Intramolecular and Intermolecular Pathways to Nortricyclane in Bamford–Stevens Reactions[1,2]

Alex Nickon* and Nick H. Werstiuk[3]

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received January 21, 1972*

Abstract: Our objective was to distinguish, unambiguously, intramolecular and intermolecular pathways to a cyclopropane ring produced in Bamford–Stevens reactions under typical "aprotic" and "protic" conditions. Thermal decomposition of the sodium salts of norbornan-2-one-*6-exo-d* and *-6-endo-d* tosylhydrazones (**2b** and **3b**) in diglyme containing an excess of sodium methoxide produced deuterionortricyclane with no deuterium loss from either precursor. Therefore, the three-membered ring was formed entirely by an intramolecular 1,3 insertion, or its equivalent. On the other hand, in ethylene glycol the nortricyclane obtained from the *6-exo-d* substrate lost 21% of its label and that from the *6-endo-d* substrate lost 52%. In this solvent, therefore, at least 52% of the cyclopropane product arises *via* an intermolecular path that allows incorporation of an external proton. A cationic route involving protonation of a diazohydrocarbon to give a diazonium ion followed by 1,3 elimination can be supported more strongly than a cationic route involving protonation of a carbene. The preference for loss of the endo proton from C-6 parallels the behavior observed in other 1,3 eliminations in the norbornyl system.

The alkaline decomposition of tosylhydrazones (Bamford–Stevens reaction)[4] is of importance for the synthesis of olefins and cyclopropyl compounds, and its mechanistic features involve carbanion, carbonium ion, and carbene chemistry.[5] Diazohydrocarbons have been established as key intermediates whose subsequent breakdown gives olefins, insertion products, and rearrangement products in ratios that depend strongly on solvent; *e.g.*, aprotic solvents favored skeletally rearranged olefins.

Consideration of the types of products and how their ratios varied with solvent led Powell and Whiting[6] and Friedman and Shechter[7] to propose that the intermediate diazohydrocarbons decomposed *via* carbenoid paths in "aprotic" media and *via* cationic paths in "protic" media. Subsequent work revealed that other factors also influenced the course of tosylhydrazone and diazohydrocarbon reactions, including the type and concentration of alkali, the presence of metal cations and Lewis acids, the polarity of aprotic media, the acidity and proton equivalence of protic media, structural constraints in the substrate, etc.[8–12] These studies also made it clear that carbenes and carbonium ions can behave similarly with respect to hydride shifts, carbon skeleton rearrangements, and formation of cyclopropyl "insertion" products, and therefore that product ratios are not reliable criteria for the differentiation of carbenoid and cationic pathways. A striking example of unexpected behavior is the Bamford-Stevens reaction of cyclopropylcarboxyaldehyde tosylhydrazone from which the product of apparent insertion (*i.e.*, bicyclobutane) is favored in protic medium and the skeletally rearranged olefin (*i.e.*, cyclobutene) is favored in aprotic medium.[10a]

Our objective was to establish whether the cyclopropane ring in nortricyclane produced in a Bamford–Stevens reaction under typical "aprotic" and "protic" conditions actually arises from an intramolecular or an intermolecular path, or from both paths. We recently communicated our findings that in the aprotic solvent, diglyme, the three-membered ring is formed exclusively by an intramolecular route, whereas in the protic medium, ethylene glycol, a path involving incorporation of an external proton is substantially involved.[2] We now present the details and some extensions of that study.[13]

Methods

Formation of the tricyclic hydrocarbon nortricyclane (**4**) from norbornan-2-one tosylhydrazone (**1b**) by either intra- or intermolecular mechanisms must necessarily

(1) This work was supported by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society. The mass spectrometer was obtained with instrument grants from the Atomic Energy Commission and the National Science Foundation.

(2) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, 88, 4543 (1966).

(3) Taken largely from the Ph.D. dissertation of N. H. Werstiuk, The Johns Hopkins University, 1966.

(4) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(5) For reviews see: (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 3, p 47; (b) W. Kirmse, *Progr. Org. Chem.*, 164 (1964); (c) R. A. More O'Ferrall, *Advan. Phys. Org. Chem.*, 5, 331 (1967).

(6) J. W. Powell and M. C. Whiting, *Tetrahedron*, 7, 305 (1959); (b) J. W. Powell and M. C. Whiting, *ibid.*, 12, 168 (1961).

(7) (a) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, 81, 5512 (1959); (b) L. Friedman and H. Shechter, *ibid.*, 82, 1002 (1960); (c) L. Friedman and H. Shechter, *ibid.*, 83, 3159 (1961).

(8) C. H. DePuy and D. H. Froemsdorf, *ibid.*, 82, 634 (1960).

(9) (a) J. W. Wilt and C. A. Schneider, *Chem. Ind. (London)*, 21, 865 (1963); (b) J. W. Wilt and W. J. Wagner, *J. Org. Chem.*, 29, 2788 (1964); (c) J. W. Wilt, J. Kosturik, and R. C. Orlowski, *ibid.*, 30, 1052 (1965); (d) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *ibid.*, 31, 1543 (1966).

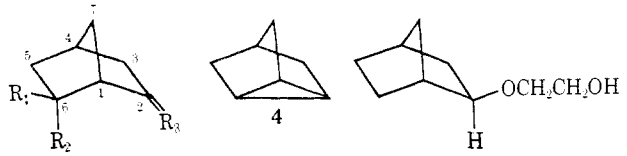
(10) (a) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Amer. Chem. Soc.*, 87, 659 (1965); (b) J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, 87, 935 (1965); (c) G. M. Kaufman, J. A. Smith, G. G. Van der Stouw, and H. Shechter, *ibid.*, 87, 935 (1965); (d) J. H. Bayless, F. D. Mendicino, and L. Friedman, *ibid.*, 87, 5790 (1965); (e) F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, 88, 3870 (1966); (f) J. H. Bayless, L. Friedman, F. B. Cook, and H. Shechter, *ibid.*, 90, 531 (1968).

(11) (a) R. H. Shapiro, *Tetrahedron Lett.*, 3401 (1966); (b) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, 89, 471, 1442 (1967); (c) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *ibid.*, 90, 4762 (1968); (d) R. H. Shapiro and M. J. Heath, *ibid.*, 89, 5734 (1967); (e) R. H. Shapiro, *Tetrahedron Lett.*, 345 (1968); (f) R. H. Shapiro and K. Tomer, *Chem. Commun.*, 460 (1968).

(12) (a) G. L. Closs, R. A. Moss, and S. H. Oak, *J. Amer. Chem. Soc.*, 88, 364 (1966); (b) K. B. Wiberg and J. M. Lavanish, *ibid.*, 88, 365, 5272 (1966); (c) W. Kirmse and K. Horn, *Chem. Ber.*, 100, 2698 (1967); (d) H. Philip, M. K. Lowery, and J. Havel, *Tetrahedron Lett.*, 5049 (1967); (e) J. E. Herz and E. Gonzales, *Chem. Commun.*, 1395 (1969).

(13) Meanwhile, others have also obtained direct evidence for competition between intramolecular and intermolecular paths in protic medium.[10e,f,11b]

involve a hydrogen at C-6. Therefore, the availability of norbornan-2-one-*6-exo-d* **2a** and norbornan-2-one-*6-endo-d* **3a** from homoketonization routes[14] provided a direct opportunity to get the desired information. Creation of the three-membered ring by any intramolecular process (*e.g.*, carbene insertion) would result in no deuterium loss, whereas any reasonable path involving external proton incorporation would require some deuterium loss from at least one of the deuterated epimers. The use of substrates having deuterium remote from the carbonyl group obviates complications that might arise by an exchange at enolizable sites during formation or decomposition of tosylhydrazones.[15] An additional advantage is that under either protic or aprotic conditions norbornan-2-one tosylhydrazone gives nortricyclane (**4**) as the predominant hydrocarbon product; the olefin, norbornene, is a minor product.[7c]



1, $R_1 = R_2 = H$
2, $R_1 = D$; $R_2 = H$
3, $R_1 = H$; $R_2 = D$

a, $R_3 = O$
b, $R_3 = NNHTS$

Our project gives no information on the mechanism of olefin formation, but some recent work with open-chain systems deals with that aspect.[10f]

The tosylhydrazones **1b**, **2b**, and **3b** were prepared[16] and each was heated in an "aprotic" medium (diglyme containing 8.9–9.1 equiv of sodium methoxide) and in a "protic" medium (ethylene glycol containing 3.4–3.6 equiv of dissolved sodium).[7,11b,17] The large excesses of alkali were used to ensure complete conversion of the tosylhydrazone to its sodium salt[18] and therefore to preclude the likelihood that free tosylhydrazone or toluenesulfinic acid could serve as a proton source, a possibility known to occur when there is a deficiency of alkali.[10a,11b]

The proportions of nortricyclane and norbornene in the hydrocarbon product were determined by analytical glpc, and pure nortricyclane was isolated by preparative glpc. Its deuterium content was assayed by mass spectroscopy and in some cases was independently checked by combustion analysis (falling drop method).

(14) (a) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Amer. Chem. Soc.*, **85**, 3713 (1963); (b) A. Nickon and J. L. Lambert, *ibid.*, **88**, 1905 (1966); (c) A. Nickon, J. L. Lambert, and J. E Oliver, *ibid.*, **88**, 2787 (1966); (d) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

(15) For example, loss of some enolizable deuterium occurs during formation and/or alkaline decomposition of camphor-*3-d*$_2$ tosylhydrazone to camphene-*d* in ethylene glycol.[14c] The presence of exchangeable hydrogens can complicate interpretation of Bamford–Stevens reactions conducted in deuterated media (see ref 10e, f, 11b, 12b).

(16) D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

(17) P. K. Freeman and D. G. Kuper, *ibid.*, **30**, 1047 (1965).

(18) (a) For example, the NH in acetone mesylhydrazone has $pK_a = 8.5$.[6a] (b) The 1 equiv of methanol released on formation of the sodium salt has been shown to be ineffective as a proton source when an excess of alkali is used.[10a,11b] (c) In other systems it has been shown that the difference between a slight deficiency of sodium methoxide (0.8 equiv) and a slight excess (1.1 equiv) can dramatically alter the course of the reaction. Possibly, free tosylhydrazone or toluenesulfinic acid can catalyze proton transfer from the liberated methanol or from adventitious proton sources.[10a]

Table I. Decomposition of Norbornan-2-one Tosylhydrazones

		Nondeuterated (**1b**)	6-*exo*-Deuterio (**2b**)[a]	6-*endo*-Deuterio (**3b**)[b]
Concn (*M*) of substrate	Aprotic	0.26	0.26	0.26
	Protic	0.18	0.21	0.21
Concn (*M*) of alkali	Aprotic	2.11	2.36	2.36
	Protic	0.65	0.72	0.72
% nortricyclane in hydrocarbon[c]	Aprotic	99	99[d]	99[d]
	Protic	93	93[e]	92[e]
% loss of original deuterium[f]	Aprotic		0	0
	Protic		21[g]	52

[a] Prepared from ketone **2a** having 10.3% d_0, 89.7% d_1, 0% d_2; 95–98% configurationally pure *exo-d*. [b] Prepared from ketone **3a** having 13.4% d_0, 86.6% d_1, 0% d_2; 90–95% configurationally pure *endo-d*. [c] The only other hydrocarbon was norbornene. [d] The yield after isolation by preparative glpc was *ca.* 40%. Similar losses on glpc collection were experienced in separate controls with authentic samples. [e] The yields after separation and purification by preparative glpc were 11% from **2b** from 7% from **3b**. [f] Determined mass spectroscopically and corrected for slight errors (<1.5%) caused by a large M − 1 peak. Correction factors were obtained from independent combustion analyses on some of the samples. [g] The value differs slightly from that (19%) originally reported (ref 2) because of refinement in mass spectral calculations.

The results are summarized in Table I. In a separate run with natural abundance substrate **1b** in ethylene glycol we also examined the nonvolatile as well as volatile products and obtained 35% of a compound identified as the hydroxy ether **5**, and *ca.* 1% of two unknown components. The hydroxy ether **5** had mass and nmr spectra consistent with its assigned structure ($C_9H_{16}O_2$). Because of overlapping signals, we could not assess the configurational homogeneity of hydroxy ether **5** by nmr; however, we believe it to be largely (if not entirely) exo from this fact: solvolysis of *exo*-norbornyl brosylate in ethylene glycol gave us a hydroxy ether whose nmr was identical with that of **5** except for minor differences in fine structure.[19] Powell and Whiting also observed formation of glycol monoethers (25–35% yields) in Bamford–Stevens reactions of cyclohexanone and decalone sulfonylhydrazones conducted in ethylene glycol.[6]

Results and Discussion

Aprotic Medium. The nortricyclane obtained from either the *6-exo-d*-epimer **2b** or the *6-endo-d* epimer **3b** had lost no deuterium (Table I) and, therefore, the cyclopropyl ring is derived exclusively by an intramolecular path. Clearly, diglyme at 140–150° in the presence of 8–9 equiv of sodium methoxide functions as an aprotic medium despite the fact that 1 equiv of methanol is liberated by the tosylhydrazone on salt formation and despite the possibility of some solvent breakdown under the hot alkaline conditions.[20] The results also establish that no deuterium is lost from the substrate, from any intermediate, or from the product under the experimental conditions.

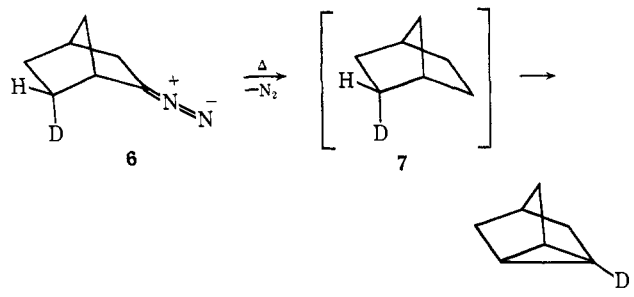
The results are understandable in terms of current views[5,7] in which the sulfonylhydrazone anion loses toluenesulfinate anion to give a thermally unstable diazohydrocarbon **6**. Loss of nitrogen from **6** produces a carbene **7**, which undergoes 1,3 insertion to form

(19) Solvolysis of *exo*-norbornyl brosylate produces exo substitution products with high stereoselectivity. For references see G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 201 (1966).

(20) W. H. Snyder, J. Parascandola, and M. Wolfinger, *J. Org. Chem.*, **31**, 2037 (1966).

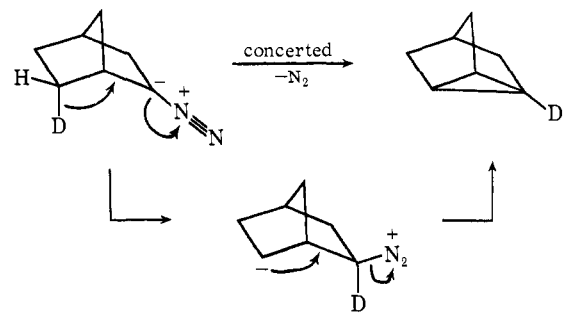
a cyclopropane ring. This intramolecular pathway is illustrated with the *6-endo-d* isomer in Scheme I, each step of which has ample precedent.[10c]

Scheme I



Although the sequence shown is completely satisfactory we wish to point out that variants in which the movement of the deuterium accompanies or precedes loss of nitrogen (Scheme II)[21] are also consistent with

Scheme II



the deuterium results and cannot be convincingly ruled out by any information in the literature. Interestingly, the three substrates **1b**, **2b**, and **3b** give comparable proportions of olefin, indicating that if any isotope effect accompanies insertion into the *6-endo-d* bond it plays no effective role in determining the nortricyclane–norbornene ratio under the experimental conditions.[22]

Protic Medium. In hot ethylene glycol containing 3.4 equiv of base, the nortricyclane from *6-exo-d* substrate **2b** lost 21% of the original amount of deuterium, and that from *6-endo-d* precursor **3b** lost 52%. Consequently, under these protic conditions there exists a path to the three-membered ring that permits unequal deuterium loss from the 6-exo and 6-endo position and incorporation of an external proton. The excess of alkali virtually ensures that the external proton source is ethylene glycol rather than the parent tosylhydrazone.[10a,11b] We must first consider the possibility that deuterium is lost by exchange in nortricyclane or by other side reactions (*e.g.*, homoenolization[14] in substrates or intermediates).

That the deuterium loss is not a result of exchange in the product is clear because both deuterium precursors gave different extents of isotope loss, and is supported by the known resistance of nortricyclane to exchange of its hydrogens even under more drastic alkaline treatment.[23] To ensure that nortricyclane and norbornene are not interconverted by alkali[24] we separately showed that a 60:40 mixture of the two hydrocarbons remained unaltered after alkaline treatment that was considerably more vigorous than that used in our experiments.

There is no information in the literature bearing on the question of the occurrence of homoenolization-like processes in tosylhydrazones or diazohydrocarbons of fused ring systems, but the following facts tend to dismiss this possibility. (a) Wolff–Kishner reductions of both labeled ketones **2a** and **3a** are known to proceed without any deuterium loss.[14a] The experimental conditions and the intermediates in those reductions represent the closest available analogies to the alkaline tosylhydrazone medium. In addition, the acidity of the NH and of the enolizable protons at C-3 would further diminish any likelihood of homoenolization-like processes involving C-6. (b) Homoenolization in bicyclo[2.2.1]-heptanones is not only a much slower process[14] than is the present Bamford–Stevens decomposition (see Experimental Section), but is known to prefer *6-exo-d* over *6-endo-d*, just the opposite of the result in Table I. (c) No homoenolization occurred in diglyme (*vide supra*) and although it might be argued that the tosylhydrazone anion has limited solubility in this solvent and may have little opportunity to undergo exchange, the derived diazohydrocarbon should remain in solution prior to its thermal decomposition. (d) No loss of deuterium from the methyl groups occurs during Bamford–Stevens reaction of the tosylhydrazone of isobutraldehyde-d_6 (diglyme, $NaOCH_3$, 160°).[22c]

Our results in the protic medium are most simply, and satisfactorily, explained by the view that a diazonium ion, or a carbonium ion, is formed as an initial ionic intermediate by protonation of a diazohydrocarbon or of a carbene, respectively.[6,7] Scheme III uses the *6-endo-d* substrate to illustrate these cationic paths involving diazohydrocarbon protonation[25] and carbene protonation.[26] Intramolecular paths, as discussed earlier for the aprotic runs, may compete with the processes in Scheme III but could not affect the deuterium content and so the higher deuterium loss in Table I (52% from **3b**) represents the minimum contribution from nonintramolecular paths in ethylene glycol.[27,28]

(21) (a) Powell and Whiting (ref 6b) invoked concerted hydrogen shift and nitrogen loss to account for olefins in Bamford–Stevens reactions. For kinetic evidence against concertedness when the migrating group is SCH_2CH_3, see J. H. Robson and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 7112 (1967). (b) Transannular insertions in monocyclic systems (C_7–C_{10}) produce only cis fused bicyclic products. Consequently, if carbanions are intermediates, they do not undergo pyramidal inversion; see ref 7c and A. C. Cope, M. Brown, and G. L. Woo, *J. Amer. Chem. Soc.*, 87, 3107 (1965).

(22) (a) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, 78, 3224 (1956); (b) H. M. Frey, *ibid.*, 80, 5005 (1958); (c) W. Kirmse, H.-D. v. Scholz, and H. Arold, *Justus Liebigs Ann. Chem.*, **711**, 22 (1968).

(23) P. G. Gassman and F. V. Zalar, *J. Amer. Chem. Soc.*, 88, 3070 (1966).

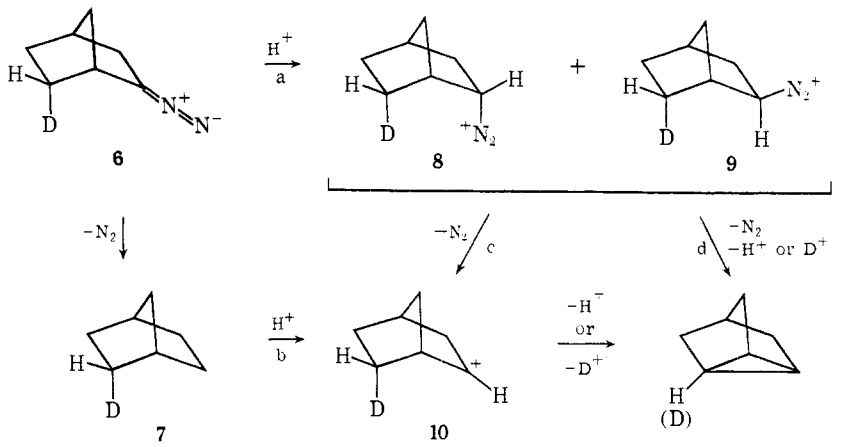
(24) The hydrocarbons can be equilibrated (*ca.* 4:1 ratio) with a silica–alumina catalyst. See Experimental Section and also P. von R. Schleyer, *ibid.*, 80, 1700 (1958).

(25) (a) For proton transfer to diazohydrocarbons see: D. Bethell and J. D. Callister, *J. Chem. Soc.*, 3801, 3808 (1963); D. W. Thomas and K. Biemann, *J. Amer. Chem. Soc.*, 87, 5447 (1965); G. L. Closs, R. A. Moss, and S. H. Goh, *ibid.*, 88, 365 (1966). (b) Step a may be reversible: L. Friedman, "Carbonium Ions," Vol. 2, G. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 655–713. (c) Interventions of hydrogen-bonded or N-protonated intermediates[12b] prior to eventual C protonation are detailed variations that could be incorporated into the interpretation.

(26) For protonation of carbenes and the reverse process see: (a) W. Kirmse, L. Horner, and H. Hoffman, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958); (b) W. Kirmse, *ibid.*, **666**, 9 (1963); (c) R. A. Olofson, S. W. Walinsky, J. P. Marino, and J. I. Jernow, *J. Amer. Chem. Soc.*, 90, 6554 (1968).

(27) The following line of reasoning suggests that the contribution from intermolecular ionic paths that do not scramble deuterium is *ca.* 54%, and that from ionic paths that scramble the deuterium is less than 4%. Let I = per cent of reaction *via* ionic paths that *do not* scram-

Scheme III



The carbonium ion path (path b) formally produces the norbornyl cation **10** which subsequently loses H^+ or D^+ to produce nortricyclane. If cation **10** is initially classical and can lose a proton before undergoing a Wagner–Meerwein or other degenerate rearrangement, then a different deuterium loss from exo and endo substrates is expected since the exo and endo bonds differ sterically and stereoelectronically. However, it is known that the norbornyl cation produced from *exo*-2-norbornyl tosylate in strongly alkaline medium becomes degenerate before it captures a nucleophile to give exo products.[29,30] By the same token, if ion **10** during its lifetime undergoes one Wagner–Meerwein shift the exo and endo bonds at C-6 become interconverted, and this scrambling requires that the norbornyl cation from either substrate **2b** or **3b** experiences the same deuterium loss. It is clear from Table I that the 6-exo and 6-endo positions do not become equivalent during the Bamford–Stevens reaction, and therefore protonation of a carbene (path *b*) or other sequences (*e.g.*, paths a + c) that produce a scrambled norbornyl cation (classical or nonclassical) cannot be the only ionic pathway, and may even be a minor one.[27,28] Consequently we favor paths a + d involving protonation of the diazohydrocarbon **6** to give a diazonium ion (**8** and **9**) followed by bimolecular 1,3 elimination. In the pathway a + d the exo–endo distinction at C-6 is maintained, and the preference for abstraction of endo deuterium (*cf.* 52% in **3b** *vs.* 21% in **2b**) is in line with other examples of 1,3 eliminations in the norbornyl system.[29,31a] Exo protonation of **6** should be preferred on steric grounds and would lead to more endo diazonium species **8** than exo diazonium species **9**.[31b] However, both of these epimers could undergo 1,3 eliminations,[29] and their proportion is not critical to any of our conclusions.[32]

Formation of the glycol monoether **5** largely, if not exclusively, with exo stereochemistry is also understandable in terms of nucleophilic attack on **8** and **9** by the solvent because the substitution products produced on deamination of *exo*- or *endo*-norbornylamines are known to be largely exo.[33,34] Interestingly, the high ratio of nortricyclane/norbornene (even if corrected for contribution from an intramolecular path[27]) also seems consistent with diazonium intermediates since deamination of *exo*- and *endo*-norbornylamines is known to produce high ratios of these two hydrocarbons.[25b] We recognize, however, that the experimental conditions being compared are dissimilar and so this parallelism provides suggestive, but not compelling, support.

Although the *cationic* path a + d is sufficient to account for our results we wish to point out that the commonly used term "cationic" may be too restrictive, since one can conceive of *anionic* routes that could lead to the same results (*e.g.*, see Scheme IV). A path analogous to that shown could accommodate the stereochemical results reported for the formation of bicyclobutane.[10f,12b] An intramolecular variant of this path in which N^- performs the abstraction to give an intermediate RN=NH could also accommodate the interesting view[10e] that bicyclobutane can arise in part from an ionic path that does not involve an external proton.[35]

ble the C-6 hydrogens; S = per cent ionic paths that do scramble the C-6 hydrogens (*e.g.*, *via* degenerate norbornyl cation); in alkaline solvolysis this pathway is known to result in loss of 0.31 of the C-6 deuterium;[28] C = per cent insertion paths (*i.e.*, paths that involve zero deuterium loss); Y = positive isotope effect (k_H/k_D) for H abstraction at C-6 in path *I*; P = ratio of rate of abstraction of a C-6 endo hydrogen to that of a C-6 exo hydrogen in path *I*. We have $I + S + C = 100\%$; % D loss from the *6-endo-d* substrate = $PI/Y + 0.31S + 0.0C = 52$; % D loss from the *6-exo-d* substrate = $I/PY + 0.31S + 0.0C = 21$. For 1,3 eliminations in KO-*t*-Bu–*t*-BuOH the nonscrambling ionic path has been shown to involve Y values of 1.6–1.8 (av = 1.7) and P values of 1.5–1.7 (av = 1.6). If we assume these average values hold approximately for the present ethylene glycoxide system the equations can be solved and lead to the following (rounded) figures: $I = 54\%$; $C = 42\%$; $S = 4\%$.

(28) The 0.31 figure in footnote 27 reflects largely the deuterium isotope effect (k_H/k_1, = 2.2) for proton loss from a scrambled norbornyl cation and applies strictly to KO-*t*-Bu–*t*-BuOH.[29] The derived value for *I*, however, does not depend on this figure, and the derived value for *S* is relatively insensitive to it. For example, if this isotope effect ranged from 1.0 to 10 the value of *S* would range only from *ca.* 3 to 13%.

(29) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, 89, 3914, 3915, 3917 (1967).

(30) *E.g.*, the *exo-tert*-butyl ether produced from *exo*-2-tosylate in 0.93 *M* KO-*t*-Bu–*t*-BuOH has the C-H bonds at C-6 scrambled.[29] The norbornyl cation produced in conventional buffered solvolysis in acetic acid also becomes degenerate before conversion to products.[19] We recognize that the gegenion situations in solvolyses are different from those in carbene protonations and could affect the lifetime of cationic intermediates.

(31) (a) N. H. Werstiuk and I. Vancas, *Can. J. Chem.*, 48, 3963 (1970); N. H. Werstiuk, *Chem. Commun.*, 1499 (1970); (b) P. Yates and J. D. Fenwick, *J. Amer. Chem. Soc.*, 93, 4618 (1971).

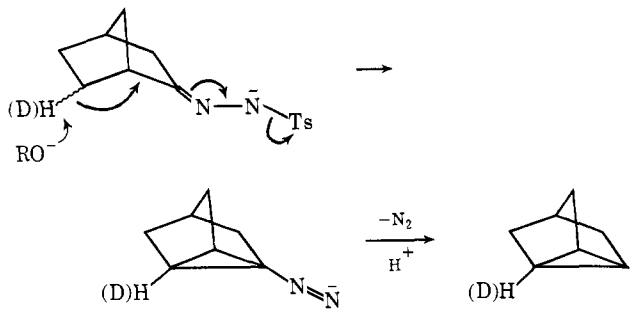
(32) Any α elimination (*e.g.*, in **8**) would produce carbene **7**, which does not introduce any additional intermediates. The question of α elimination as a competitive pathway in the formation of cyclopropyl rings in 1,3 elimination has been examined and will be reported separately (A. Nickon and J. Morgan, unpublished results).

(33) (a) J. A. Berson and A. Remanick, *J. Amer. Chem. Soc.*, 86, 1794 (1964); (b) E. J. Corey, J. Casanova, P. A. Walahencherry, and R. Webster, *ibid.*, 85, 169 (1963).

(34) Compare the formation of *exo-tert*-butyl ether on the treatment of either *exo*- or *endo*-norbornyl tosylates under strong alkaline conditions (KO-*t*-Bu–*t*-BuOH).[29]

(35) D. J. Cram and J. S. Bradshaw, *J. Amer. Chem. Soc.*, 85, 1108 (1963).

Scheme IV



Although we do not favor anionic paths[36] they have not, to our knowledge, been ruled out experimentally, and until such time perhaps the term cationic should be replaced by the less restrictive term ionic in discussions of Bamford–Stevens pathways.

Experimental Section

General. Melting points were taken in capillary tubes in a Herschberg apparatus equipped with thermometers calibrated against a set standardized by the National Bureau of Standards. The melting points are corrected and rounded to the nearest 0.5°. Infrared spectra were recorded on Perkin-Elmer Model 137 and 21 spectrophotometers equipped with NaCl optics and prisms and Perkin-Elmer Model 337 and 521 spectrometers equipped with gratings. Band positions are uncalibrated and are expressed in reciprocal centimeters. Perkin-Elmer Model 226, Aerograph Model A-700, and Varian-Aerograph Model 204 gas chromatographs were used for glpc analyses. Product ratios were obtained by tracing and weighing glpc peaks. Nuclear magnetic resonance spectra were recorded on a Varian Model A-60 spectrometer in CCl_4 or $CDCl_3$ with tetramethylsilane as the internal reference. Mass spectra were obtained on Consolidated Electrodynamics Model 21, 03C and Perkin-Elmer-Hitachi RMU-6-A mass spectrometers. All solutions were dried over anhydrous Na_2SO_4 or $MgSO_4$. Pentane was stirred over 30% fuming sulfuric acid, washed with bicarbonate, and distilled. Diglyme was shaken over KOH pellets and distilled. Ethylene glycol was purified by distillation from sodium.

Deuterium Assay. Mass spectroscopic assay of the norcamphor-*6-exo-d* and -*6-endo-d* gave values of 89.7 and 86.6% d_1, respectively. These are reliable values in that the M − 1 peak in norcamphor is 4% of M^+. The deuterium assay on several nortricyclanes was done by the falling drop method[38] as a check on the mass spectroscopic values because in the hydrocarbon the M − 1 peak is 40% of M^+. The deuterionortricyclane obtained from **3b** under "aprotic" conditions assayed mass spectrometrically and by the falling drop method showed values of 89.0 and 87.7% d_1, respectively. The methods gave values of 40.4 and 41.7% d_1, respectively, for the deuterionortricyclane obtained from **3b** under "protic" conditions. Since values obtained by the falling drop method, in this case, are more reliable than the mass spectrometric values they are used in deuterium loss calculations. The deuterium assays on the deuterionortricyclanes which were obtained from tosylhydrazone **2b** under "aprotic" (92.5% d_1) and "protic" (71.2% d_1) conditions were determined mass spectrometrically and are corrected by interpolation: −1.4 for the former and −0.3 for the latter. Our work also shows that fingerprint infrared spectroscopy may be used to determine the amount of deuterium on the three-membered ring in nortricyclane-d_1 in a d_0–d_1 mixture. A comparison of the fingerprint regions (Figure 1) of nortricyclane and nortricyclane-d_1 (86.6% d_1 species) recorded in CS_2 shows that a strong bond at 668 cm^{-1} with virtually base-line separation from adjacent peaks is present in the d_1 species but absent in d_0. Therefore, the intensity of the band is useful at least as a qualitative measure of the amount of d_1 present in a d_1–d_0 mixture when the deuterium is on the three-membered ring.

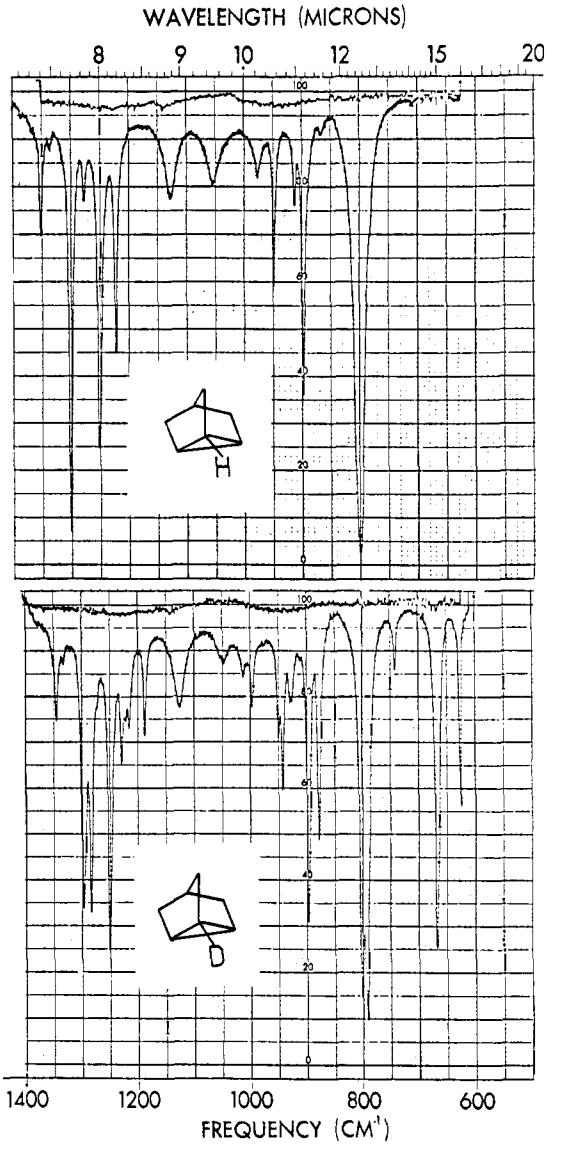


Figure 1. The ir fingerprint regions (CS_2) of nortricyclane and nortricyclane-d_1.

Methanol-*O*-*d*. Methanol-*O*-*d* (350 g) was prepared from dimethyl carbonate (800 g) and D_2O as described by Streitwieser, *et al.*[39] That the methanol-*O*-*d* was 90–95% isotopically pure was determined by nmr by comparison of the integral of the C_{13} satellite of the methyl group to that of the integral for OH.

Acetic Acid-*O*-*d*- in Deuterium Oxide. Acetic anhydride (distilled from molecular sieve, bp 139–140°, 190 g, 1.86 mol) and deuterium oxide (110 ml, 6.12 mol) each were added to each of two dried flasks, protected from atmospheric water by silica gel tubes, and refluxed for 20 hr. The nmr integral data showed that the solution contained *ca.* 5.6% OH.

Isomerization of Norbornene.[24] Norbornene (500 g, 5.3 mol) was purified by distillation from sodium to yield 450 g of a white solid. Silica–alumina catalyst[40] (16.5 g) was added and the mixture was refluxed for 2 hr. Monitoring the reaction by glpc showed that the equilibrium mixture of 80% nortricyclane–20% norbornene had

(36) Among other things, one might expect anionic routes to favor olefin formation by analogy to the mechanism for the Caglioti reaction[37] and to the reaction of tosylhydrazones with alkyllithiums.[11e,d]

(37) (a) R. Caglioti and M. Magi, *Tetrahedron*, **19**, 1127 (1963); (b) M. Fisher, Z. Pelah, D. H. Williams, and C. Djerassi, *Chem. Ber.*, **98**, 3236 (1965); (c) F. Y. Edamura and A. Nickon, *J. Org. Chem.*, **35**, 1509 (1970).

(38) Analyses were performed by J. Nemeth, Urbana, Ill.

(39) A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

(40) The original catalyst (S-90) used was supplied by Houdry Chemical Co. Subsequent experiments with a deactivated silica–alumina catalyst ($^3/_{16}$-in. extrusions, high pore volume, obtained from Grace and Co., Baltimore, Md) required careful monitoring since prolonged heating tended to convert the norbornene to a motor oil like liquid.

been reached after 1.5 hr. The norbornene–nortricyclane mixture was distilled, bp 96–105° (750 mm), to yield 350 g of a white solid.

1-Acetoxynortricyclane (1-Acetoxytricyclo[2.2.1.0^{2,6}]heptane). The ester (134 g, 98% pure by glpc) was prepared from a mixture of 110 g of norbornene and nortricyclane as reported previously.[41a,41b]

Homoketonization of 1-Acetoxynortricyclane. Acid Medium. To each of the prepared CH_3COOD–D_2O solutions contained in a flask stopped with a serum cap, acetoxynortricyclane (36.6 g, 0.25 mol, 98% pure) was added with a 50-ml syringe. To each solution, D_2SO_4 (99.8% d_2, 10 g, 0.10 mol) and D_2O (99.7% d_2, 25 ml, 1.25 mol) were added with 5- and 50-ml syringes, respectively. The mixture was stirred at 25 ± 3° for 44 hr. Water (250 ml) was added to each ketonization mixture and each was extracted with purified pentane (one 250-ml portion, four 150-ml portions). The pentane layers from both extractions were combined and dried. The pentane was distilled off through a 1-m Vigreux column to yield an oily residue with the odor of acetic acid. To the oil was added 100 ml of a solution made up of methanol (100 ml), water (50 ml), and KOH (5 g). The solution was stirred at 25 ± 3° for 21 hr and was worked up by the addition of water (150 ml) and extraction with pentane (one 200-ml portion, four 100-ml portions). The solvent was distilled off and the alkaline washing procedure was repeated twice more to yield 43 g (78%) of norbornan-2-one after the solvent was removed under vacuum. A sublimed sample had mp 90–92° (lit.[16] 92–93°), and mass spectrometric analysis showed 13.4% d_0, 86.6 d_1, and 0% d_2; ir (CS_2) 1740 (s), 965 (m), 940 (s), 870 (s), and 775 (m) cm^{-1} was identical with the spectrum of norbornan-2-one-*6-endo-d*[14d] and indicated that the deuterium at C-6 was at least 90–95% stereochemically pure endo.

Alkaline Medium. To each of two 500-ml flasks (dried in the oven and flushed with N_2) fitted with a condenser and stoppered with a rubber septum was added methanol-*O-d* (180 ml, 4.5 mol, 90–95% d_1) with a 50-ml syringe. While dry N_2 was bubbled through the solution, potassium (1.5 g, 0.04 mol) was added to each flask followed by 1-acetoxynortricyclane (37.5 g, 0.26 mol). The solution was stirred at 25 ± 3° for 2.5 hr. Water (200 ml) and NaCl (75 g) were added and the solution was extracted with purified pentane (one 200-ml portion, three 150-ml portions). The pentane was distilled off and the residue was treated with one 225-, 150-, and 300-ml portion of the MeOH–H_2O–KOH wash solution to wash deuterium out of the enolizable sites as described above. The pentane was distilled off through a 1-m Vigreux column and the last trace of solvent was removed by aspirator vacuum to yield 48 g (87%) of norbornan-2-one-*d*. A sublimed sample had mp 91–92° (lit.[16] mp 92–93°). Mass spectral analysis showed 10.3% d_0, 89.7% d_1, and 0% d_2 species; ir (CS_2) 1740 (vs), 973 (s), 973 (s), 936 (s), 878 (m), 842 (s) cm^{-1} was identical with the spectrum of norbornan-2-one-*6-exo-d* reported previously[14d] and established that the deuterium at C-6 was at least 95–98% stereochemically pure exo.

Norbornan-2-one Tosylhydrazone. This tosylhydrazone (3.4 g, 60%, mp 205–207°) (lit.[16] mp 206.5–208°) was prepared from tosylhydrazine (4.0 g, 0.22 mol) and norbornan-2-one (2.4 g, 0.22 mol, mp 90–92°) as described by Farnum.[16]

Norbornan-2-one-*6-exo-d* Tosylhydrazone. The tosylhydrazone (6.3 g, 74%, mp 204–206°) was obtained similarly from norboran-2-one-*6-exo-d* (3.4 g).

Norboran-2-one-*6-endo-d* Tosylhydrazone. The tosylhydrazone (6.3 g, 74%, mp 204–206°) was prepared similarly from norbornan-2-one-*6-endo-d* (3.4 g).

Decomposition of Tosylhydrazones. Protic Medium. Run 1. Norbornan-2-one tosylhydrazone (0.6 g, mp 205–207°) was added to purified ethylene glycol (10 ml). Sodium (0.2 g) was dissolved in the solution as N_2 was swept over the mixture. The resulting clear solution was heated and at 130° N_2 evolution began and became brisk at 170°. The mixture was heated at 200° for 30 min, then poured into water (40 ml) saturated with NaCl. The mixture was extracted with 50:50 pentane–ether (two 30-ml portions). Analysis of the extract by glpc (10 ft × 1/8 in., 10% SE-30 on Chromosorb W; temperature programming 85 → 230°) showed that the hydrocarbon fraction was composed of 7% norbornene and 93% nortricyclane. The glycol monoether **5** (35%) and two minor components (1%) with retention times between norbornene and the ether were also present. The solvent was evaporated off and the glycol monoether **5** (0.07 g) was isolated and purified from the residue by preparative glpc: nmr ($CDCl_3$) δ 3.65 (br m, 5, OCH), 2.70 (s, 1, OH), 2.25 (m, 2, bridgehead C–H), 1.7–0.85 (m, 8, norbornyl envelope).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.23; H, 10.25. Found: C 69.18; H, 10.41.

Run 2. Norbornan-2-one-*6-exo-d* tosylhydrazone (2.5 g, 0.0093 mol, mp 204–206°) was added to purified ethylene glycol (45 ml) in a flask set up with a condenser, thermometer, and nitrogen inlet. Nitrogen was bubbled through this solution for *ca.* 10 min, then sodium (0.75 g, 0.033 mol) was added and the mixture was heated to 170°. Brisk N_2 evolution occurred. A temperature of 170° was maintained for 30 min and then raised to 215° for 20 min. The solution was cooled and the hydrocarbons that had sublimed into the condenser were washed down with ether (3 ml) and the mixture was shaken to form a homogeneous solution. An aliquot (5 ml) was added to water (10 ml) and extracted with ether (5 ml). Analytical glpc (9 ft × 1/8 in., 15% Squalane on Chromosorb W column) showed norbornene and nortricyclane in the ratio 7.1:92.9. The remaining reaction mixture was heated to 180° and nitrogen was vented (15 min) through the solution and through a "V" tube cooled in Dry Ice. The hydrocarbon that collected in the tube was taken up in ether. Nortricyclane (0.090 g, 11%, >99% pure by glpc) was isolated pure by preparative glpc (20 ft × 3/8 in., diethylene glycol succinate on Chromosorb W, 65°). The deuterium content was determined mass spectrometrically, 71.2% d_1 and 28.8% d_0 species. The quantity of norbornene was too small to be collected. No attempt was made to isolate the glycol monoether in this run.

Glpc analysis of a duplicate of run 2 with 0.5 g of tosylhydrazone showed norbornene and nortricyclane in a ratio of 7.1:92.9.

Run 3. Norbornan-2-one-*6-endo-d* tosylhydrazone (2.5 g, 0.0093 mol, mp 204–206°) was carried through the procedure as described in run 2. Glpc analysis of the hydrocarbon fraction showed norbornene (7.6%) and nortricyclane (92.4%). The deuterionortricyclane (0.060 g, 7%) was isolated by preparative glpc, and assayed for deuterium mass spectroscopically (40.4% d_1 and 59.6% d_0) and by the falling drop method (41.7% of one deuterium atom per molecule). The small quantity of norbornene could not be collected efficiently.

Analytical glpc analysis of the hydrocarbon fraction of a duplicate run 3 with 0.5 g of tosylhydrazone showed norbornene (7.8%) and nortricyclane (92.2%).

Aprotic Medium. Run 1. Norbornan-2-one-*6-exo-d* tosylhydrazone (2.0 g, 0.0074 mol, mp 204–206°) was added to purified diglyme (28 ml) in a flask equipped with a condenser, thermometer, and nitrogen inlet. Freshly prepared sodium methoxide (3.2 g, 0.065 mol) was added. The mixture was refluxed (150–170°) and the hydrocarbon, along with some methanol and diglyme, was vented with N_2 (0.5 hr) into a "V" tube cooled with liquid nitrogen. The hydrocarbon (41%) was collected from this solution by preparative glpc and assayed for deuterium mass spectrometrically, 92.5% d_1 and 7.5% d_0 species.

A duplicate of run 1 was carried out with 0.5 g of tosylhydrazone. In this case N_2 was not vented through the solution mixture but rather was poured into water (10 ml) and extracted with ether (5 ml). Glpc analysis of the ether extract showed norbornene (0.2%) and nortricyclane (99.8%).

Run 2. Norbornan-2-one-*6-endo-d* tosylhydrazone (2.0 g, 0.0074 mol, mp 204–206°) was carried through the procedure as described in run 1 above. The hydrocarbon fraction consisted of norbornene (0.3%) and nortricyclane (99.7%) as was determined by analytical glpc of the methanolic solution. The deuterionortricyclane (0.27 g, 40%) was isolated pure by preparative glpc from the methanolic solution collected in the "V" tube, and assayed for deuterium mass spectrometrically and by the falling drop method. Mass spectrometry showed 89.0% d_1 and 10.0% d_0 species; the falling drop method showed 87.7% of one deuterium atom per molecule.

Solvolysis of Norbornyl Brosylate in Ethylene Glycol. Norbornyl brosylate (0.27 g, mp 55.5–57°) and solid $NaHCO_3$ (0.20 g) were added to purified ethylene glycol (5 ml) and the mixture was heated for 6 hr at 50°. The mixture was poured into water (25 ml) and extracted with purified pentane (one 25-ml portion and one 10-ml portion). The glycol monoether **5** (0.025 g) was isolated and purified by preparative glpc (10 ft × 1/4 in., 15% Carbowax on Chromosorb W, temp 200°); nmr ($CDCl_3$) δ 3.60 (br m, 5, OCH), 2.24 (m, 2, bridgehead CH), 2.15 (s, 1, OH), 1.7–0.85 (m, 8, norbornyl envelope).

(41) (a) H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); (b) H. Hart and R. A. Martin, *J. Amer. Chem. Soc.*, **82**, 6362 (1960).