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CYCLOPROPYLIDENE-BICYCLO[1.1.0]BUTANE INTERACTIONS. THE GENERATION AND INTRAMOLECULAR REARRANGEMENT OF TETRACYCLO[5.1.0.0^{2,4}.0^{3,5}]OCTANYLIDENES

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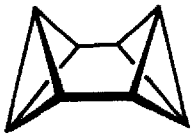
Pentacyclic (CH)$_8$ hydrocarbon **1** can be viewed not only as the most highly condensed valence isomer of cyclooctatetraene, but also as a formal (2+2) dimer of tetrahedrane. The effective cyclic conjugation of two bicyclo[1.1.0]butane rings in **1** should form the basis for interesting spectral properties.[2] Furthermore, its highly strained nature should promote unusual chemical reactivity. In anticipation that double carbenoid C-H insertion of readily accessible 4,4,8,8-tetrabromotricyclo[5.1.0.0^{3,5}]octanes (**2**)[3] or more conventional monocyclization[4] of tetracyclic dibromides such as **3a** could provide expedient synthetic entries to **1**, we have exposed several such halides to methyllithium. This approach was prompted in particular by our earlier observation that closure of **4** to **5** proceeds in exceptionally high (91%) yield.[5] However as



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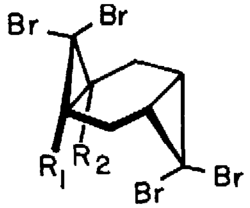
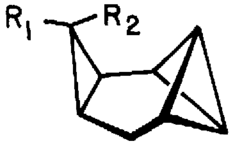
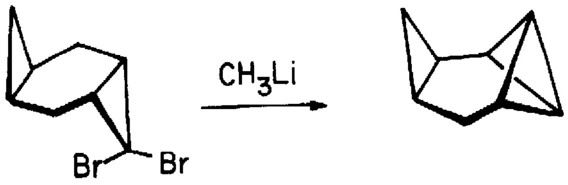


2a, R$_1$ = R$_2$ = H
b, R$_1$ = CH$_3$, R$_2$ = H
c, R$_1$ = R$_2$ = CH$_3$



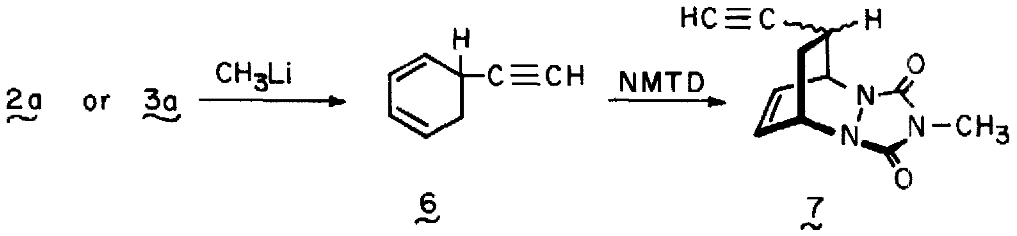
3a, R$_1$ = R$_2$ = Br
b, R$_1$, R$_2$ = H, CH(CH$_3$)OCH$_2$CH$_3$



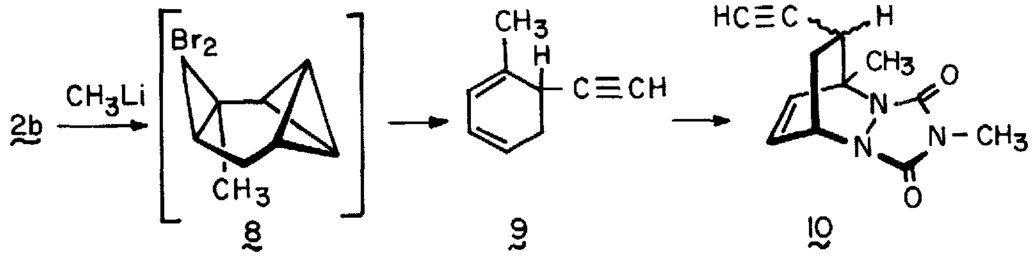
4 **5**

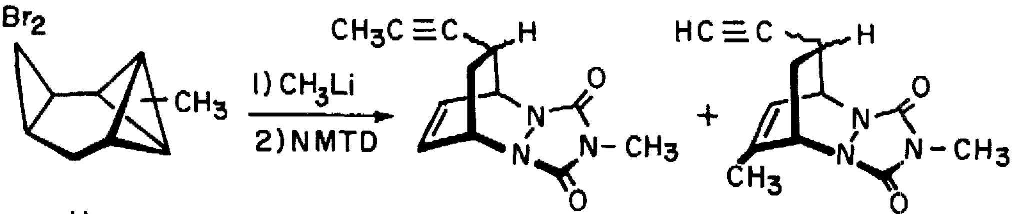
Christl and Lechner have also experienced recently,[6] the precedented insertion does not operate. The unanticipated deep-seated structural bond reorganization which occurs instead forms the subject of this report.

Sequential treatment of homobenzvalene[7] with dibromocarbene (from $CHBr_3$ and KO*t*Bu) to give 3a and with excess methyllithium in ether at 0° led to the formation of 5-ethynyl-1,3-cyclohexadiene (6, *ca* 30% yield)[6] as the only characterizable product. Its structure was substantiated spectroscopically and by cycloaddition to N-methyltriazolinedione (NMTD). The adduct so obtained (7) is characterized by multiplets at δ6.40-6.20 (1, olefinic), 5.50-5.40 (1, olefinic), 5.20-5.00 (2, $>C\underline{H}\text{-}N<$), 2.70-2.10 (2, $-CH_2-$), and 1.95 (2, $>C\underline{H}C{\equiv}C\underline{H}$) in addition to a singlet at 3.01 (3, methyl). The identical hydrocarbon was produced upon reaction of 2a with methyllithium, but in lower yield. The rationale that 2a likely reacts by initial closure to 3a prior to extensive skeletal rearrangement is supported by the isolation of substantial amounts of the ether insertion product 3b.

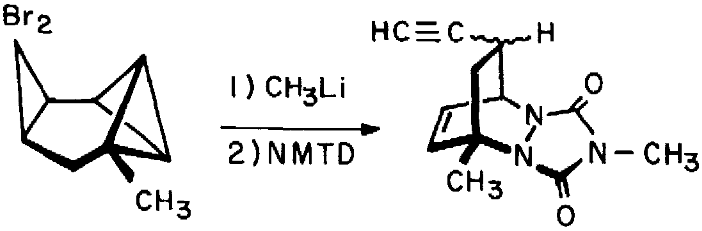


Through the use of methyl labeling, it proved possible to map rather systematically the origins of the carbon atoms in 6. When recourse was made to 2b, for example, there was obtained a single diene shown conclusively to be 9 by its conversion to 10. That carbenoid cyclization of the less hindered cyclopropylidene in 2b gains kinetic dominance (to give 8 initially) can be inferred from the regioselectivities observed with 11 (60% syn; 40% anti)[7a] and 14, the alternative possible "semi-reacted" products of 2b. However, none of these three tetracyclic dibromides gave 10. Rather, 11 afforded approximately equal amounts of 12 and 13 while 14 gave rise ultimately to adduct 15.



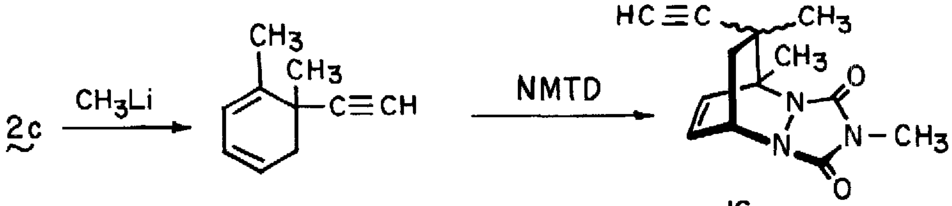


11 **12** **13**



14 **15**

Adherence to a similar kinetic bias would require that **2c** cyclize preferentially in that manner which would generate a transient intermediate different from anti-**17**. To test this rationale, **2c** and **17** (isomer ratio unknown) were independently treated as above. In contrast to **2c** which underwent conversion to **16**, **17** afforded an 80:20 mixture of **18** and **19**. In view of the mutually exclusive characteristics of these rearrangements, it is concluded that **2c**, like **2b**, experiences more efficient alkyllithium attack at its less sterically encumbered cyclopropane ring.



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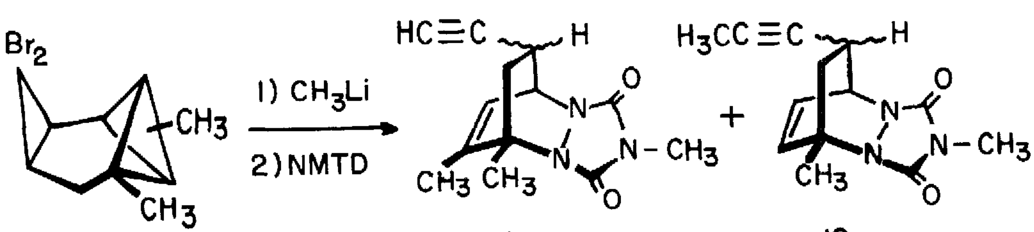
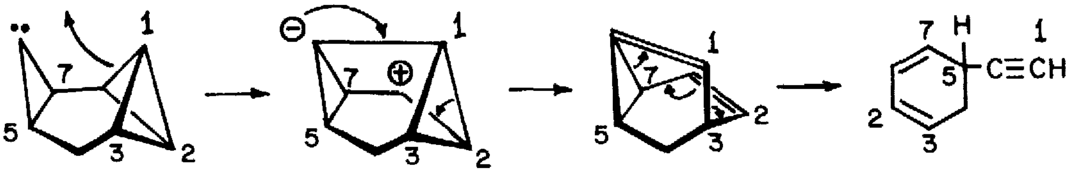


17 **18** **19**

The ultimate purpose of this work was to engage carbenes such as **20** in intramolecular C-H insertion. However, this potential route to **1** and its derivatives fails because of the incursion of a more facile rearrangement leading to 5-ethynyl-1,3-cyclohexadienes. As a consequence of Christl and Lechner's ^{2}H and ^{13}C labeling studies and the present work, the movement of *five* (C-1,2,3,5,7) of the eight constituent carbon atoms can be traced as shown in **6**. The most reasonable mechanism which can place C-1 at the terminal acetylenic site while simultaneously causing C-2 and C-3 to emanate as π-bonded partners and C-5/C-7 to remain as adjacent ring atoms is that advanced earlier by the Würzburg group. In brief, the carbenoid center is intercepted by the neighboring bicyclobutane edge bond in an electronic reorganization which conjoins C$_1$ and C$_8$ in a highly strained bicyclo[2.2.2]octa-2,5-diene framework (**21**), Diels-Alder retrogression of which delivers product. Thus, although the cyclopropylidene ring in **20** is so fixed that C-H insertion at C-4 seems geometrically plausible, this process clearly suffers from excessive energy requirements. However, because this very same molecular construction does also serve to constrain the carbenic center in close proximity to the C-1/C-8 bond, electron density is preferentially removed from this site in a most unusual 1,3 shift.[9]



20 **21** **6**

References and Footnotes

(1) The Ohio State University Dissertation Fellow, 1975-1976.
(2) Compare W. R. Moore and C. R. Costin, J. Amer. Chem. Soc., **93**, 4910 (1971).
(3) W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, J. Amer. Chem. Soc., **86**, 3126 (1964)
(4) W. R. Moore, H. R. Ward, and R. F. Merritt, J. Amer. Chem. Soc., **83**, 2019 (1961); W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, Tetrahedron Lett., 2365 (1970); W. R. Moore and J. B. Hill, ibid., 4343 (1970); W. R. Moore and B. J. King, J. Org. Chem., **36**, 1877 (1971); L. A. Paquette, G. Zon, and R. T. Taylor, ibid., **39**, 2677 (1974).
(5) R. T. Taylor and L. A. Paquette, Angew. Chem., **87**, 488 (1975); Angew. Chem. Intern. Ed. Engl., **14**, 496 (1975).
(6) M. Christl and M. Lechner, Angew. Chem., **87**, 815 (1975); Angew. Chem. Intern. Ed. Engl., **14**, 765 (1975).
(7) (a) R. T. Taylor and L. A. Paquette, accompanying paper; (b) M. Christl and G. Brüntrup, Angew. Chem., **86**, 197 (1974); Angew. Chem. Intern. Ed. Engl., **13**, 208 (1974); (c) G. W. Klumpp, and J. J. Vrielink, Tetrahedron Lett., 539 (1972).
(8) Footnore 5 of reference 6 indicates that G. Szeimies and K. Mannhardt have made similar observations.
(9) This research was supported in part by the National Science Foundation.