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EVIDENCE FOR HOMOQUADRICYCLENE, A POSSIBLE CARBON YLIDE

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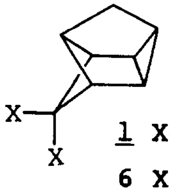
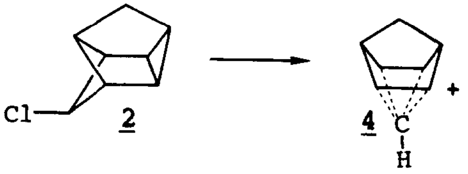
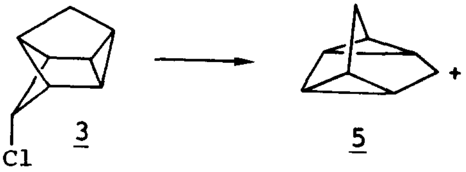
Summary. The endo-epimer of the formal homo-1,4 adduct of monochlorocarbene and norborna-2,5-diene on treatment with lithium 2,2,6,6-tetramethylpiperidide in THF in the presence of diphenylisobenzofurane (DPIBF) gave a single Diels-Alder adduct. The same cyclo-adduct was obtained by subjecting the homo-1,4 adduct of dibromocarbene and norborna-2,5-diene to lithiummethyl in THF. By single crystal X-ray analysis the adduct is shown to be the result of the normal Diels-Alder cyclo-addition of DPIBF to the least hindered side of tetracyclo[3.2.1.0.^{2,7}0.^{4,6}]oct-2-ene, a novel anti-Bredt olefine, best considered as a carbon ylide.

We recently reported that the homo-1,4 adduct[1] obtained from norborna-2,5-diene and dichlorocarbene (1) is a useful intermediate for studying complex rearrangements of C_8H_9 cations of the cage type.[2] A good illustration is provided by the exo and endo monochloro epimers (2 and 3) which are easily prepared by reductive dechlorination of 1. They rearrange differently on ionization, yielding two distinct families of cations, the square pyramidal and bis-cyclopropyl carbinyl species 4 and 5 respectively.[3] We now describe how 1 and its dibromo analogue 6[4] can be exploited to produce homoquadricyclene 7, an unusual anti-Bredt olefine which is perhaps the first example of a carbon ylide.

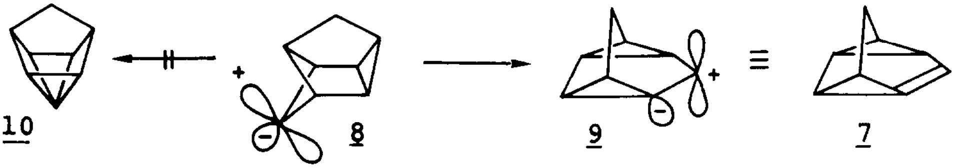


1 X=Cl
6 X=Br

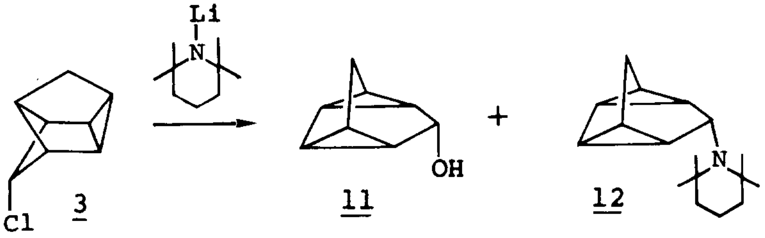




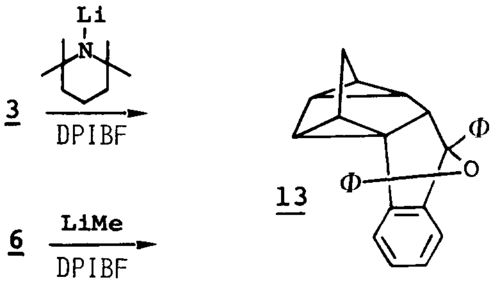
Our experimental approach is based on the premise that a carbene would behave like a cation, as both are electrophilic,[5] and that it would rearrange in the same way. Accordingly, the cyclobutylidene 8 should mimic the ionization of the endo-epimer 3 and give the zwitterionic intermediate 9. Normally, such a rearrangement would be completed by mutual annihilation of charges to give the corresponding olefine 7.^{6} In the present instance, formation of the bridgehead olefine 7 might be foiled by its twisted and strained geometry. The alternative, namely the insertion of the carbene into the cyclopropane ring to give the hypothetical structure containing a pyramidally substituted carbon atom (10), although structurally intriguing, would not be favoured for reasons of energy.



The experimental realization of these expectations was achieved by treating the endo-chloro epimer 3 with lithium 2,2,6,6-tetramethylpiperidide in THF at 25° for 1 h. Apart from a small amount (0.1%) of exo alcohol 11, undoubtedly derived from moisture, the main product (80.0%)^7 was the exo-2,2,6,6-tetramethylpiperidinohomoquadricyclane 12. Significantly, both products are the result of a suprafacial displacement process. The stereospecificity of rearrangement and substitution can be rationalized by several mechanisms in which the carbene 8 need not be invoked.



However, the choice of mechanism was narrowed when the same treatment of 3 by base was carried out in the presence of diphenylisobenzofurane (DPIBF). In addition to 11 (∿1.0%), and 12 (9.5%), a single Diels-Alder adduct 13 (84%) was formed. Confirmation that the immediate precursor of 13 was the formal anti-Bredt olefine 7 was obtained by an independent trapping experiment. Treatment of the gem-dibromo analogue 6 with lithiummethyl in THF at 25° for 20 min. in the presence of DPIBF gave exactly the same adduct 13 in 88% yield.



The structure of 13 was determined by single crystal X-ray analysis (Fig.). All interatomic distances were normal,[8] however the feature of interest was the unique exo/endo configuration of the olefine/diene adduct. Although there are four possibilities for cycloaddition, only the one expected of a dissymmetric dienophile had occurred. Clearly, DPIBF had approached the double bond of homoquadricyclene 7 on the least hindered exo face adopting the endo orientation in keeping with the Alder-Stein rule.[9]

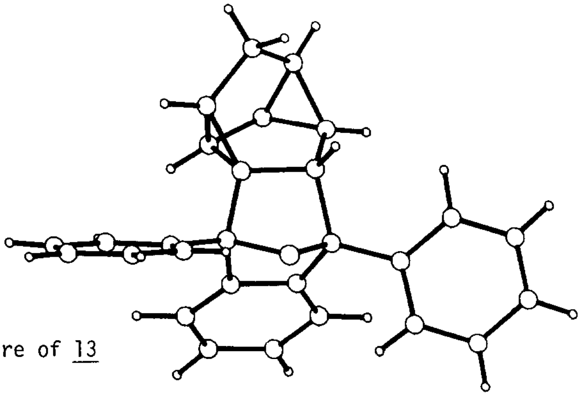


Fig. Crystal structure of 13

We believe that these two results satisfy the criterion for a common intermediate, namely 8, which has rearranged to a molecule which behaves like 7, a transient intermediate which falls well within the least accessible category of anti-Bredt olefines ($S < 5$).[10]

The nature of the double bond remains unknown, but polarization is probably in the sense indicated by 9, which would be favoured by the structural elements of the parent molecule.[11] Evidence for the reality of this novel chemical entity, a carbon ylide, is currently being sought.

BIBLIOGRAPHY AND NOTES

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2) C.W. Jefford, J. Mareda, J.C. Perlberger & U. Burger, J. Am. Chem. Soc. 101, 1370 (1979).

3) C.W. Jefford, S. Genevay-Höck, A. Delay, J. Mareda & U. Burger, Tetrahedron Lett. 2549 (1979); C.W. Jefford & V. de los Heros, Tetrahedron Lett. 913 (1980).

4) Although hitherto unknown, 6 was prepared by the conventional addition of dibromocarbene to norborna-2,5-diene (J.A. Zuber, Doctoral Thesis, University of Geneva, 1982).

5) An illustration is provided by the similarity of stereochemical criteria for hydride shifts in the two species (cf. A. Nickon, F. Huang, R. Wegelin, K. Matsuo & H. Yagi, J. Am. Chem. Soc. 96, 5264 (1974); L.S. Press & H. Shechter, ibid. 101, 509 (1979).

6) Both calculation and experiment predict and confirm that this is so for cyclobutylidene which gives methylidenecyclopropane (W.W. Schoeller, J. Am. Chem. Soc. 101, 4811 (1979); U. Brinker & G. Schenker, J. Chem. Soc. Chem. Comm. 679 (1982).

7) In addition to 11 and 12 there were eight other unidentified compounds formed in 20% yield. The exo configuration of the substituents 11 and 12 was assigned from the absence of vicinal coupling for the geminal proton. The general structure was determined by oxidative cleavage of 12 to the known homoquadricyclanone (N.A. LeBel & R.N. Liesemer, J. Am. Chem. Soc. 87, 4301 (1965).

8) Crystal data will be published in the full paper.

9) K. Alder & G. Stein, Angew. Chem. 50, 510 (1937).

10) G. Köbrich, Angew. Chem. Int. Ed. 12, 464 (1973); K.J. Shea, Tetrahedron 36, 1683 (1980)

11) The twisted and bent ethylene fragment possesses pyramidal and trigonal carbon atoms respectively and fulfills the structural conditions for sudden polarization (B.R. Brooks & H.F. Schaeffer, J. Am. Chem. Soc. 101, 307 (1979).

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