must be less than 0.2.

No conclusions can be drawn about the precise distribution of the unpaired electron in either radical. Electron spin resonance studies of the kind recently reported for cyclopropylcarbiny1 and allylcarbiny1 radicals (10) should give direct information on this point, but would offer no test of the possible consequence of delocalization of the unpaired electron. These different approaches to determination of nonclassical character thus complement one another.

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