

Communications to the Editor

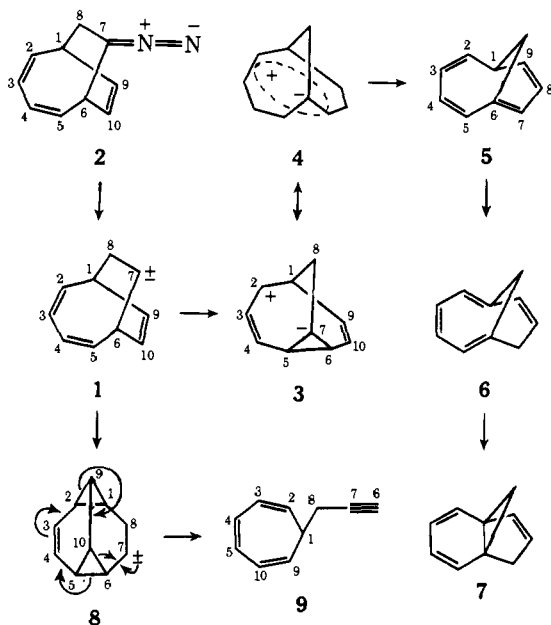
Carbenic Rearrangement and Fragmentation of Bicyclo[4.2.2]deca-2,4,9-trien-7-ylidene and Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene

Sir:

We wish to report the thermal and photochemical properties of bicyclo[4.2.2]deca-2,4,9-trien-7-ylidene (**1**) and elaborate further the intramolecular chemistry of bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (**17**).¹ These potentially degenerate carbenes are of interest because of their deep-seated rearrangement processes and products and because of their transannular interactions resulting in carbon-skeleton fragmentation to give acetylenic cycloheptatrienes.

Isomerization of **1** at 220 °C, as generated from 7-diazo-bicyclo[4.2.2]deca-2,4,9-triene (**2**) by pyrolysis of the sodium salt of bicyclo[4.2.2]deca-2,4,9-trien-7-one *p*-tosylhydrazone,² and collection of the volatile products (~100%) at -78 °C yields bicyclo[4.3.1]deca-2,4,6,8-tetraene (**5**, 81%), tricyclo[4.3.1.0^{1.6}]deca-2,4,7-triene (**7**, 5%), and 1-propargyl-2,4,6-cycloheptatriene (**9**, 14%). Although thermal rearrangement of α -hydrogen is usually a facile carbenic process,³ isomerization of **1** by migration of hydrogen from C₈ to the carbenic center, C₇, to give bicyclo[4.2.2]deca[2,4,7,9-tetraene² (**10**) or its subsequent derivatives was not detected.

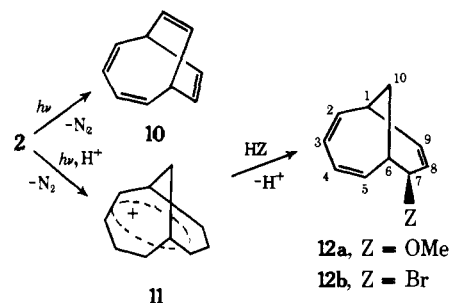
Tetraene **5** is a strained bridgehead olefin.^{4,5} It is sensitive to heat and to oxygen and at present cannot be efficiently separated preparatively from **7** and **9**. The mixture of **5**, **7**, and **9** can be kept at -78 °C without rapid alteration and is a satisfactory source of **5** for direct study and for use in synthesis. The isomeric products (**5**, **7**, and **9**) were characterized and analyzed by IR and NMR methods; **7**⁶ and **9**⁷ are separable from **5** by gas-liquid chromatography and were identified by comparison with authentic samples.



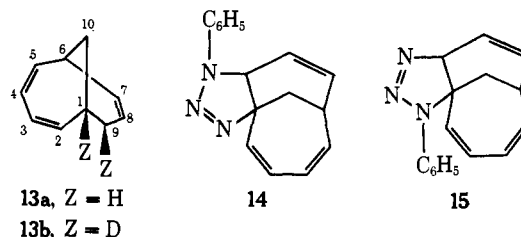
Participation of its π -electron systems appears to be important in isomerization of **1** to **5**, **7**, and **9**.^{8a} Formation of **5** from **1** involves the equivalent of a 1,2-shift of C₅ of the diene bridge to C₇, possibly via **3** and **4** in which use is made of

bishomotropylum character (**4**) of the rearrangement process. Triene **7** presumably is formed from **5** and possibly **6**; the mechanistic aspects of such a process are as yet unclear^{8b} but are consistent with properties of **5** to be described later. Acetylene **9** is of note in that it may be derived from **1** by intramolecular cycloaddition of the C₂-C₅ diene and C₉-C₁₀ monoene bridges, cyclopropylcarbonyl fragmentation⁹ of **8**, and reorganization.¹⁰

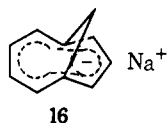
Photolysis of **2**, as generated by irradiation (Hanovia medium pressure mercury lamp through Pyrex) of the sodium salt of bicyclo[4.2.2]deca-2,4,9-trien-7-one *p*-tosylhydrazone suspended in ethyl ether at 25 °C, results in significant hydrogen migration from C₈ to C₇ to yield **10**² and thus the photochemical and thermal carbenic processes of **2** are decidedly different. In methanol **2** photolyzes efficiently to *exo*-7-methoxybicyclo[4.3.1]deca-2,4,8-triene¹¹ (**12a**); in the protic environment, apparently cationic carbon-skeleton rearrangement and solvent capture by the bishomotropylum bicyclo[4.3.1]decatrienyl cation¹² (**11**) occur.



As expected the bridgehead double bond in tetraene **5** is highly reactive. Diimide and dideuterodiimide reduce **5** selectively at -40 °C to bicyclo[4.3.1]deca-2,4,7-triene (**13a**, 60%) and 1,9-dideuterobicyclo[4.3.1]deca-2,4,7-triene (**13b**, 53%), respectively. The structures of **13a**^{13a} and **13b**^{13c} are assignable on the basis of their IR, mass, and NMR spectra. Bicyclic triene **13a** is identical with that obtained by addition of hydrogen bromide to **10** in methylene chloride and reduction of the resulting *exo*-7-bromobicyclo[4.3.1]deca-2,4,8-triene (**12b**) with lithium triethylborohydride¹⁴ in tetrahydrofuran at 20-25 °C. The potential of **5** for reaction as a 1,3-dipolarophile at its C₆-C₇ double bond is revealed by its addition of phenyl azide at 0 °C to give a *N*-phenyltriazole (mp 92-94 °C, **14** or **15**) for which the position of the phenyl group is not yet established.¹⁵

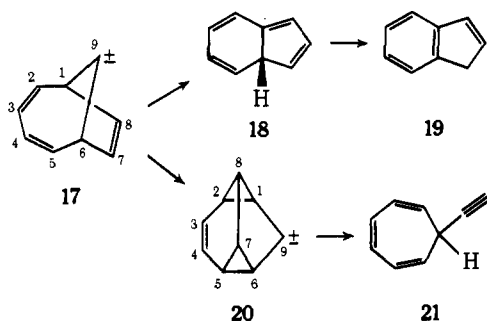


Of particular interest is that **5** reacts essentially quantitatively with sodium dimsyl in dimethyl sulfoxide at -78 °C and warming to room temperature to give the 10 π electron anion, 1,5-methanocyclononatetraenyl anion^{6a,b} (**16**). The structure of **16** is established from its NMR spectrum⁶ and upon its



conversion to **7** upon protonation. Indeed vacuum pyrolysis of the sodium salt of bicyclo[4.2.2]deca-2,4,9-trien-7-one *p*-tosylhydrazone, reaction of the condensate with sodium dimethyl sulfoxide, and acidification of the product is an advantageous method for preparing **7** (>54% isolated). Such an overall process might be the source of **7** from pyrolysis of **2** in a basic environment.

Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (**17**), presumably generated by decomposition of 9-diazobicyclo[4.2.1]nona-2,4,7-triene as derived from thermolysis of the dry sodium salt of the *p*-tosylhydrazone of bicyclo[4.2.1]nona-2,4,7-trien-9-one, has been reported¹ to give indene (**19**, 95%). A simple path for conversion of **17** to **19** (and is analogous to that suggested for conversion of **1** to **5**) is rearrangement to bicyclo[4.3.0]nona-2,4,6,8-tetraene (**18**) which undergoes 1,5-sigmatropic isomerization to **19**. It has now been found that **17**, as generated thermally, also yields 1-ethynyl-2,4,6-cycloheptatriene¹⁶ (**21**, 5%). Acetylene **21** may result from cyclopropylcarbinyl collapse of **20** as formed by cycloaddition of the C₂-C₅ diene and C₇-C₈ monoene moieties within **17** or its precursors.¹⁷ The overall behavior of **1** and **13** is thus formally identical. Study of possible degeneracy and the significance of bicycloaromatic interactions in isomerization of **1** and **17** will be initiated.



Acknowledgment. We should like to acknowledge support of this research by the National Science Foundation, a dissertation year fellowship to T. V. Rajanbabu by the Stauffer Chemical Company, and the initial observations by J. B. Press relative to the properties of **1**.

References and Notes

- (1) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 5366 (1972).
- (2) J. B. Press and H. Shechter, *J. Org. Chem.*, **40**, 2446 (1975).
- (3) W. Kirmse, "Carbene Chemistry", Academic Press, New York, N.Y., 1971, pp 236, 457.
- (4) Progress in synthesis of bridgehead olefins has been reviewed by G. Köbrlich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973).
- (5) ¹H NMR (CDCl₃) δ 2.2 (m, 1 H), 2.7 (m, 1 H), 2.9 (m, 1 H), 5.6 (m, 1 H), 5.9 (m, 4 H), and 6.3 (m, 2 H); ¹³C NMR (CDCl₃, -40 °C) δ 139.3 (1 C), 138.7 (1 C), 135.3 (1 C), 128.0 (1 C), 125.8 (2 C), 121.4 (1 C), 36.4 (1 C), and 32.8 (1 C) (the ¹³C resonance of C₆ is of too low intensity to be recorded).
- (6) (a) Prepared previously by P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, **88**, 3461 (1966). (b) We should like to thank Dr. Radlick and his colleagues for a sample of **7**.
- (7) P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc., C*, 1062 (1967).
- (8) (a) In the present interpretation **2** is assumed to convert first to **1** which then yields **8**. It cannot be ruled out, however, that sodium bicyclo[4.2.2]deca-2,4,9-trien-7-one *p*-tosylhydrazone or/and **2** undergo intramolecular cycloaddition of their C₂-C₅ diene and C₉-C₁₀ monoene bridges before conversion (in part) to **8**. (b) 1,7-Hydrogen migration in **5** to give **8** is symmetry forbidden.
- (9) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).
- (10) An alternate, less likely mechanism involves isomerization of **1** to bullvalylidene and then cyclopropylcarbinyl fragmentation to **8**.
- (11) M. R. Willcott, J. F. M. Oth, J. Thio, G. Pilnke, and G. Schröder, *Tetrahedron Lett.*, 1579 (1971).
- (12) G. Schröder, J. Prange, B. Pritze, J. Thio, and J. F. M. Oth, *Chem. Ber.*, **104**,

3406 (1971).

- (13) (a) NMR (CDCl₃) δ 1.69–2.10 (m, 4 H, H₉ and H₁₀), 2.77 (br m, 1 H, H₁), 3.13 (br m, 1 H, H₆), and 5.80 (m, 6 H, olefinic H); (b) **13a** is also described by M. Fus, University of Koln, West Germany, 1968; (c) NMR (CDCl₃) δ 1.69–2.10 (m, 3 H, H₉ and H₁₀, coupling simplified), 3.13 (br m, 1 H, H₆), and 5.80 (m, 6 H, olefinic H). It is noted that the absorption at δ 2.77 has disappeared (bridgehead H₁).
- (14) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95**, 1669 (1973).
- (15) The adduct is of proper analysis; NMR (CDCl₃) δ 7.25 (m, 5 H, aromatic), 6.00 (m, 6 H, H₂, H₃, H₄, H₅, H₆, H₉), 4.45 (dd, 1.5 Hz, 4 Hz, 1 H, H₇), 3.15 (br m, bridgehead H₁), 2.25 (d, 13 Hz, 1 H, H₁₀, endo), 1.6 (dd, 12 Hz, 5 Hz, 1 H, H₁₀, exo). The triazole loses nitrogen readily upon heating and in mass spectral analysis.
- (16) R. M. Hoskinson, *Aust. J. Chem.*, **23**, 399 (1970).
- (17) (a) An alternate, more complicated mechanism might involve rearrangement of **17** to barbarylidene and subsequent cyclopropylcarbinyl fragmentation similar to that in footnote 10. (b) Pyrolysis of the sodium salt of barbaralene *p*-tosylhydrazone gives **21** (~100%).

T. V. Rajan Babu, H. Shechter*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received July 19, 1976

Stereochemical Rigidity and Enantiomerization of Bis(diisopropylamino)dialkylaminoboranes

Sir:

There is considerable interest in the conformational and dynamical behavior of aminoboranes;¹⁻³ however, with the exception of a brief report and discussion of a B-N torsional barrier in bis(dimethylamino)methylphenylaminoborane, [(CH₃)₂N]₂BN(CH₃)(C₆H₅),² little is known of the stereochemical dynamics of tris(amino) boranes. Recently, we have begun an investigation of the properties of these compounds, which are isoelectronic with the biologically important guanidinium ions. This communication reports the detection of stereochemically rigid (on the NMR time scale) bis(diisopropylamino)dialkylaminoboranes and the determination of the barrier to and the permutational mode of a concerted rotation which occurs about the two B-N(*i*-C₃H₇)₂ bonds.

At ambient temperature, the ¹H spectrum of bis(diisopropylamino)diethylaminoborane,⁴ [(*i*-C₃H₇)₂N]₂BN(C₂H₅)₂ (**I**), exhibits four resonances: a septet (δ 3.58, *J* = 7.0 Hz) arising from the isopropyl methine protons; a quartet (δ 2.93, *J* = 7.0 Hz) from the ethyl methylene protons; a doublet (δ 1.21, *J* = 7.0 Hz) from the isopropyl methyl protons; and a triplet (δ 0.95, *J* = 7.0 Hz) from the ethyl methyl protons. At -110 °C, in contrast, the ethyl resonances are typical of an ABX₃ system (δ_{CH₂} ~ 2.73, *J*_{AB} = 12 Hz, δ_{CH₃} 0.78), the isopropyl methyl resonances consist of two broad doublets (δ 1.13, *J* = 6.5 Hz, and δ 0.96, *J* = 6.0 Hz), and there are two well separated resonances arising from anisochronous isopropyl methine protons (δ ~ 3.51 and 3.27).

The noise-decoupled ¹³C spectrum at -105 °C exhibits resonances assigned to the isopropyl methine carbon (δ 62.4), the ethyl methylene carbon (δ 53.2), the ethyl methyl carbon (δ 28.2), and four peaks attributable to isopropyl methyl carbons occupying four diastereotopic sites (δ 41.5, 41.2, 37.7, and 37.0). On warming, the ethyl and the isopropyl methine peaks do not change, but the isopropyl methyl resonances undergo coalescence and sharpen to a single peak by -48 °C. Further warming to 30 °C does not affect the spectrum. Chemical shifts at 30 °C are isopropyl methine, δ 61.8; ethyl methylene, δ 53.9; isopropyl methyl, δ 38.7; and ethyl methyl, δ 27.5.

The stereochemical relationships between groups in **I** cannot be determined unequivocally from either ¹H or ¹³C spectra alone. However, the observation of two separate isopropyl methine proton resonances and four separate isopropyl methyl carbon resonances indicates that there are two distinct isopropyl sites and that within each of these sites, the methyl