the other extreme model systems **7** and **8** for which the rate-determining activated complex resembles a phenonium ion.[19] Such inverse isotope effects are observed when electron deficiency develops at nonhyperconjugating isotopically substituted sites in the activated complex.[1,18] Since the para-d effect for solvolysis of **1** is also large and inverse, we conclude that the rate-determining activated complex (for substitution with retention) closely resembles a phenonium ion.

The secondary kinetic β-isotope effect on the (major) aryl assisted pathway for **1** is expected to be very small.[20] Therefore, we conclude that the observed kinetic β effect on the solvolysis of **1** is largely due to competing rate-determining elimination of the β hydrogen atom in the (minor) aryl unassisted pathway. The magnitude of the kinetic β effect is congruent with this proposal that the rate-determining and product-determining steps are the same for the aryl unassisted pathway. The magnitude of the kinetic α-isotope effect is also consistent with the proposed dual path mechanism, since participation by neighboring carbon does not substantially lower the α effect below that expected for rate-determining ion-pair formation.[21,22]

Thus, the present results provide direct evidence that solvolysis of **1** involves rate-determining formation (or destruction) of a phenyl bridged species in the aryl assisted pathway and rate-determining elimination, probably from an open threo ion pair, in the aryl unassisted pathway. Crossover between the two pathways, in the usual sense of the term,[2] is unimportant because hindered secondary intimate ion pairs are remarkably resistant to nucleophilic attack at carbon and may maintain their stereochemical integrity.[23,24] The rate–product data for acetolysis of *threo*-3-aryl-2-butyl brosylates can be accounted for in a similar fashion as well. The observation of curved Hammett plots may be viewed as resulting from *substitutent induced* changes in the relative rate constants for ionization, phenyl bridging, and elimination.[25] For deactivated derivatives of **1**, ionization to the intimate ion pair is probably rate determining; increased elimination fractions are expected and indeed found.[2b]

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[19] H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Amer. Chem. Soc.*, **87**, 1280 (1965).

[20] (a) W. H. Saunders, *et al.*, *ibid.*, **80**, 2421 (1958); **82**, 3586 (1960); (b) S. L. Loukas, M. R. Velkou, and G. Gregoriou, *Chem. Commun.*, 251 (1970).

[21] B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, **92**, 3462 (1970).

[22] V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

[23] S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc. Spec. Publ.*, **No. 19**, 109 (1965).

[24] (a) H. L. Goering, R. G. Briody, and G. Sandrock, *J. Amer. Chem. Soc.*, **92**, 7401 (1970); (b) H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964); (c) H. L. Goering and R. W. Thies, *ibid.*, **90**, 2967, 2968 (1968).

[25] There is a delicate balance among various rate constants for complex solvolysis schemes.[23,24] Substituent induced changes in rate-determining steps should be anticipated.[26]

[26] V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971).

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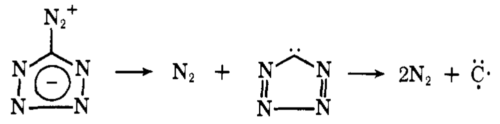
Formation of Atomic Carbon in the Decomposition of 5-Tetrazolyldiazonium Chloride

Sir:

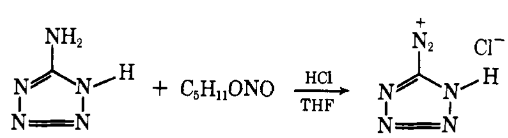
The formation and reactions of atomic carbon have been studied by a variety of methods including the production of energetic carbon atoms by nuclear transformation[1] and the preparation of lower energy carbon species in carbon arcs.[2] We have previously observed the formation of carbon atoms in the decomposition of quadricyclanone *p*-tosylhydrazone.[3]

In an attempt to devise a readily available chemical system for preparing and reacting carbon atoms, the decomposition of species related to 5-diazotetrazole (**1**)[4] has been studied. It was anticipated that **1** would decompose to three molecules of nitrogen and a carbon atom. Attempts to prepare **1** in a suitable nonaqueous solvent or in the gas phase have been unsuccessful due to extreme lability of the compound.



1

However, the corresponding diazonium chloride, 5-tetrazolyldiazonium chloride (**2**), can be isolated. We have prepared **2** by dropwise addition of isoamyl nitrite (10 mmol) to a solution of 5-amino-1*H*-tetrazole (**3**) (9.8 mmol) in 20 ml of THF–5 ml of HCl at 0°.



3 2

The diazonium chloride may be extracted into ether and the ether removed at reduced pressure to yield crystalline **2**. The infrared spectra (NaCl plate) of the extremely explosive salt[5] shows ν_{max} 2275 cm^{-1}.

The decomposition of **2** has been studied by coating the salt on the walls of a 500-ml flask and evacuating and immersing the flask in a water bath at 80°. Thermal decomposition of **2** in the presence of two substrates, ethylene and ethylene oxide, has been examined.

When **2** (0.75 mmol) was allowed to decompose at 80° in a system containing 550 mm (17.1 mmol) of ethylene, the products were: nitrogen (0.9 mmol), methane (2.3×10^{-3} mmol), allene (1.9×10^{-3} mmol), propyne (1.2×10^{-3} mmol), and hydrogen cyanide (1.6×10^{-2} mmol).[6] It is proposed that carbon atoms

$$\mathbf{2} + H_2C{=}CH_2 \xrightarrow{\Delta} N_2 + CH_4 + H_2C{=}C{=}CH_2 + CH_3C{\equiv}CH + HCN$$

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[1] A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 201 (1964).

[2] P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 1135 (1965); P. S. Skell and R. R. Engel, *ibid.*, **88**, 3749 (1966); P. S. Skell and R. R. Engel, *ibid.*, **88**, 4883 (1966); P. S. Skell and R. R. Engel, *ibid.*, **89**, 2912 (1967).

[3] P. B. Shevlin and A. P. Wolf, *Tetrahedron Lett.*, 3987 (1970).

[4] J. Thiele, *Justus Liebigs Ann. Chem.*, **270**, 59 (1891).

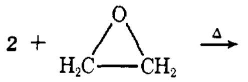
[5] It should be emphasized that **2** is extremely explosive and should be handled with great care. We recommend that no more than 0.75 mmol of **2** be isolated at one time. Ethereal solutions of **2** are somewhat more stable but explosions have occurred after standing at −70° for 1 hr.

[6] In all reactions the products were separated by gas chromatography and characterized by their ir spectra.

are produced in the decomposition of **2**. The allene and propyne result from addition of these carbon atoms to ethylene. Skell and coworkers[7] have observed allene and propyne as the principal products in the reaction of arc-generated carbon atoms with ethylene at −196°. Reaction of ethylene with higher energy carbon-11 atoms produced by nuclear transformation yields allene, propyne, acetylene, propylene, cyclopropane, and vinylacetylene.[8]

The hydrogen cyanide formed in the decomposition of **2** is most probably the result of insertion of a carbon atom into the N–H bond of another molecule of **2** followed by decomposition to HCN. While the mechanism of methane formation is uncertain, it appears that the most likely pathway is a series of hydrogen abstractions either by ^3P carbon or by CH produced during the decomposition of **2**.

The pyrolysis of **2** in the presence of ethylene oxide has also been examined. It has been shown,[9] in a similar system, that arc-generated carbon atoms react with propylene oxide to give carbon monoxide and propylene. Decomposition of **2** (0.75 mmol) in a reactor containing 145 mm (4.6 mmol) of ethylene oxide gave: nitrogen (1.4 mmol), carbon monoxide (0.4 mmol), ethylene (0.06 mmol), methane (0.16 mmol), and acetylene (0.05 mmol).



$$N_2 + CO + H_2C{=}CH_2 + CH_4 + HC{\equiv}CH$$

In this system ethylene and carbon monoxide are postulated to be the result of abstraction of oxygen from ethylene oxide by atomic carbon. Since the carbon monoxide yield exceeds that of ethylene in this reaction, it is proposed that a portion of the carbon monoxide is the result of hydrogen abstraction from ethylene oxide followed by decomposition of the resulting radical to carbon monoxide and a methyl radical. Abstraction of hydrogen from ethylene oxide in the gas phase is known to yield carbon monoxide and methyl radicals.[10,11] In the present case the abstracting species is probably either ^3P carbon or CH.

The formation of acetylene parallels the chemistry of energetic carbon atoms produced by nuclear transformation.[1] However, the mechanism of acetylene formation may not be similar since neat pyrolysis of **2** also produces acetylene in smaller yield. When **2** (0.75 mmol) was allowed to decompose in a degassed system the products were: nitrogen (0.43 mmol), hydrogen cyanide (0.09 mmol), and acetylene (0.03 mmol). In this reaction the most likely origin of the acetylene is either dimerization of atomic carbon to C_2 followed by hydrogen abstraction, or dimerization of CH. Hydrogen abstraction by C_2 has been observed in the reactions of arc-generated carbon species.[12] The results of the neat pyrolysis render the mechanism of acetylene production in the ethylene oxide system uncertain.

Thermal decomposition of **3** represents a convenient method for generating and studying the reactions of atomic carbon. While the spin state of the reacting carbon atom is unknown, the most probable species would appear to be ^1S.[6,13] Efforts toward the preparation of pure **1** are continuing in order to study its gas-phase photolysis.

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[7] P. S. Skell, J. E. Villaume, J. H. Plonka, and F. A. Fogone, *J. Amer. Chem. Soc.*, **93**, 2699 (1971).

[8] C. Makay, P. Polak, H. E. Rosenberg, and R. Wolfgang, *ibid.*, **84**, 308 (1962).

[9] P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, **89**, 1748 (1967).

[10] W. R. Trost, B. deB. Darwent, and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 353 (1948).

[11] R. Gomer and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, 72, 101 (1950).

[12] P. S. Skell and J. H. Plonka, *ibid.*, **92**, 5620 (1970).

[13] M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, **92**, 3505 (1970).

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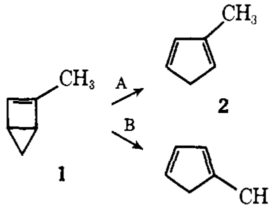
The Thermal Rearrangement of 2-Methylbicyclo[2.1.0]pent-2-ene

Sir:

Bicyclo[2.1.0]pent-2-ene undergoes a facile thermal valence isomerization to cyclopentadiene.[1] The 2-methyl homolog **1** undergoes an analogous reaction at a similar rate.[2,3] Whether this thermal isomerization of **1** follows path A to 2-methylcyclopentadiene (**2**) or path B to 1-methylcyclopentadiene (**3**) is of considerable mechanistic importance, but the ready thermal equilibration of the isomeric dienes,[4] leading to a mixture containing **2** and **3** in the ratio 55:45 approximately, complicates a study of the thermal ring opening of **1**. It has recently been reported[3] that the thermal isomerization of **1** leads to **3** only, following path B and so providing evidence that the reaction is concerted and follows a symmetry-allowed path[5] described as $[{}_\sigma 2_s + {}_\sigma 2_a]$. The isomerization was carried out at 43°, and the diene **3** produced was trapped *in situ* as its adduct with *N*-phenylmaleimide, no trace of the isomeric adduct being found; it was stated that the *N*-phenylmaleimide was unreactive toward the starting bicyclopentene **1**, but reacted with the methylcyclopentadiene produced faster than **3** rearranged to **2**.



1 **2** **3**

In our original study[2] of the thermal reaction of **1** we observed only the mixture of isomers **2** and **3** that re-

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[1] J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968); J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *ibid.*, **88**, 846 (1966).

[2] S. McLean and D. M. Findlay, *Can. J. Chem.*, **48**, 3107 (1970).

[3] J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

[4] S. McLean and P. Haynes, *Tetrahedron*, **21**, 2313, 2329 (1965).

[5] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.