tonitrile saturated with 9,10-dicyanoanthracene (DCA) produced **8** in 72% yield.[12,13] This latter reaction is presumed to occur via a sensitized-electron-transfer process to give a cation radical intermediate, which may be associated with DCA anion radical. Ample discussion of this mechanism for the photosensitized dimerization of 1,3-cyclohexadiene exists.[14,15]

In summary, we believe that our results indicate that **8**, and not **4**, is the real product of a cation radical mediated dimerization of **1**. The formation of **4**, as catalyzed by **3**, appears to be a protic acid catalyzed process, while the dimerization of 1,3-cyclohexadiene apparently involves the intermediacy of cation radicals. This indicates that great care should be taken in evaluating the mechanistic discussions associated with cation radical reactions initiated by aminium cation radicals. We propose that the systematic use of the series of reactions discussed above will constitute a standard approach for distinguishing when aminium cation radicals lead to a protic acid catalyzed process and when they are involved in a cation radical chain process.

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(11) The rate of formation of **8** was at least 100 times slower than the rate of formation of **4** in the absence of base. Careful examination of the reaction of **1** with **3** in the absence of base showed the presence of trace amounts (<1%) of **8**. It should be noted that the room temperature reaction of **1** with **3** in the presence of di-*tert*-butylpyridine also gave **8** and none of **4** when acetonitrile was used as solvent.

(12) ^{1}H NMR ($CDCl_3$) δ 5.261 (1 H, heptet, J = 1.4 Hz), 5.017 (1 H, hextet, J = 1.5 Hz), 1.90–1.86 (2 H, m), 1.86–1.76 (1 H, m), 1.749 (3 H, d, J = 1.4 Hz), 1.713 (3 H, d, J = 1.4 Hz), 1.65–1.56 (1 H, m), 1.610 (3 H, d of t, J = 1.5, 1.0 Hz), 1.088 (3 H, s), 0.932 (3 H, s), 0.885 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 132.51 (d), 130.79 (d), 130.05 (s), 129.91 (s), 39.78 (s), 38.50 (s), 31.49 (t), 29.07 (q), 27.91 (t), 25.96 (q), 25.32 (q), 23.23 (q), 21.07 (q), 19.24 (q); IR (neat) 3060, 2960, 2915, 1660, 1455, 1398, 1375, 1200, 1090, 1063, 1032, 986, 840 cm^{-1}. A satisfactory elemental analysis and exact mass molecular weight has been obtained for **8**.

(13) Of special significance is the fact that no trace of **4** could be detected in either of the reactions which produced major amounts of **8**.

(14) Libman, J. *J. Chem. Soc., Chem. Commun.* **1976**, 361. Jones, C. R.; Allman, B. J.; Mooring, A.; Spahic, B. *J. Am. Chem. Soc.* **1983**, *105*, 652.

(15) The electron-transfer-sensitized dimerization of 1,3-cyclohexadiene has also been studied by others: Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870. We thank Professor Schuster for informing us of his results prior to publication.

Temperature Dependence of Stereoselectivity as a Criterion for Mechanism. Rearrangement of Bicyclo[2.1.1]hexene-*5-d* and Two Phenyl Derivatives

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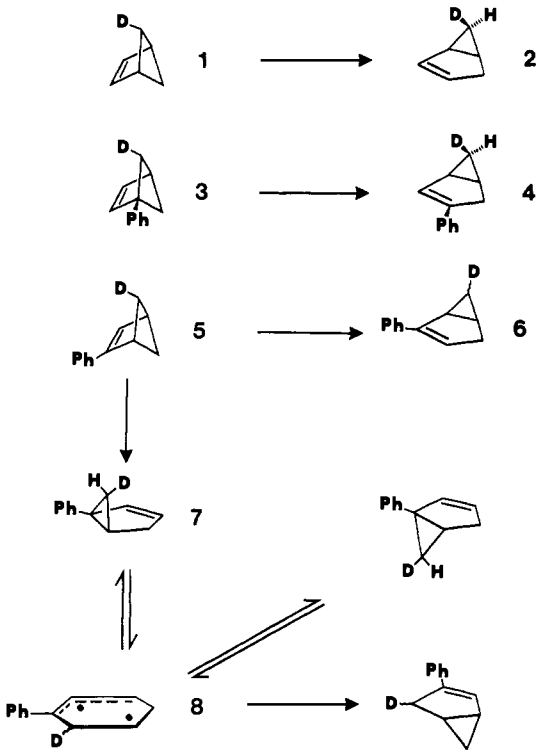
The study of stereochemical changes at a chiral or prochiral center[1] can provide useful insights into mechanism. Reactions that occur with complete retention or complete inversion are generally thought of in terms of single or sequential pathways but not parallel pathways. Reactions that occur with 50% retention are generally considered to involve an intermediate that has lost the stereochemical information of the reactant; the alternative explanation of parallel inversion and retention pathways with coincidentally equal rates is implicitly treated as too improbable to be worth consideration. Problems arise when the reaction exhibits partial loss of stereochemistry. In this case parallel mechanisms are generally invoked but the single experimental observation (inversion/retention ratio) is insufficient to distinguish among the possible combinations of inversion, retention, and intermediate formation.

Scheme I. Main Thermal Reactions of the Bicyclo[2.1.1]hexenes[a]



[a] Only a single stereoisomer is shown for each reactant, although both were used. Only the major stereoisomer of the products from migration of the labeled bridge is shown in each case. See Table I for more details of product ratios.

In the case of sigmatropic rearrangements the allowed and forbidden pericyclic mechanisms can be expected to exhibit pure retention or pure inversion. Unfortunately, the problem of interpretation of partial stereoselectivity, described above, is compounded in this case by the possibility that a biradical might have properties that allow it to retain some stereochemical information.[2] Thus a single pathway leading to a biradical intermediate could, perhaps, exhibit overall stereochemistry that ranges anywhere from complete stereoselectivity to complete loss of stereochemical information. This single fact has been the source of much of the contention in the study of hydrocarbon rearrangement mechanisms. In the present communication we show that by studying the temperature dependence of stereoselectivity one can considerably reduce the number of mechanistic possibilities. We further show that the stereochemistry of biradical reactions might be even more surprising than had previously been considered.

The reactions studied were the formal [1.3]-sigmatropic rearrangements of bicyclo[2.1.1]hexane-5-*d*[3] and its 1- and 2-phenyl derivatives (see Scheme I). Both *exo* and *endo* stereoisomers of these compounds[4] were used in the study. Experiments were conducted on dilute solutions of the compounds in dry, degassed isooctane. The stereochemistry of deuterium incorporation in the products was determined by ^{1}H and ^{2}H NMR, using previously reported assignments for the bicyclo[3.1.0]hex-2-ene ring system.[5]

(1) We use these terms despite their imprecision (Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319–3328) because the alternatives are so cumbersome in this case.

(2) Borden, W. T. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1980; Vol. 2. Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; p 311.

(3) For a study on the rearrangement of the unlabeled compound, see: Frey, H. M.; Hopkins, R. E.; O'Neal, H. E.; Bond, F. T. *J. Chem. Soc. D* **1969**, 1069. The stereochemistry of the rearrangement of 5-methylbicyclo[2.1.1]hexene was reported in: Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607–2610.

(4) Newman-Evans, R. H.; Carpenter, B. K., unpublished results.

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Table I. Rearrangements of Compounds **1**, **3**, and **5**

reactn	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[a] cal/(mol K)	KIE[b]	stereoselectivity	
				T, °C	% retentn
1 → **2**	34.8 ± 0.3[c]	3.9 ± 0.6[c]	1.07 ± 0.03	135.2	1.9 ± 0.4
				165.7	2.7 ± 0.3
				197.0	6.9 ± 0.5
3 → **4**	28.9 ± 0.2[d]	0.0 ± 0.6[d]	1.25 ± 0.05	80.0	9.1 ± 0.3
				110.5	9.3 ± 0.4
				140.6	9.2 ± 0.4
				165.7	8.8 ± 0.3
5 → **6**	35.7 ± 0.3[e]	1.6 ± 0.6[e]	*f*	*f*	*f*
5 → **7**	32.7 ± 0.2[e]	0.0 ± 0.5[e]	1.26 ± 0.05	124.9	12.1 ± 0.3
				144.6	11.7 ± 0.6
				160.2	12.7 ± 0.7
				181.3	11.7 ± 0.3

[a] Determined from unlabeled compounds. [b] Intramolecular kinetic isotope effect; see text for explanation. [c] Rate constants measured at six temperatures from 130.1 to 175.3 °C. [d] Rate constants measured at seven temperatures from 82.6 to 133.5 °C. [e] Rate constants measured at seven temperatures from 130.1 to 181.3 °C. [f] Insufficient material to make the measurements.

The stereoselectivity was determined by integration of the ^2H NMR spectrum. All reactions showed good first-order kinetics over more than 4 half-lives. Bicyclo[2.1.1]hexenes recovered from partial reaction showed no sign of label scrambling. Products were, with one exception, found to be stable to the reaction conditions. The exception was 1-phenylbicyclo[3.1.0]hex-2-ene (**7**), which slowly epimerized and rearranged to 3-phenylbicyclo[3.1.0]hex-2-ene, presumably by way of the cyclohexene-1,5-diyl (**8**).[6] The reported regio- and stereoselectivity of the rearrangement of 2-phenylbicyclo[2.1.1]hexene is corrected for this secondary reaction. Results for all of the compounds are summarized in Table I.[7]

Cursory examination of the results might make it appear that the rearrangements of bicyclo[2.1.1]hexene and the two phenyl derivatives are mechanistically similar since all three show high but incomplete stereoselectivity with a preference for inversion of configuration. However, determination of the temperature dependence of the stereoselectivity reveals that this apparent similarity is misleading. The stereoselectivity of rearrangement of the parent compound shows clear temperature dependence, strongly suggesting the existence of parallel reaction pathways with different activation energies. The stereoselectivities of rearrangement of the phenyl-substituted compounds, on the other hand, are temperature independent, within our experimental precision. It seems improbable that there would be two parallel pathways with identical activation energies for even one compound, but to observe it for two is, in our opinion, too unlikely to be worth serious consideration. We prefer instead a mechanism involving a single rate-determining step leading to an "intermediate" (not necessarily a local minimum on the potential energy surface) that can collapse to give the product with both possible stereochemistries. This suggestion, that the phenyl-substituted compounds rearrange by a mechanism substantially different from that of the parent, is supported by the observation that the intramolecular isotope effects (ratio of unlabeled to labeled bridge migration) are very similar for the 1-phenyl and 2-phenyl compounds but very different from that for the parent (see Table I).

A plausible identity for the "intermediate" is a singlet biradical. This would explain why **5** reacts by preferential cleavage of the distal carbon–carbon bond despite the fact that the product so derived is thermodynamically less stable than that from cleavage of the proximal bond. The biradical from cleavage of the distal bond contains a 1-phenylallyl unit whereas the biradical from cleavage of the proximal bond contains a cross-conjugated 2-phenylallyl moiety.

If one accepts a biradical mechanism for rearrangement of **3** and **5** then it becomes intriguing to inquire what leads to the observed preference for inversion of configuration. It is not a least motion process, as invoked for the formally analogous rearrangement of 7,7-dimethylbicyclo[4.1.1]octadiene,[8] since, in the present case, least motion would give retention of configuration. One can not invoke a biradical in a potential energy well with barriers of different heights leading to the products with retention and inversion of stereochemistry since this would give a temperature-dependent stereoselectivity even if formation of the biradical were rate determining. It may well be that experimental determination of the temperature dependence of stereoselectivity in several other systems will be necessary before this phenomenon can be properly understood.

Acknowledgment. Support of this work by the NIH (Grant GM 27022) is gratefully acknowledged.

(5) Srinivasan, R.; White, L. S.; Rossi, A. R.; Epling, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7299–7304.

(6) Cooke, R. S.; Andrews, U. H. *J. Org. Chem.* **1973**, *38*, 2725–2727; *J. Am. Chem. Soc.* **1974**, *96*, 2974–2980.

(7) A referee has inquired why the activation entropies seem to be smaller for the phenyl-substituted compounds than for the parent if the former are biradical processes and the latter largely a pericyclic reaction. Two factors probably play a role. The first is statistical: the parent compound has a choice of four equivalent bonds to break whereas the phenyl-substituted compounds each have a choice of only two. This means that the effective activation entropy must be lower for the substituted compounds by R ln 2 or 1.38 cal/(mol K). The second effect concerns rotation about the bond to the phenyl group. This is likely to be more restricted in the putative biradicals because of p_π–p_π overlap. It is interesting to note, then, that when the phenyl would have to be at the nodal position of the allyl radical moiety (as in **5** → **6**) the activation entropy is a little higher.

(8) Borden, W. T.; Lee, J. G.; Young, S. D. *J. Am. Chem. Soc.* **1980**, *102*, 4841–4843.

Crossed-Beam Study of an Acid–Base Reaction of Neutral Molecules

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Crossed molecular beams are one of the few experimental ways of determining the detailed dynamics of a chemical reaction: examining how the chemical bonds are made and broken during the reactive collision.[1] We report here a crossed-beam study of one of the oldest chemical reactions, the reaction of an acid and a base to form a salt.

$$HI + (n\text{-}Bu)_3N \rightarrow I^- + (n\text{-}Bu)_3NH^+ \qquad (1)$$

This is also a chemiionization reaction in that the reactants are neutral but the products are ions. Only the two product ions in (1) were seen. The details of the apparatus have been described previously.[2] Briefly, two supersonic nozzle beams are crossed at right angles in a vacuum chamber. The product ions are collected, mass analyzed, and detected by an electron multiplier. The beam of HI is prepared by passing a mixture of HI and He through a glass nozzle which can be heated. The beam of tri-*n*-butylamine is prepared by injecting the liquid amine into a flowing stream of He which then passes through a similar nozzle. In both cases the reactants form less than 2% of the beam, and we expect negligible concentrations of dimers or polymers in the beams. The ion collector is mounted on the rotatable lid of the vacuum chamber so that the angular distribution of the product ions can be taken. Ions are formed in a grid cage, which forms a field-free region. Those that pass through the entrance to the

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(2) Alben, K. T.; Auerbach, A.; Ollison, W. M.; Weiner, J.; Cross, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3274. Auerbach, A.; Cross, R. J.; Saunders, M. *Ibid.* **1978**, *100*, 4908. Lee, L.; Russell, J. A.; Su, R. T. M.; Cross, R. J.; Saunders, M. *Ibid.* **1981**, *103*, 5031. Russell, J. A.; Hershberger, J. F.; McAndrew, J. J.; Cross, R. J.; Saunders, M. *J. Phys. Chem.* **1984**, *88*, 4494.

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