phatic copper(I) compounds, since these reactions give fundamentally different types of products. For example, thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I) at room temperature in ether gives butane (50%) and 1-butene (50%), but no detectable octane. Details of these reactions will be discussed in later papers.

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Nortricyclene Precursors in Bamford–Stevens Reactions[1]

Sir:

Diazohydrocarbons can be generated and decomposed in hot alkoxide solutions of aldehyde and ketone tosylhydrazones.[2,3] Studies of product ratios revealed a strong solvent dependence and led to the generalization that cationic paths prevail in "protic" media whereas carbenoid intermediates are involved under "aprotic" conditions.[4,5] Subsequent investigations uncovered additional complexities and have made it clear that carbenes and energetic cations can behave similarly with respect to carbon skeleton rearrangements, hydride shifts, and the formation of insertion products, and therefore product ratios are not reliable criteria for the existence of carbenoid or cationic precursors.[3,6–9] We wish to report direct experimental evidence that distinguishes insertion and cationic mechanisms in a bicyclo[2.2.1]heptane system and imposes restrictions on the nature of the cations.

Thermal decomposition of norbornan-2-one tosylhydrazone with an excess of alkali in diglyme and in ethylene glycol gives a hydrocarbon mixture that consists almost entirely of nortricyclene (*ca.* 99%[4d] and 93%, respectively). The experiments described below establish that (i) the three-membered ring arises completely by an intramolecular insertion path in the diglyme system, (ii) in ethylene glycol a cationic path competes in which an external proton is incorporated on carbon,[10] (iii) protonation of 2-carbenanorbornane[11] to the corresponding carbonium ion is not the only cationic path (and may even be a minor one), and (iv) an ionic progenitor of nortricyclene exists which is not the norbornyl cation encountered in solvolytic studies.

Norbornan-2-one (**1a**, mp 90–92°), 6-*exo*-deuterionorbornan-2-one (**2a**, mp 91–92°; 10.3% d_0, 89.7% d_1, 0% d_2), and 6-*endo*-deuterionorbornan-2-one (**3a**, mp 90–92°; 13.4% d_0, 86.6% d_1, 0% d_2)[12,13] were converted to their corresponding tosylhydrazones.[14] Each derivative was thermally decomposed in "aprotic" medium (diglyme containing an excess of dissolved sodium methoxide) and in "protic" medium (ethylene glycol containing an excess of dissolved sodium). The nortricyclene was isolated and assayed for deuterium mass spectroscopically. Results are summarized in Table I.

Table I. Decomposition of Norbornan-2-one Tosylhydrazones

		Non-deuterated (**1b**)	6-*exo*-Deuterio (**2b**)	6-*endo*-Deuterio (**3b**)
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
% nortricyclene in hydrocarbon	Aprotic	>99	>99	>99
	Protic	93.2	92.9	92.3
% loss of original deuterium[a]	Aprotic	. . .	0	0
	Protic	. . .	19	52

[a] Independent combustion analyses indicated that the mass spectroscopic assays are accurate to *ca.* ±1.5%.

In the "aprotic" runs the nortricyclene had the same deuterium content as did its corresponding deuterated precursor. Therefore the new ring arose from the diazohydrocarbon entirely by an insertion path (path A) involving intramolecular transfer of hydrogen (in the case of **4**) or deuterium (in the case of **6**).[15] This is the behavior expected for a carbenoid intermediate or its equivalent.

In the "protic" runs each labeled substrate lost an appreciable fraction of its deuterium. Consequently a substantial proportion of the nortricyclene is produced from an intermediate that acquired an external proton. Importantly, the different deuterium loss from each substrate (*cf.* 19 and 52%)[16] reveals the existence of an intermediate whose behavior is that expected for neither a bridged norbornyl cation nor a pair of equilibrated classical norbornyl cations, because these species do not preserve the original stereochemical distinction at C-6 and require that the fraction of isotope loss be identical from each substrate.[17] These

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the National Science Foundation for financial support.

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

[3] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, Chapter 3, p 47.

[4] (a) J. W. Powell and M. C. Whiting, *Tetrahedron*, **1**, 305 (1959); (b) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (c) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **82**, 634 (1960); (d) L. Friedman and H. Schechter, *ibid.*, **83**, 3159 (1961).

[5] For relevant observations and comments on the "protic" and "aprotic" character of solvents see ref 3, 4b, and 8.

[6] (a) J. W. Wilt, J. M. Kosturik, and R. C. Orlowski, *J. Org. Chem.*, **30**, 1052 (1965); (b) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *ibid.*, **31**, 1543, (1966).

[7] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

[8] (a) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **87**, 659 (1965); (b) J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, **87**, 661, (1965).

[9] J. H. Bayless, F. D. Mendicino, and L. Friedman, *ibid.*, **87**, 5790 (1965).

[10] *Cf.* K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 365 (1966), and also ref 8a.

[11] For this nomenclature see ref 3, p 3.

[12] A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963).

[13] (a) A. Nickon and J. L. Lambert, *ibid.*, **88**, 1905 (1966); (b) A. Nickon, J. L. Lambert, and J. E. Oliver, *ibid.*, **88**, 2787 (1966); (c) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

[14] D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

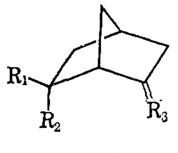
[15] In nortricyclene the cyclopropyl C–H stretching vibration appears as a doublet at *ca.* 3070 cm^{-1} in CS_2, whereas the deuterated nortricyclene showed a single band at this position with reduced intensity.

[16] The different outcome from each labeled compound also establishes that the deuterium is not lost from nortricyclene after its formation. Loss of deuterium by homoenolization is not expected under the experimental conditions.[12,13]

[17] A classical norbornyl cation that is neutralized by proton loss before it can undergo Wagner–Meerwein or other rearrangements could preserve the *exo–endo* distinction at C-6. Such behavior, though conceivable, is presently contrary to known experience with the norbornyl cation: J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

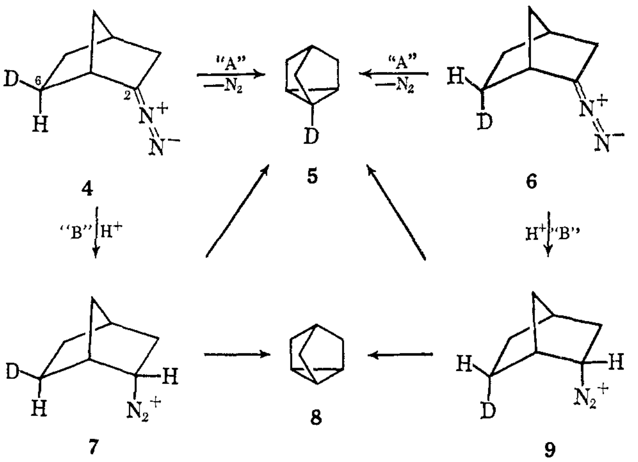
results also exclude protonation of the carbene as the sole cationic pathway, because such protonation must formally produce a norbornyl cation.

We suggest as the *simplest* interpretation that an important reactive species preceding nortricyclene is a diazonium ion or its equivalent, derived possibly by protonation of the corresponding diazohydrocarbon (path B).[18,19] Because *exo* protonation should be favored sterically,[20] the C–N bond is probably largely in the *endo* configuration (**7** and **9**). Unimolecular and bimolecular 1,3 elimination from **7** or **9** can lead to deuterated or nondeuterated nortricyclene (**5** and **8**, respectively) according to whether an *exo* or *endo* hydrogen (or deuterium) is abstracted from C-6.



a, $R_3 = O$;
b, $R_3 = NNHTs$

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



The greater isotope loss from presecursor **9** indicates that for the bimolecular component there is a stereoelectronic preference for cleavage of the *endo* bond at C-6 in the 1,3-elimination step.

(18) For proton transfer to diazohydrocarbons see: (a) D. Bethell and J. D. Callister, *J. Chem. Soc.*, 3801, 3808 (1963); (b) D. W. Thomas and K. Biemann, *J. Am. Chem. Soc.*, **87**, 5447 (1965); (c) G. L. Closs, R. A. Moss, and S. H. Goh, *ibid.*, **88**, 365 (1966).

(19) Intervention of hydrogen-bonded[18c] or N-protonated intermediates[10] prior to eventual C-protonation are detailed variations that can be incorporated into the interpretation.

(20) H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

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Stabilization Energies of Triphenylmethyl Anions from Electromotive Force Measurements. Concerning Saturation of π Electronic Effects[1,2]

Sir:

The stabilization energies of *para*-substituted trityl (triphenylmethyl) cations relative to unsubstituted trityl cation were recently obtained from the standard free energy change of reaction 1 through the use of emf cell measurements[3]

$$R^+ + {}^1\!/_2(R_0\text{-}R_0) \rightleftarrows R_0^+ + {}^1\!/_2(R\text{-}R) \qquad (1)$$

where $R_0 \equiv$ trityl, $R \equiv$ substituted trityl, and $\Delta F°(R+) = -nFE° \equiv SE(R^+)$.

We wish to report the similar use of emf cell measurements to obtain the first measures of stabilization energies of *meta*- and *para*-substituted trityl anions, *i.e.*

$$R^- + {}^1\!/_2(R_0\text{-}R_0) \rightleftarrows R_0^- + {}^1\!/_2(R\text{-}R) \qquad (2)$$

where R_0 and R are as above and $\Delta F°(R^-) = -n\text{FE}° \equiv SE(R^-)$.

The actual observable was the reversible emf[4] for reaction 3 in purified dimethyl sulfoxide[5] (DMSO) at

$$R^-(Na^+) + Ag^+(NO_3^-) \rightleftarrows {}^1\!/_2(R\text{-}R) + Ag \qquad (3)$$

25°. The modified three-electrode emf cell[6] used to measure the potential of reaction 3 contained two platinum disk electrodes which were separated by an ultrafine glass frit. The third electrode consisted of an Ag| 0.02 *M* $AgNO_3$ (DMSO) reference electrode and was separated from the Pt electrode in the $R^-|R\text{-}R$ compartment by an ultrafine glass frit. Tetramethylammonium tetrafluoroborate (0.20 *M*) was used as a supporting electrolyte and an atmosphere of ultrahigh-pure argon or nitrogen was maintained in the cell throughout the course of the experiment. Concentrations of R^- and R-R were varied[7] by electrolytic oxidation of the trityl anions and were followed by connecting the cell in series with a hydrogen–oxygen gas coulometer.[8] Variation of $[R^-]$ from 4.5 to 6.5×10^{-2} *M* and [R-R] from 1.0×10^{-3} to 1.0×10^{-2} *M* gave emf values which followed the Nernst equation to a precision of ±0.005 v.

The standard free energy change, $\Delta F°(R^-)$, was obtained from $\Delta E°$ for reaction 3 for the substituted trityl anions relative to the unsubstituted anion and is assumed to be only slightly affected by the liquid junction potential and by any small variations in ion-pair formation. Table I lists values of $E°(2)$ for reaction 2 and corresponding $\Delta F°(R^-)$ values. Also listed are values of $\delta\Delta$, the fluorine nmr shielding change on formation of 4-fluoro-4′-X-substituted trityl anion from its methane relative to the corresponding change for the unsubstituted 4-fluorotrityl system. This substituent shielding effect is expected to be a measure (1 ppm $\cong$ 1 kcal) of the relative stabilization

(1) This work was supported in part by the National Science Foundation.

(2) Taken in part from the Ph.D. Dissertation of L. D. McKeever, University of California, Irvine, 1966; work performed in part at the Pennsylvania State University.

(3) E. D. Jenson and R. W. Taft, *J. Am. Chem. Soc.*, **86**, 116 (1964).

(4) H. E. Bent and N. B. Keevil, *ibid.*, **58**, 1228 (1936), established the reversibility of cells involving the trityl anion system by measuring $E°$ for the reaction: $C(C_6H_5)_3\cdot + Na \rightleftarrows Na^+(C_6H_5)_3C^-$.

(5) E. J. Corey and M. Chaykovski, *ibid.*, **84**, 866 (1962); **87**, 1345 (1965).

(6) The basic design of the emf cell was privately communicated by Professor Peter H. Given, Pennsylvania State University.

(7) The trityl anions were generated by treating the corresponding triarylmethane with an equimolar amount of dimsylsodium, prepared according to the technique of Corey.[5] Initial concentrations of R^- were obtained by applying the "double titration" technique of H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

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