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	stereoselectivity % 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 ^{2}H 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

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(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.

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.

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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.

$$HI + (n\text{-}Bu)_3N \rightarrow I^- + (n\text{-}Bu)_3NH^+ \qquad (1)$$
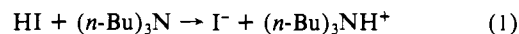
This is also a chemiionization reaction in that the reactants are neutral but the products are ions. Only the two product ions in (1) were seen. The details of the apparatus have been described previously.[2] Briefly, two supersonic nozzle beams are crossed at right angles in a vacuum chamber. The product 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
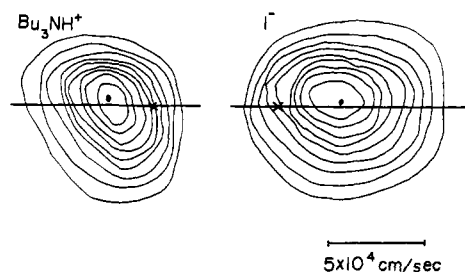
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Figure 1. Cartesian probability contours for both ion products in the reaction of HI and tri-*n*-butylamine at a relative energy of 3.65 eV. The relative velocity is 3.65 × 10⁵ cm/s. The lines are a portion of the relative velocity vector; × is the position of the center of mass. The contour diagrams are shown side by side for clarity, but the center of mass is the same point in space for both diagrams. ● is the position of maximum intensity, and the contours are 90%, 80%, 70%, ... of the maximum. The HI beam goes to the right and the amine beam to the left. The spread in the two beam velocities is roughly 1.3 × 10⁴ cm/s (hwhm).

detector pass through a retarding potential energy analyser, an ion lens, and a quadrupole mass filter before they are detected by an electron multiplier. In a typical experiment we first take the angular distribution of one of the product ions with the retarding potential off to collect all the ions at a particular angle. Then, at each angle, the voltage on the retarding grid is scanned to obtain the energy distribution. This then is normalized to the raw angular distribution. There are several coordinate systems that can be used, but we prefer a Cartesian distribution[3] with an origin at the center of mass, $P_C(u_x, u_y, u_z)$, where **u** is the product velocity.

Figure 1 shows the Cartesian contour diagrams for the product ions at an initial relative energy of 3.65 eV. The straight line is the initial relative velocity vector which extends well beyond both edges of the two diagrams. × is the position of the center of mass, and ● is the position of the maximum in the product intensity. The curves surrounding the maximum are contours at 90%, 80%, ... of the intensity of the maximum. The reaction occurs by way of a direct, modified stripping process so that the I⁻ is found in the direction of the HI beam and the ammonium ion along the amine beam. If the reaction were to proceed by way of a collision complex whose lifetime was comparable to or longer than the duration of a rotation, product intensity would be symmetric about the center of mass, which is not observed. The heat of the reaction is readily computed from the proton affinity of tri-*n*-butylamine,[4] the dissociation energy of HI,[5] the ionization potential of H, and the electron affinity of I to be 79.5 kcal/mol (3.45 eV). The reactants thus have 4.6 kcal/mol in excess of the heat of the reaction. At the 100% contour the final translational energy is 3.0 kcal/mol so that most of the energy of the products is found in translation. It should be noted however, that the energy spread of the two beams is larger than this so that there is a considerable uncertainty in the fraction of energy that appears in translation vs. internal modes. Since the tri-*n*-butylamine is tetrahedral as is the final ammonium ion, one would expect little if any vibrational energy in the N–C bending or stretching modes. One might expect vibrational energy in the N–H stretch, but this is apparently not so. The reaction may occur on two or more potential energy surfaces.

A simple model of the reaction is that the HI passes near the tri-*n*-butylamine, and the proton jumps from the I to the N. The product ions are then gradually decelerated by the Coulombic attraction as they separate. The reaction is direct in that the reactive intermediate lives less than one rotational period.

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Registry No. (*n*-Bu)₃N, 102-82-9; HI, 10034-85-2.

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2-Azaadamant-1-ene and 4-Azaprotoadamant-3-ene

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We report the preparation of matrix-isolated 2-azaadamant-1-ene (**1**), the most highly twisted bridgehead imine observed so far, and some of its unusual properties. Two byproducts, 4-azaprotoadamant-3-ene (**2**) and 3-noradamantylnitrene (**3**), have also been identified.
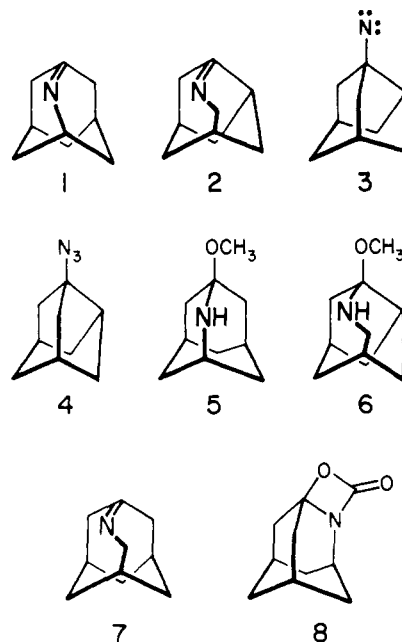
Irradiation of 3-azidonoradamantane (**4**) in methanol solution at room temperature produces the methanol adducts **5** and **6**, presumably originating in **1** and **2**, respectively.[2,3] When **4**, isolated in solid argon or polyethylene at 12 K,[4] is irradiated at 308 nm,[5] its UV and IR peaks gradually disappear and a new set of peaks appears. Concurrently, N₂ is formed (Raman).

The new IR and UV peaks belong to two distinct ESR-inactive species, one red and one colorless. The spectra are readily separated (Figures 1 and 2) since the red species is slowly destroyed by irradiation at 488 nm (Ar⁺ laser) or rapidly at 254 nm (low-pressure Hg arc). Visible light has no effect on the colorless species, but UV irradiation slowly destroys it. Both species are stable indefinitely in the matrix in the dark (in polyethylene matrix at least up to 100 K) and are destroyed upon warm-up. The structures of the secondary photoproducts and warm-up products are not known.

Irradiation (308 nm) of **4** in a methanol-doped Ar matrix yields the same two products (UV, IR). On subsequent warm-up to ~36 K the red species disappears and several IR bands characteristic

(1) (a) University of Utah. (b) On sabbatical leave from the University of Marburg, Marburg, West Germany. (c) University of Wisconsin—Milwaukee. (d) Presented at the 187th National American Chemical Society Meeting, St. Louis, MO, April 1984.
(2) Sasaki, T.; Eguchi, S.; Okano, T.; Wakata, Y. *J. Org. Chem.* **1983**, *48*, 4067.
(3) The use of ethanol and dibutylamine as trapping reagents produced similar results: Jawdosiuk, M.; Kovacic, P. *J. Chem. Soc., Perkin Trans. 1* in press.
(4) The characteristic IR bands of **4** (Ar, 12 K) are 2099 (*as* N₃ stretch), 1258 (*sym* N₃ stretch), 721 and 564 (N₃ bend) cm⁻¹. The UV spectrum (polyethylene, 12 K) shows maxima at 216 and 288 nm. ¹³C NMR (CDCl₃) δ 34.1, 37.4, 43.0, 43.4, 47.9, 72.1.
(5) XeCl excimer laser.