

was heated further at a rate of 5 °C/min up to 120 °C for 30 min to detect the 2-chloroethyl vinyl ether, the thioethers, and the corresponding 2-hydroxyethyl compounds.

The aqueous layer was extracted thoroughly with Spectrograde chloroform and dried (Na₂SO₄), and the extract was similarly analyzed by GC and GC/MS.

Polarographic Measurement of Rates of Decomposition. Kinetic measurements of the rates of aqueous decomposition of S-CENU and O-CENU were made by differential pulse polarography following the disappearance of the electrochemically active nitroso group as described previously.²⁵ Measurements were made in a PAR 174A polarograph using a three-electrode cell thermostated at 37 °C. All solutions contained 50 mM potassium phosphate buffer (pH 7.2) and 10⁻² M potassium chloride as the supporting electrolyte together with 10⁻⁴ M nitrosourea with 5% acetonitrile. Polarographic potentials were measured and are recorded with respect to the saturated calomel electrode.

Acknowledgment. This investigation was supported by Grant 1-R01-CA21488-01 awarded by the National Cancer Institute, DHEW, and by a grant from the Alberta Provincial Cancer Hospitals Board. We thank Dr. Alan Hogg and his associates for the mass spectral determinations.

Registry No. S-CENU, 66929-50-8; α ₂-S-CENU, 81141-99-3; β ₂-S-CENU, 81142-00-9; O-CENU, 73944-53-3; α ₂-O-CENU, 81142-01-0; β ₂-O-CENU, 81177-94-8; CCNU, 13010-47-4; dicyclohexylurea, 2387-23-7; 2,3-dihydrothiophene, 1120-59-8; cyclohexyl isocyanate, 3173-53-3; 2-chloroethyl vinyl thioether, 81142-02-1; 2,2'-dichlorodiethyl sulfide, 505-60-2; 2-hydroxyethyl vinyl sulfide, 3090-56-0; acetaldehyde, 75-07-0; vinyl chloride, 75-01-4; 2-chloroethyl vinyl ether, 110-75-8; 2,2'-dichlorodiethyl ether, 111-44-4; 2-

hydroxyethyl-2'-chloroethyl ether, 628-89-7; 2,3-dihydrothiophene-5-d, 81142-03-2; 2,3-dihydrothiophene-4-d, 81142-04-3; 2,2-dideuterio-2,3-dihydrothiophene, 81142-05-4; 3,3-dideuterio-2,3-dihydrothiophene, 81142-06-5; 2-[(2-hydroxyethyl)thio]-2,2-dideuterioethylamine, 81142-07-6; 2-mercaptoethanol, 60-24-2; 2-chloro-2,2-dideuterioethylamine hydrochloride, 78604-36-1; 2-[(2-chloroethyl)thio]-2,2-dideuterioethylamine HCl, 81142-08-7; 1-[2-[(2-chloroethyl)thio]-2,2-dideuterioethyl]-3-cyclohexylurea, 81157-74-6; 1-[2-[(2-chloroethyl)thio]-1,1-dideuterioethyl-3-cyclohexyl-1-nitrosourea, 81142-09-8; chloroacetic acid, 79-11-8; 2-chloro-1,1-dideuterioethanol, 77081-40-4; 2-[(2-aminoethyl)thio]-1,1-dideuterioethanol, 81142-10-1; 2-mercaptoethylamine hydrochloride, 156-57-0; 1-[2-[(2-chloro-2,2-dideuterioethyl)thio]ethyl]-3-cyclohexylurea, 81142-11-2; 2-[(2-chloro-2,2-dideuterioethyl)sulfinyl]ethanamine hydrochloride, 81142-12-3; 2-[(2-chloro-2,2-dideuterioethyl)thio]ethylamine hydrochloride, 81142-13-4; phthalic anhydride, 85-44-9; diglycolamine, 929-06-6; 2-(2-phthalimidoethoxy)ethanol, 69676-63-7; (2-phthalimidoethoxy)acetaldehyde, 81142-14-5; (2-phthalimidoethoxy)acetic acid, 69676-65-9; 2-(2-aminoethoxy)-1,1-dideuterioethanol, 81142-15-6; (2-aminoethoxy)acetic acid hydrochloride, 81142-16-7; 1-[2-(2-chloro-2,2-dideuterioethoxy)ethyl]-3-cyclohexylurea, 81142-17-8; 2-amino-1,1-dideuterioethanol, 59099-87-5; 1,1-dideuterio-2-phthalimidoethanol, 81142-18-9; 2-(2-amino-1,1-dideuterioethoxy)ethanol, 81142-19-0; ethyl chloroacetate, 105-39-5; (2-phthalimido-1,1-dideuterioethoxy)acetic acid, 81142-20-3; ethyl (2-phthalimido-1,1-dideuterioethoxy)acetate hydrochloride, 81142-21-4; 1-[2-(2-chloroethoxy)-2,2-dideuterioethyl]-3-cyclohexylurea, 81142-22-5; ClCH₂CH₂OCd₂CH₂Cl, 81142-23-6; CD₂=CHOCH₂CH₂Cl, 81157-75-7; CH₂=CDOCH₂CH₂Cl, 81142-24-7; CH₃CDO, 4122-13-8; ClC₂H₄S₂CD₂CH₂Cl, 81142-25-8; CH₂=CDSCH₂CH₂Cl, 81142-26-9; CD₂=CHSCH₂CH₂Cl, 81157-76-8; CD₂=CHSCH₂CH₂OH, 81157-77-9; ClCD₂CH₂SCH₂CH₂Cl, 81142-27-0; CH₂=CHSCH₂CD₂Cl, 81142-28-1; ClCD₂CH₂OCH₂CH₂Cl, 81142-29-2; CH₂=CDCl, 4984-12-7; CH₂=CHOCH₂CD₂Cl, 81142-30-5; CH₂DCHO, 7086-00-2.

Supplementary Material Available: Table III containing aqueous decomposition and mass spectral data for the CENUs (3 pages). Ordering information is given on any current masthead page.

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Chemistry of 2-Carbenabicyclo[3.2.1]octadiene¹

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Pyrolytic decomposition of the lithium or potassium salt of the tosylhydrazone of bicyclo[3.2.1]octa-3,6-dien-2-one (11) or photolysis of the lithium salt of 11 results in the formation of bicyclo[3.2.1]octa-2,6-diene (12), tricyclo[3.2.1.0.2⁷]oct-3-ene (13), tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (14), semibullvalene (15), 5-ethynyl-1,3-cyclohexadiene (16), and *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (17). The formation of the C₈H₈ fraction (15-17) is ascribed to insertion and rearrangement reactions of singlet 2-carbenabicyclo[3.2.1]octadiene, whereas the formation of the C₈H₁₀ fraction (12-14) appears to be the result of hydrogen abstraction reactions of the corresponding triplet carbene or closely related species.

Homoaromatic character for the bicyclo[3.2.1]octadienyl carbanion 1 has been proposed by Brown^{2,3} and Winstein,^{4,5} evidence supporting antiaromaticity of the related carbocation 2 (Chart I) has been provided by Diaz,⁶ and studies

have been carried out on the related free radical.⁷ In recent molecular orbital studies, Grutzner⁸ and Schleyer⁹ conclude, however, that homoaromaticity is not important in the bicyclo[3.2.1]octadienyl anion and similar systems. Our interests in homoaromatic carbenes and in systems with potential for carbene to carbene rearrangements provided the impetus to consider the chemistry of 2-carbenabicyclo[3.2.1]octa-3,6-diene (3). Qualitative MO

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(3) Brown, J. M. *Chem. Commun.* 1967, 638.

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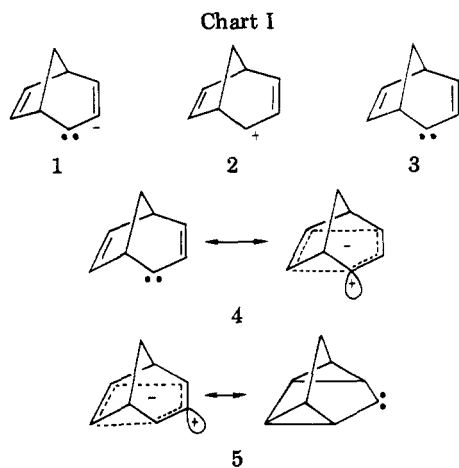
(5) See also: Bos, H.; Klumpp, G. W. *Tetrahedron Lett.* 1978, 1865. Trimitsis, G. B.; Tuncay, A. *J. Am. Chem. Soc.* 1976, 98, 1997. Trimitsis, G. B.; Tuncay, A. *Ibid.* 1975, 97, 7193. Dauben, W. G.; Tweig, R. J. *Tetrahedron Lett.* 1974, 531. Moncur, M. V.; Grutzner, J. B. *J. Am. Chem. Soc.* 1973, 95, 6449. Goldstein, M. J.; Natowsky, S. *Ibid.* 1973, 95, 6451.

(6) Diaz, A. F.; Sakai, M.; Winstein, S. *J. Am. Chem. Soc.* 1970, 92, 7477. See also: Jefford, C. W.; Mareda, J.; Perlberger, J.-C.; Burger, U. *Ibid.* 1979, 1370.

(7) Japenga, J.; Klumpp, G. W.; Stapersma, J. *Tetrahedron* 1977, 33, 2847.

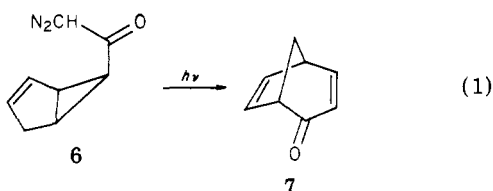
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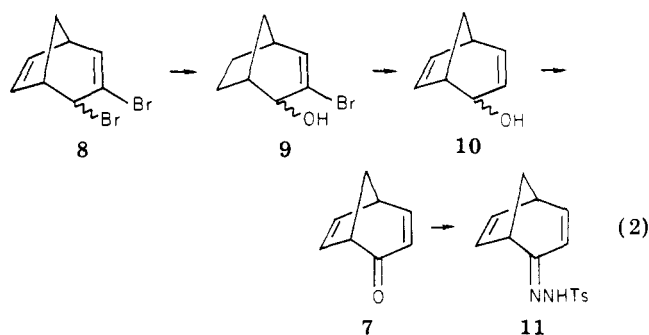


theory suggests that in the lowest singlet the C-2 electron pair could be delocalized in the p-orbital system rather than localized in the C-2 sp^2 orbital in order to achieve homoaromaticity (4). Comparison with the closely related 3-carbenatetracyclooctane 5 studied by Bergman¹⁰ reveals that the two species are related by a 1,2 hydrogen shift and may, in fact, be part of the same intermediate manifold, thus providing the potential for a carbene to carbene rearrangement.

Since decomposition of the alkali metal salt of the tosylhydrazone related to 3 was the method chosen to generate bivalent 3, the first synthetic goal was the preparation of bicyclo[3.2.1]octa-3,6-dien-2-one (7). Previously we had generated bicyclooctadienone 7 by a Wolf rearrangement-Cope rearrangement sequence of diazomethyl ketone 6¹¹ (eq 1), but we chose, on this occasion, to use a modified



procedure of Strothers and co-workers.¹² Hydrolysis of 2,3-dibromobicyclooctadiene 8 (eq 2) was carried out by

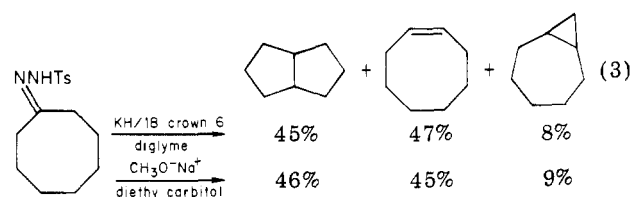


using aqueous acetone and calcium carbonate (75% yield). Debromination of 9 was accomplished by Strothers with sodium-ammonia, but after some experimentation, we decided to use alkyllithium reagents. In our hands, the sodium-ammonia reaction led to excessive reduction of the carbon-carbon double bonds. The transformation of 9 to

10 was effected by *n*-butyllithium in 38% yield, while *sec*-butyllithium afforded a 45% yield of the epimeric alcohols 10. Pyridinium dichromate¹³ in DMF was used to oxidize epimeric alcohols 10 to bicyclooctadienone 7 (36%), and subsequent treatment of 7 with 1 equiv of tosylhydrazine in methanol at room temperature with pyridine as a catalyst produced tosylhydrazone 11 (39%). Attempts to use more vigorous conditions such as refluxing in acidic ethanol led to varying amounts of an undesired side product, tentatively identified as the 3-tosyl adduct of 11.

With tosylhydrazone 11 in hand, the corresponding lithium and potassium salts were made and decomposed under a variety of conditions. The volatile products were separated by preparative VPC and identified by spectral comparison with the spectroscopic data of authentic samples. The first method of carbene generation employed was the pyrolysis of the dry lithium salt of tosylhydrazone 11 in a flask under vacuum with collection of the volatile products in traps maintained at dry ice temperature (the static method).¹⁴ The dry salt was also decomposed by dropping it onto a hot Pyrex surface (the drop static method).¹⁵ In addition, the lithium salt was photolyzed in anhydrous THF (0.0039 M). The irradiation was carried out through quartz at about 10 °C with a 450-W Hanovia high-pressure mercury lamp. Irradiation was discontinued when an equivalent amount of nitrogen had been collected. The fourth method of generating the carbene involved the thermal decomposition of the potassium salt of the tosylhydrazone in diglyme in the presence of 18-crown-6 ether. Complexation of the potassium ion with the crown ether was used to increase the solubility of the salt in diglyme and possibly to lower the temperature needed to initiate diazo compound formation.

Since thermolysis of the salt of a tosylhydrazone with crown ether as a complexing agent is not commonly used, a model system was investigated. Cyclooctanone tosylhydrazone (eq 3) was chosen since it is readily available



and the chemistry of its carbene well documented. The results obtained agreed extremely well with those of Friedman and Shechter,¹⁶ who had generated the carbene by treatment of the tosylhydrazone with 1.2 equiv of sodium methoxide in diethyl carbitol. This appears to be good evidence that the complexed potassium ion conditions provide the same results as more conventional methods of carbene generation.

The results of the decomposition of tosylhydrazone 11 with the product compositions obtained are shown in Table I. Compounds 12–14 were identified by comparison of their NMR spectra with spectra of authentic samples available from previous work in this laboratory.^{17,18} Compounds 15 and 17 were identified by comparison of

(10) Bergman, R. G.; Rajadhyaksha, V. J. *J. Am. Chem. Soc.* 1970, 92, 2163.

(11) Freeman, P. K.; Kuper, D. G. *Chem. Ind. (London)* 1965, 424.

(12) Stothers, J. B.; Swenson, J. R.; Tan, C. T. *Can. J. Chem.* 1975, 53, 581.

(13) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* 1979, 399.

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(16) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* 1961, 83, 3159.

(17) Freeman, P. K.; Kinnel, R., unpublished results.

(18) Rao, V. N. M. Ph.D. Thesis, University of Idaho, 1965.

Table I. Percent Composition of Products from Decomposition of Tosylhydrazone 11

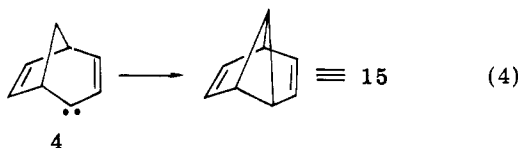
conditions	% yield					
	12	13	14	 + 16	17	unknown
dry salt (Li ⁺) pyrolysis (static)	44	7	10	24	9	6
dry salt (Li ⁺) pyrolysis (static drop)	58	7	7	11	5	11
photolysis (Li ⁺ salt) in THF	39	31	18	9	3	
KH/18-crown-6, diglyme	19	12	10	13	17	28

their NMR spectra with the data of Zimmerman¹⁹ and Bergman,¹⁰ respectively, while 16 was identified by comparison with an NMR spectrum of 16 obtained from Professor Murahashi.^{20,21} The products 15 and 16 are grouped together in Table I as they were not resolved under the VPC conditions used. An NMR spectrum of the two together was obtained from the dry salt pyrolysis (static) run, and the integrations indicate that 16 and 15 are present in roughly a 4:1 ratio. One further compound was present in the amounts shown but was never identified.

The reason that a number of different methods was employed to generate carbene 3 is that in each case the yield of volatile products was low, ranging from 1.5% to 3.0%. Unfortunately, no single variation of tosylhydrazone salt decomposition improved the yield to any great extent. Spectral analysis of the residue suggests that intermolecular insertion reactions leading to intractable high molecular weight materials are responsible for the low yields of carbene which escape to form the volatile fraction.

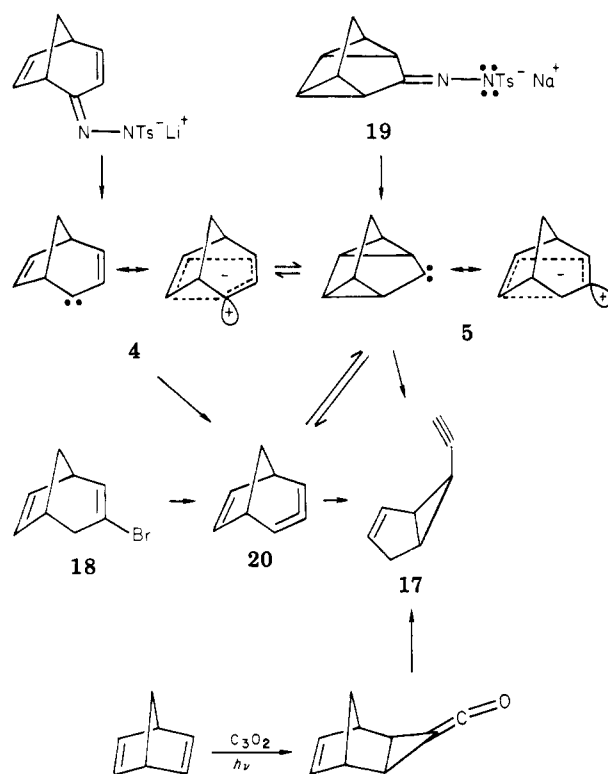
Examination of the products in Table I shows that they can be divided into two groups on the basis of molecular formula. Products 15–17 have the formula C₈H₈ which is the same as the parent carbene 4. The remaining hydrocarbons 12–14 have the formula C₈H₁₀, indicating that two hydrogen atoms have been abstracted by the carbene intermediate.

A consideration of the C₈H₈ components suggests that the formation of semibullvalene (15) may be readily explained as the result of insertion of the carbene into the syn C₈-H bond (eq 4). A similar process occurs in 7-carbenanorborene,²² 2-carbenanorborene,²³ and a number of less closely related examples.



The presence of *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (17) deserves more attention than the rather obvious 15. This is the same product that was obtained from bromide 18 by treatment with KO-*t*-Bu/Me₂SO and by pyrolysis of the sodium salt of tosylhydrazone 19 and ascribed to bishomoaromatic carbene 5 by Bergman and Rajadhyaksha.¹⁰ Klumpp and van Dijk²⁴ photolyzed carbon suboxide in the presence of norbornadiene and obtained ethynyl-

Scheme I

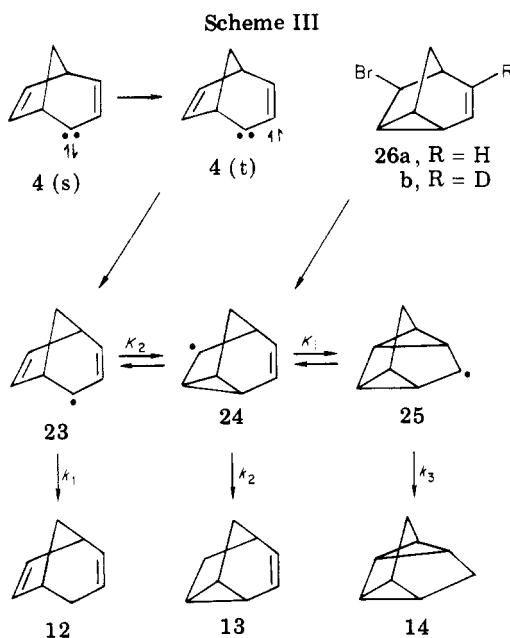
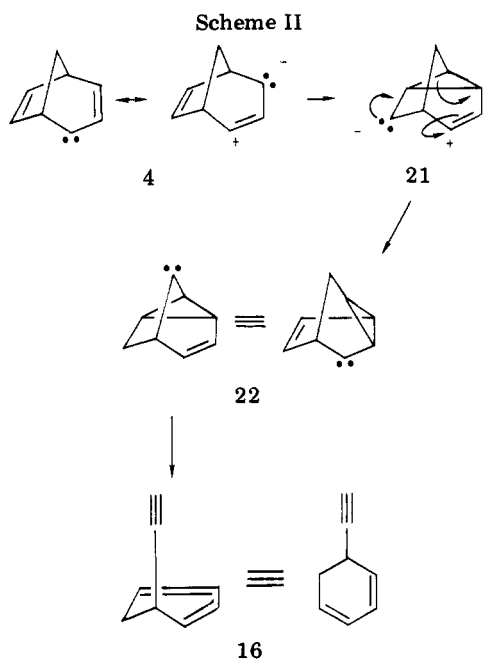


bicyclohexene 17, suggesting allene 20, carbene 5, or 5 with charges reversed as possible intermediates. Our first thought was that the product-determining intermediate is bishomoaromatic 5 formed from carbene 4 by 1,2 hydrogen migration or via the allene 20. The recent work of Balci and Jones,²⁵ which reports the trapping of twisted allene 20 from potassium *tert*-butoxide treatment of bromide 18 and the formation of optically active 17 in a reaction of bromide 18 with potassium methoxide, suggests an important role for allene 20. It is conceivable that ethynylbicyclohexene 17 is formed directly from allene in all the reactions of Scheme I; however, it is also possible that an equilibrium of 20 and 5 is set up and that both participate as product-determining intermediates. The relative importance of allene 20 and carbene 5 as direct precursors for ethynylbicyclohexene 17 must rely on additional experimentation.

The formation of the third C₈H₈ hydrocarbon, 5-ethynyl-1,3-cyclohexadiene (16) can be understood in terms of the mechanism provided in Scheme II. If one considers carbene 4 as homoaromatic, then a rearrangement analogous to the carbanionic allylcarbinyl to cyclopropylcarbinyl rearrangement²⁶ leads to 21, which can reopen to carbene

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 (20) Okumura, K.; Murahashi, S.-I. *Tetrahedron Lett.* 1977, 3281.
 (21) Murahashi, S.-I., private communication.
 (22) Moss, R. A.; Whittle, J. R., *Chem. Commun.* 1969, 341.
 (23) Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* 1966, 88, 4543.
 (24) Klumpp, G. W.; van Dijk, P. M. *Recl. Trav. Chim. Pays-Bas* 1971, 90, 381.

(25) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* 1981, 103, 2874.



22, which in turn would be expected to undergo a cyclopropylcarbene fragmentation reaction²⁷ to generate ethylcyclohexadiene 16.

The formation of the C₈H₁₀ fraction, 12–14, each component containing an additional two hydrogen atoms relative to initial carbene 4, strongly suggests a triplet hydrogen abstraction process. Carbene 4, which would be generated as a singlet from the singlet diazo compound,

(26) Wilson, S. E. *Tetrahedron Lett.* 1975, 4651. Maercker, A.; Geuss, R. *Chem. Ber.* 1973, 106, 773. Maercker, A.; Streit, W., *Angew. Chem., Int. Ed. Engl.* 1972, 11, 542. Moncar, M. V.; Grutzner, J. B.; Eisenstadt, A. *J. Org. Chem.* 1974, 39, 1604. Staley, S. W.; Reichard, D. W. *J. Am. Chem. Soc.* 1969, 91, 3998. Grutzner, J. B.; Winstein, S. *Ibid.* 1968, 90, 6562.

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Table II. Composition of Products from Tricyclic Bromide 26a

reagent	% yield		
	12	13	14
(<i>n</i> -Bu) ₃ SnH	98.7	1.3	<0.1
Na/ <i>t</i> -BuOH	97.5	2.5	<0.1

Table III. Composition of C₈H₁₀ Products from 11

conditions	% yield			% of total volatile products
	12	13	14	
dry salt (Li ⁺)	72	11	16	61
pyrolysis (static)				
dry salt (Li ⁺)	81	10	10	72
pyrolysis (static drop)				
photolysis (Li ⁺ salt) in THF	44	35	20	88
KH/18-crown-6, diglyme	46	29	24	41

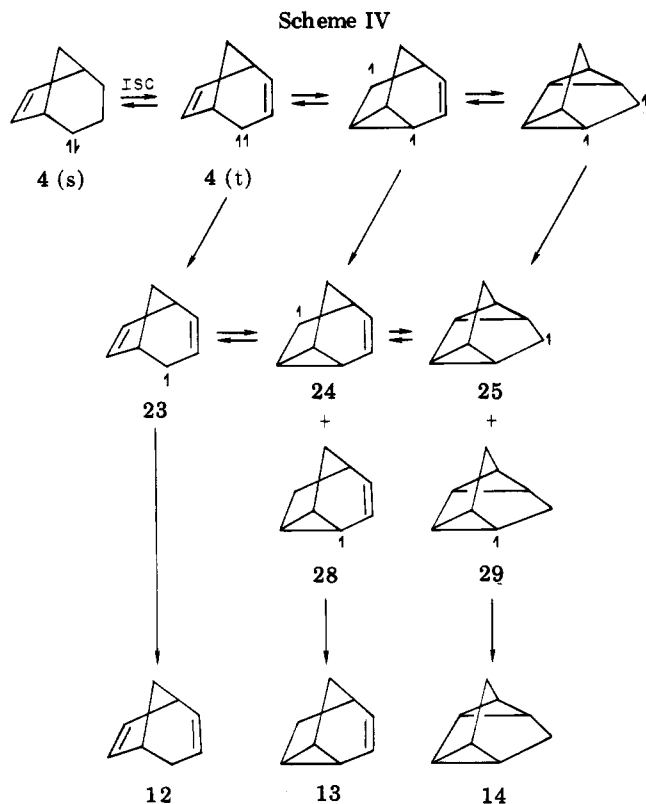
might undergo intersystem crossing to the triplet which could abstract a hydrogen atom to form radical 23. This radical might well be in equilibrium with radical species 24 and 25, each of which could abstract a second hydrogen atom leading to the observed products 12–14 (Scheme III).

This particular radical system has been studied by Klumpp and co-workers,⁷ who treated tricyclic bromide 26b with tri-*n*-butyltin hydride or sodium in *tert*-butyl alcohol and THF, both free-radical conditions, and obtained hydrocarbon product 12 with deuterium scrambling as would be expected from labeled allylic radical 23. No comment was made as to the presence of possible minor hydrocarbon products 13 and 14.

We decided to repeat the above experiment and search for minor concentrations of 13 and 14. The debromination of 26a was carried out by using both tri-*n*-butyltin hydride and sodium in *tert*-butyl alcohol. For the tri-*n*-butyltin hydride case, the hydrocarbon products were produced in an overall yield of 19%, with the percent composition shown in Table II, while a similar product composition was obtained with sodium in *tert*-butyl alcohol with the yield of hydrocarbons found to be 29% (Table II). A comparison of the product compositions of these known radical processes with that obtained from the carbene route shows noticeable differences. No tetracyclooctane and only a very small amount (<3%) of the tricyclooctene 13 was found in the radical reaction. Table III shows the relative amounts of the three C₈H₁₀ hydrocarbons produced by the various methods of carbene generation.

For comparison of the results of the radical reaction with those of the carbene process, considerable insight into the various individual processes in operation is needed. The ratio of products 12/13/14 will depend upon the point of entry into the manifold, the equilibria K_1 and K_2 , and the rates of hydrogen abstraction, k_1 , k_2 , and k_3 (Scheme III). Since, in the norbornenyl-nortricyclyl radical equilibrium, Kuivila²⁸ has provided evidence that the product ratio depends very little on the hydrogen donor, which may vary from organotin hydride to cumene to norborn-2-ene-5-carboxaldehyde, we assume for the purposes of discussion that the rates of hydrogen abstraction (k_1^{Sn} , k_2^{Sn} , and k_3^{Sn}) by the radical from tri-*n*-butyltin hydride are nearly equivalent and that the rates k_1^{THF} , k_2^{THF} , and k_3^{THF} for hydrogen abstraction from THF by the proposed radical

(28) Warner, C. R.; Strunk, R. J.; Kuivila, H. G. *J. Org. Chem.* 1966, 31, 3381. Martin, M. M.; DeJongh, D. C. *J. Am. Chem. Soc.* 1962, 84, 3526. Wilt, J. W.; Levin, A. A. *J. Org. Chem.* 1962, 27, 2319.



in the carbene case are also nearly equivalent. In the tri-*n*-butyltin hydride reaction, if equilibration of the three radical species is not complete, 13 would be formed from the parent radical in excess, so that 2.5% would be an upper limit to the percentage of 13 to be expected from the carbene. If the radical species are present in equilibrium, the hydrocarbon ratio shown in Table II should also be that of the carbene.

For the carbene process, if equilibration is complete, the percentage of products given in Table III would be representative. If complete equilibration is not obtained, an excess of 12 from the parent radical would be expected. Even so, from the carbene reaction, a significantly larger percentage of 13 and 14 was obtained than that for the tri-*n*-butyltin hydride radical process. This would point to the possibility that the intermediates for the carbene process might be better represented by a set of intermediates other than the equilibrating radicals of Scheme III.

A logical alternative to the radical intermediate would be a diradical process (Scheme IV). The singlet carbene 4(s) might undergo intersystem crossing to the triplet 4(t), followed by equilibration with two other diradical species. The triplet 4(t) and the two diradicals could abstract hydrogen atoms to give a set of five radicals. The three radicals 23–25 would be in equilibrium, while radicals 28 and 29 cannot equilibrate and would have to go directly on to products 13 and 14, respectively. This mechanism would give larger amounts of products 13 and 14 than the radical process of Scheme III.

In summary, we see two facets for the chemistry of 2-carbenabicyclo[3.2.1]octa-3,6-diene: (a) rearrangement and insertion chemistry, with evidence for rearrangement of the initial singlet carbene to additional neutral species, either carbene or allene, and (b) radical chemistry derived from initial triplet carbene. While at the present time the chemistry uncovered does not shed great light on the homoaromaticity of 2-carbenabicyclo[3.2.1]octa-3,6-diene, the large fraction of products derived from the triplet state does provide a hint that the initially generated singlet may

have a longer lifetime than is normal for most dialkyl-carbenes.

Experimental Section

Melting points were determined by using a Büchi melting point apparatus and are uncorrected. All boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727B infrared spectrophotometer. Proton NMR spectra were recorded on a Varian Associates EM-360 (60 MHz) or HA-100 (100 MHz) spectrometer, while carbon-13 NMR spectra were run on a Varian Associates FT-80A spectrometer. Mass spectra were obtained on a Varian-MAT CH-7 mass spectrometer interfaced to a System 150 data system. High-resolution mass spectra were carried out by the University of Oregon Chemistry Department. VPC analyses were carried out on an Aerograph A-90-P2 chromatograph equipped with a thermal-conductivity detector. The following columns were used: (a) 19 ft × 0.25 in., aluminum, containing 15% Carbowax 20M on chromosorb G, 60/80 mesh; (b) 4 ft × 0.25 in., aluminum, containing 10% SE-30 on Chromosorb P, 60/80 mesh; (c) 14 ft × 0.25 in., aluminum, containing 7% SE-30 on Chromosorb G, 60/80 mesh; (d) 15 ft × 0.25 in., aluminum, containing 6% DC-200 on Anakrom AS, 60/80 mesh; (e) 9 ft × 0.25 in., aluminum, containing 10% SE-30 on Chromosorb P, 60/80 mesh; (f) 11 ft × 0.25 in., aluminum, containing 15% DC-710 on Chromosorb P, 60/80 mesh; (g) 4 ft × 0.25 in., aluminum, containing 4% Carbowax 4000 on Chromosorb P, 60/80 mesh; (h) 6 ft × 0.25 in., aluminum, containing 7% OV-17 on Chromosorb P, 60/80 mesh; (i) 5 × 0.25 in., aluminum, containing 7% SE-30 on Chromosorb P, 60/80 mesh.

Silver Nitrate Assisted Hydrolysis of 3,4-Dibromobicyclo[3.2.1]octa-2,6-diene (8). A 100-mL flask fitted with a magnetic stirrer and reflux condenser was charged with 20.26 g (0.0767 mol) of dibromide 8 in 25 mL of acetone and 25 mL of water. To this solution was added 12.9 g (0.076 mol) of silver nitrate which gave an immediate precipitate of silver bromide. The mixture was vigorously stirred and heated at reflux for 1 h, during which time a sizable amount of silver bromide precipitated. After the mixture cooled, the silver bromide was removed by filtration and the filtrate diluted with 200 mL of water. This diluted filtrate was extracted with three 75-mL portions of ether. The combined ether extracts were washed twice with 100 mL of 5% sodium bicarbonate and once with 100 mL of water and dried over magnesium sulfate. The ether was removed on a rotary evaporator and the residue distilled through a short-path distillation apparatus [58–82 °C (0.18 mm)] to give 11.4 g (0.0570 mol) of a colorless liquid in 75% yield. On the basis of the NMR spectrum, this is a mixture of the exo and endo isomers of the desired 3-bromobicyclo[3.2.1]octa-3,6-dien-2-ol (9): NMR (60 MHz, CDCl₃) δ 6.99 (m, 2 H, vinyl protons), 6.10 (m, 1 H, vinyl proton), 4.43 (d, *J* = 6 Hz, ¹/₃ H, H-2 of endo alcohol), 4.00 (d, *J* = 2 Hz, ²/₃ H, H-2 of exo alcohol), 3.00 (m, 2 H, bridgehead H-1 and H-5), 2.02 (m, 2 H, bridge H-8); the aliphatic region showed a somewhat higher than calculated integration, which is attributed to saturated impurities; IR (neat, 0.1 mm), 3390 (s), 3052 (m), 2945 (s), 1655 (s), 1275 (s), 1038 (s), 845 (s), 725 cm⁻¹ (s).

Hydrolysis of 3,4-Dibromobicyclo[3.2.1]octa-2,6-diene (8) with Calcium Carbonate. A 2-L flask fitted with a magnetic stirrer and reflux condenser was charged with 164.62 g (0.6236 mol) of the title dibromide 8 in 600 mL of acetone and 320 mL of water (65% acetone/35% water). To this mixture were added 76.4 g (0.764 mol) of calcium carbonate and 4 mL of Aliquat 336 (tridecylmethylammonium chloride). The resulting two-phase slurry was heated to reflux and the course of the reaction followed by VPC (column b, 175 °C, 70 mL/min), monitoring the disappearance of starting dibromide. After 9 days the reaction had essentially reached completion. The reaction mixture was cooled and the calcium carbonate removed by filtration through a Büchner funnel. This filtrate was diluted with 400 mL of brine and extracted twice with 350 mL of ether. The ether extracts were combined, washed twice with 300 mL of brine and twice with 400 mL of water, and dried over magnesium sulfate. The ether was removed on a rotary evaporator to leave a dark oil which was distilled through a short-path distillation apparatus [66–77 °C (0.18 mm)] to give 94.04 g (0.477 mol) of a colorless oil in 77% yield. The NMR spectrum of the bromo alcohols 9 is identical with that obtained from the silver nitrate assisted hydrolysis.

Debromination of 3-Bromobicyclo[3.2.1]octa-3,6-dien-2-ol (9) with *n*-Butyllithium. A 250-mL three-necked flask equipped with a reflux condenser, gas inlet, septum, and magnetic stirrer was charged with 10.063 g (0.0500 mol) of the title bromo alcohol 9 dissolved in 75 mL of anhydrous ether. The flask was flushed with dry nitrogen and cooled to -78°C . To the cold, stirred solution was added 52.3 mL (0.119 mol) of 2.28 M *n*-butyllithium in hexane via syringe over a period of 20 min. A yellow color appeared, and the solution was stirred at -78°C for 70 min. The solution was warmed to -12°C and stirred at this temperature for 25 min. Water was added dropwise, via syringe, to the rapidly stirred reaction mixture over a 20-min period while the reaction warmed from -12 to $+5^{\circ}\text{C}$. After warming to room temperature, the solution was diluted with 150 mL of brine and extracted twice with 75 mL of ether. The combined ether extracts were washed with 100 mL of brine and 150 mL of water and dried over magnesium sulfate. The ether was removed on a rotary evaporator to leave 7.74 g of a yellow oil as the crude product. This oil was distilled through a short-path distillation apparatus ($63\text{--}70^{\circ}\text{C}$ (2.6 mm)) to give 2.305 g (0.0189 mol) of a mixture of the desired *exo*- and *endo*-bicyclo[3.2.1]octa-3,6-dien-2-ol (10): 38% yield; NMR (60 MHz, CCl_4) δ 6.30 (dd, $J = 6$, 3 Hz, 1 H, vinyl proton), 6.02 (m, 1 H, vinyl proton), 5.74 (dd, $J = 6$, 3 Hz, 1 H, vinyl proton), 5.12 (m, 1 H, vinyl proton), 3.76 (broadened s, 2 H, H-2 proton superimposed on OH proton), 2.54 (m, 2 H, H-1 and H-5 bridgehead protons), 1.82 (m, 2 H, H-8 bridge protons); the aliphatic region showed a somewhat higher than expected integration indicating some saturated impurities; IR (neat, 0.1 mm) 3350 (s), 3050 (m), 3025 (m), 2940 (s), 1627 (w), 1055 cm^{-1} (s).

Debromination of 3-Bromobicyclo[3.2.1]octa-3,6-dien-2-ol (9) with *sec*-Butyllithium. A 1-L three-necked flask fitted with a magnetic stirrer, reflux condenser, gas inlet, and addition funnel was charged with 9.98 g (0.2380 mol) of sodium hydride (57.2% dispersion in mineral oil). The sodium hydride was washed with five 20-mL portions of dry hexane to remove the mineral oil. After removal of the last hexane wash, 200 mL of anhydrous ether was added to the sodium hydride, and the flask was thoroughly flushed with dry nitrogen and cooled to 0°C . A solution of 40.517 g (0.2015 mol) of the title bromo alcohol 9 in 110 mL of anhydrous ether was placed in the addition funnel and added dropwise to the cold, stirred sodium hydride suspension over a period of 30 min. This mixture was stirred at 0°C for an additional 45 min. Then the addition funnel was replaced with a septum and the reaction mixture cooled to -78°C . To this cold, stirred solution was added 242 mL (0.242 mol) of 1.0 M *sec*-butyllithium in cyclohexane via syringe over 30 min. The resulting brown solution was stirred at -78°C for 2.75 h and then warmed to 0°C for 5 min. Water was added dropwise, slowly, via syringe to the rapidly stirred solution. This was stirred at 0°C for 20 min and then poured into 300 mL of brine, and the layers were separated. The aqueous layer was extracted with 400 mL of ether, and the combined ether extracts were washed twice with 300 mL of brine and three times with 500 mL of water. After the mixture was dried over magnesium sulfate, the ether was removed on a rotary evaporator to leave about 30 mL of a reddish oil. This oil was distilled [$62\text{--}74^{\circ}\text{C}$ (4.0 mm)] to give 10.975 g (0.0898 mol, 45%) of dienol 10 as a colorless liquid whose identity was verified by comparison of its NMR spectrum with that of an authentic sample.

Oxidation of Bicyclo[3.2.1]octa-3,6-dien-2-ol (10) with Pyridinium Dichromate. The general procedure of Corey and Schmidt¹³ was followed. A solution was prepared by dissolving 54.6 g (0.121 mol) of pyridinium dichromate in 70 mL of DMF in a 250-mL flask equipped with a magnetic stirrer and Drierite drying tube. This was cooled to 0°C , and a solution of 10.975 g (0.0898 mol) of the title alcohol 10 in 30 mL of DMF was added to the cold, stirred oxidizing agent. The reaction was stirred at 0°C for 5 h, poured into 1 L of water, and extracted with five 200-mL portions of ether. The combined ether extracts were washed with three 500-mL portions of water and dried over magnesium sulfate. The ether was removed on a rotary evaporator to leave a yellow oil which was distilled [$56\text{--}62^{\circ}\text{C}$ (4.2 mm)] to yield 3.834 g (0.0319 mol, 36%) of the desired bicyclo[3.2.1]octa-3,6-dien-2-one (7) whose NMR spectrum was identical with that of an authentic sample.¹¹

Preparation of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone (11). A solution of 0.625 g (5.21 mmol) of ketone 7

in 2 mL of methanol was added to 0.9638 g (5.18 mmol) of tosylhydrazine dissolved in 9 mL of methanol in a 25 mL flask equipped with a magnetic stirrer and a Drierite drying tube. Three drops of pyridine were added to the reaction, and it was allowed to stir at room temperature. After about 2 h a white precipitate started to form. The reaction mixture was stirred for a total of 8 h at room temperature and then placed in a refrigerator overnight to complete precipitation. The white, powdery product was isolated on a Hirsch funnel and dried to give 0.569 g (1.97 mmol, 39%) of the desired tosylhydrazone: mp $149\text{--}152^{\circ}\text{C}$ dec; NMR (100 MHz, CDCl_3) δ 7.90 (d, $J = 9$ Hz, 2 H, aromatic protons), 7.35 (d, $J = 9$ Hz, 2 H, aromatic protons), 6.80–6.35 (m, 2 H, vinyl protons), 5.92 (m, 1 H, vinyl proton), 5.68 (dd, $J = 9$, 2 Hz, 1 H, vinyl proton), 3.81–3.50 (m, 1 H, bridgehead proton), 3.04 (m, 1 H, bridgehead proton), 2.48 (s, 3 H, aromatic methyl), 2.18 (m, 2 H, bridge protons); IR (Nujol mull) 3210 (m), 1602 (w), 1380 (s), 1340 (s), 1175 cm^{-1} (s); high-resolution mass spectrum, calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ m/e 288.093, found m/e 288.094.

Dry Salt Pyrolysis of the Lithium Salt of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone (11). A 100-mL three-necked flask fitted with a magnetic stirrer, gas inlet, and septum was charged with 0.7371 g (2.56 mmol) of the title tosylhydrazone 11 dissolved in 20 mL of anhydrous THF. To this tosylhydrazone solution at room temperature was added 1.71 mL (2.56 mmol) of 1.50 N methyllithium in ether. Hydrogen gas evolved, and the solution was stirred at room temperature for 15 min. The THF was evaporated by blowing dry nitrogen over the stirred solution. When most of the THF had evaporated, the white lithium salt covered the inside of the flask. The standard all-glass decomposition apparatus was set up, and the salt heated to 198°C (oil bath temperature) under vacuum (0.1 mm) while the volatile products were pumped over and collected in a trap maintained at -78°C . An estimate of the time nitrogen evolution begins and ceases can be made by watching the pressure of the vacuum pump. Nitrogen evolution started at about 120°C , and heating at 198°C was continued for 10 min after nitrogen evolution had ceased. The volatile material in the traps was washed out with pentane and the pentane removed by distillation through a 6-in. Vigreux column. The remaining yellow oil was analyzed by VPC (column a, 124°C , 75 mL/min). In addition to THF and benzene, six components, A–F, were found with retention times and percent composition as follows: THF (6.3 min), benzene (8.5 min), A (14.1 min, 44%), B (18.2 min, 7.6%), C (20.8 min, 9.5%), D (26.8 min, 23.7%), E (34.4 min, 8.8%), F (37.6 min, 6.4%). Tridecane (39.8 min) internal standard was added, and the total yield of volatile products was found to be 1.4%. These compounds were isolated by preparative VPC. Components A–C were identified as bicyclo[3.2.1]octa-2,6-diene, tricyclo[3.2.1.0^{2,7}]oct-3-ene (13) and tetracyclo[3.3.0^{2,6}.0^{4,6}.0]octane (14) by NMR spectral comparison with those of authentic samples.^{17,18} Component D is a mixture of two products, one of which is semibullvalene (15), identified by comparison of its NMR with its literature NMR.¹⁹ The other product is 5-ethynyl-1,3-cyclohexadiene (16).²⁰ A 60-MHz NMR of 16 was kindly provided by Professor Murahashi²¹ and compared to our 100-MHz spectrum. NMR integration shows the compounds 15 and 16 to be present in roughly a 1:4 ratio. Component E remains unidentified: NMR (100 MHz, CDCl_3) δ 1.67 (s superimposed on m), 1.50 (broadened d, $J = 2$ Hz). Component F has been identified as *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (17) by comparison of its NMR spectrum with the data of Bergman.¹⁰

Decomposition of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone (11) with Potassium Hydride and 18-Crown-6 in Diglyme. A 100-mL flask equipped with a reflux condenser, gas inlet, and magnetic stirrer was charged with 91.7 mg (0.504 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed with six 5-mL portions of hexane to remove the mineral oil. After removal of the last hexane wash, 10 mL of anhydrous diglyme was added. Then 112.3 mg (0.390 mmol) of the title tosylhydrazone 11 was added with evolution of hydrogen. Upon addition of 110.3 mg (0.417 mmol) of 18-crown-6 a pink color appeared in the solution, but it faded after about 5 min of stirring. The reaction was heated to 140°C for 2 h. After cooling, the reaction was diluted with 150 mL of water and extracted with four 50-mL portions of pentane. The pentane extracts were combined and washed with five 60-mL portions of water.

After the mixture was dried over sodium sulfate, the pentane was removed by distillation through a 7-in. Vigreux column. The residue was analyzed by VPC (column a, 125 °C, 65 mL/min). The results were similar to those of the previous decompositions of this tosylhydrazone except that there were a number of new compounds present, probably residual mineral oil components. The six hydrocarbons found previously were present with percent compositions as follows: bicyclo[3.2.1]octa-2,6-diene (12), 18.9%; tricyclo[3.2.1.0^{2,7}]oct-3-ene (13), 12.4%; tetracyclo[3.3.0.^{2,8}.0^{4,6}.0]octane (14), 10.5%; mixture of semibullvalene (15) and 5-ethynyl-1,3-cyclohexadiene (16), 13.0%; unknown E, 28.4%; *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (17), 16.8%. Tridecane internal standard was added, and the overall yield was found to be 1.5%.

Dry Salt Pyrolysis of the Lithium Salt of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone (11) by Addition of the Salt to a Hot Surface. A solution of 196.2 mg (0.681 mmol) of the title tosylhydrazone 11 in 15 mL of dry THF was prepared in a 50-mL flask fitted with a septum, gas inlet, and magnetic stirrer. To this tosylhydrazone solution was added 0.454 mL (0.681 mmol) of 1.50 M methyllithium in ether. The THF was removed by blowing on the stirred solution with a stream of dry nitrogen, and the salt was dried further by pumping at 0.1 mm while the flask was warmed to about 40 °C. The salt had coated the inside of the flask and had to be scraped off the glass with a spatula to transfer it to a curved test tube with a ground-glass joint. The standard all-glass decomposition apparatus was assembled and the curved test tube of salt fitted into the side neck of a three-necked flask. This flask was heated to 195 °C in an oil bath while a pressure of 0.1 mm was maintained. The curved test tube was rotated and tapped, allowing small portions of the salt to drop into the hot flask where they decomposed immediately. The volatile products were collected in the two traps kept at -78 °C. The traps were washed with pentane, and the pentane was removed by distillation through a 7-in. Vigreux column. The remaining oil was analyzed by VPC (column a, 123 °C, 75 mL/min). The same six products found in the previous decompositions were obtained in the following percent compositions: bicyclo[3.2.1]octa-2,6-diene (12), 58.3%; tricyclo[3.2.1.0^{2,7}]oct-3-ene (13), 7.2%; tetracyclo[3.3.0.^{2,8}.0^{4,6}.0]octane (14), 7.3%; mixture of semibullvalene (15) and 5-ethynyl-1,3-cyclohexadiene (16), 11.2%; unknown E, 11.2%; *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (17), 4.8%. Tridecane was added as an internal standard, and the overall yield of volatile products was found to be 2.8%.

Irradiation of the Lithium Salt of Bicyclo[3.2.1]octa-3,6-dien-2-one Tosylhydrazone (11). A 50-mL flask fitted with a magnetic stirrer, gas inlet, and septum was charged with 0.2482 g (0.861 mmol) of the title tosylhydrazone 11 dissolved in 8 mL of anhydrous THF. The flask was purged with dry nitrogen, and 0.52 mL (0.86 mmol) of 1.67 N methyllithium in ether was added with a syringe. Frothing and bubbling accompanied the gas evolution. The solution was stirred at room temperature for 15 min. The solution was diluted with anhydrous THF to a total volume of 220 mL (0.0039 M) and transferred to a vessel surrounding the quartz immersion well of a 450-W Hanovia high-pressure mercury lamp. The vessel was attached by latex tubing through a Drierite trap to a graduated cylinder inverted in a water bath so that nitrogen evolution could be monitored. The reaction solution was irradiated until an equivalent amount of nitrogen had been collected (5.5 h). The solution was poured into 600 mL of water and extracted with three 75-mL portions of pentane. The pentane extracts were combined and washed four times with 100-mL portions of water. After the mixture was dried over sodium sulfate, the pentane was removed by distillation through a 7-in. Vigreux column. The remaining oil was analyzed by VPC (column a, 111 °C, 70 mL/min). Five of the six compounds obtained in the lithium salt pyrolysis were found with percent composition as follows: bicyclo[3.2.1]octa-2,6-diene (12), 39%; tricyclo[3.2.1.0^{2,7}]oct-3-ene (13), 31%; tetracyclo[3.3.0.^{2,8}.0^{4,6}.0]octane (14), 18%; mixture of semibullvalene (15) and 5-ethynyl-1,3-cyclohexadiene (16), 9%; *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (17), 3%. Unknown E as reported for the thermal decompositions of 11 was absent. Tridecane internal standard

was added, and an overall yield of volatile products was found to be 2.7%.

The aqueous layer (with considerable particulate matter) from the pentane extraction was extracted further with 100 mL of chloroform and the chloroform layer dried over sodium sulfate. The aqueous layer was acidified with 1 N HCl and extracted a final time with two 100-mL portions of chloroform. Again the combined chloroform extracts were dried over sodium sulfate. These two chloroform extracts were examined separately but in the same manner. The chloroform was removed, and NMR spectra were taken. The first chloroform extract gave the following NMR (60 MHz, CDCl₃): δ 4.4-3.3 (br band), 2.7-1.0 (br band). These undefined absorbances were present in a ratio of 2:3. No aromatic or aromatic methyl absorbances were present. The residue from the chloroform extracts of the acidified aqueous layer gave a very similar NMR. The two chloroform extracts were combined at this point. This residue showed a TLC *R_f* value of about 0.05 or less (CH₂Cl₂, silica gel) under conditions where the starting tosylhydrazone and a known azine had large (about 0.6 or greater) *R_f* values. Pyrolysis of this material in the mass spectrometer showed no distinct molecular ion, but all molecular weights from 106 to 500 were represented in gradually decreasing intensity. This residual oil was dried by heating to 60 °C under vacuum (0.05 torr) for 24 h. The residue weighed 0.2770 g, which is 112% (weight percent) yield. This discrepancy may be due to a small amount of nonvolatile impurities from the solvent. This intractable residue seems to be the final product of the major portion of the reactant.

Debromination of *exo*-6-Bromotricyclo[3.2.1.0^{2,7}]oct-3-ene (26a) with Tri-*n*-butyltin Hydride. By use of the general procedure of Klumpp,⁷ a 5-mL flask fitted with a magnetic stirrer, reflux condenser, and gas inlet was charged with 207 mg (1.19 mmol) of the title bromide 26a, 694 mg (2.39 mmol) of freshly prepared tri-*n*-butyltin hydride, and 1.0 mg of azobisisobutyronitrile (AIBN). This solution was heated to 95 °C under a nitrogen atmosphere for 7 h. After the mixture cooled, the volatile products were collected by distillation on an Aldrich Kugelrohr [65 °C (73 mm)]. The distilled product, 22.8 mg (0.21 mmol, 19% yield) of a colorless liquid, was analyzed by VPC (column a, 126 °C, 70 mL/min). The product mixture consisted of bicyclo[3.2.1]octa-2,6-diene (12), tricyclo[3.2.1.0^{2,7}]oct-3-ene (13), and tetracyclo[3.3.0.^{2,8}.0^{4,6}.0]octane (14) in a ratio of 98.7: 1.3:0 (less than 0.08), respectively.

Debromination of *exo*-6-Bromotricyclo[3.2.1.0^{2,7}]oct-3-ene (26a) with Sodium in *tert*-Butyl Alcohol. The general procedure of Klumpp⁷ was followed. A 25-mL flask fitted with a magnetic stirrer, reflux condenser, and gas inlet was charged with 173 mg (0.94 mmol) of the title bromide 26a dissolved in 2.2 mL of dry tetrahydrofuran and 0.6 mL of dry *tert*-butyl alcohol. This solution was heated to 50 °C with rapid stirring in a nitrogen atmosphere. Then 171 mg (7.44 mmol) of sodium was added and the resulting mixture heated at reflux for 9.5 h. After the mixture cooled, methanol was slowly added to destroy the excess sodium. The resulting solution was poured into 30 mL of water and extracted with four 10-mL portions of pentane. The combined pentane extracts were washed with four 30-mL portions of water and dried over magnesium sulfate. The pentane was removed by distillation through a 7-in. Vigreux column to leave about 0.3 mL of a colorless liquid which was analyzed by VPC (column a, 120 °C, 60 mL/min). The product mixture consisted of bicyclo[3.2.1]octa-2,6-diene (12), tricyclo[3.2.1.0^{2,7}]oct-3-ene (13), and tetracyclo[3.3.0.^{2,8}.0^{4,6}.0]octane (14) in a ratio of 97.5:2.5:0 (less than 0.1), respectively. Tridecane internal standard was added, and the yield of hydrocarbons was found to be 29%. An additional compound (possibly a dimer²⁹) was present at a much longer VPC retention time, but it was not investigated.

Registry No. 7, 1122-53-8; 8, 65824-27-3; *endo*-9, 56639-02-2; *exo*-9, 56639-01-1; *exo*-10, 17757-30-1; *endo*-10, 32655-68-8; 11, 80976-41-6; 11 Li, 80976-42-7; 12, 4096-95-1; 13, 3725-23-3; 14, 765-72-0; 15, 6909-37-1; 16, 57015-38-0; *endo*-17, 28282-68-0; *exo*-26a, 40459-37-8; 2-carbenabicyclo[3.2.1]octa-3,6-diene, 80976-43-8.