in energy by more than 50 calories this can easily be detected by pronounced curvature in the Curie plot. While it is possible that one of the tetramethyleneethane diradicals, I or II, might be characterized by an exact degeneracy between the singlet and triplet states, it is clearly less likely that *both* I and II will exhibit this behavior.

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9-Phenyl-1(9)-homocubene, Probably the Most Twisted Olefin Yet Known, and the Carbene 1-Phenyl-9-homocubylidene, Its Rearrangement Product

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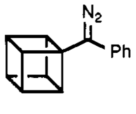
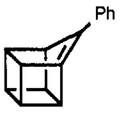
We have examined the thermal and photochemical decompositions of cubylphenyldiazomethane (**1**) and report here observations which make us believe these processes lead to 9-phenyl-1(9)-homocubene (**2**), the anti-Bredt rule olefin nonpareil.[1] By one phraseology,[2] the double bond in **2** would be called "trans in a five-membered ring". Previous to the present report, double bonds trans in six-membered rings were the limiting examples.[3] Although convenient, the descriptor "trans" is misleading. The relevant dihedral angle (2,1,9,8) in the σ frame of **2** is approximately 41°.[4] Were there no pyramidalization of C-9, the p-orbitals of the "double bond" would be orthogonal to one another.



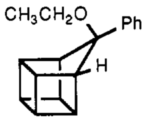
1



2

Cubylphenyldiazomethane was prepared by thermolysis of the sodium salt of the tosylhydrazone of cubyl phenyl ketone,[5] itself obtained by reaction of cubane carboxylic acid[6] with phenyllithium in ether. Its tosylhydrazone precipitated analytically pure on reaction of the ketone overnight at room temperature with excess tosylhydrazine in ethanol. When the tosylhydrazone was refluxed in ethanol with excess sodium ethoxide, it decomposed fairly rapidly. The solution turned red; aliquots showed the generation of a diazo compound (IR 2037 cm^{-1}), but it was not stable under these conditions and after 5 h was gone completely. Pyrolysis under vacuum (80–120 °C/0.005 Torr) of the dry sodium salt of the tosylhydrazone below a liquid N_2 cold finger gave 27–39% yield on the condensing surface of neat cubylphenyldiazomethane.[7] It is a red oil, labile at room temperature but stable for several days when stored at −20 °C in pentane.

Thermolysis of the tosylhydrazone in ethanolic sodium ethoxide and, separately, photolysis (Hg arc, Pyrex filter) of the diazo compound itself in ethanol gave good conversions to a 1.5:1 mixture of isomeric ethers of formula corresponding to addition of ethanol to cubylphenylcarbene. However, it was completely clear from their NMR spectra that the symmetry of the cubyl skeleton had been lost and that rearrangement into the homocubane system had occurred.[7] Whether (for the major product) this rearrangement occurred concommitantly with the loss of nitrogen or happened after cubylphenylcarbene was generated is yet a moot point.[8] The major isomer was assigned structure **3**, it being apparent from its proton and carbon NMR spectra that a single plane of symmetry bisects the molecule. This is the compound expected from addition of ethanol in the Markovnikov sense to 9-phenyl-1(9)-homocubene (**2**). The minor ether was first thought to be **4**, formed perhaps by ethanolysis with rearrangement[8] of the diazo compound or, instead, by addition of ethanol in the anti-Markovnikov sense to **2**. Although this assignment was reasonably consistent with the elementary NMR data,[7] it is in fact wrong; the true structure is **5**. The distinction between **4** and **5** was made unambiguously by using homonuclear coupled ^{13}C NMR methodology by which it was demonstrated that the quaternary carbon of the phenyl group is *not* attached to an adjacent aliphatic carbon which bears hydrogen. The origin of **5** is addressed later in this paper.



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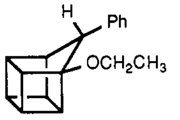

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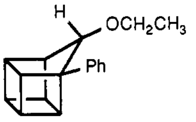

5

Following first the traditional approach, we attempted to trap the highly strained olefin **2** as a Diels–Alder adduct. Thermolysis of its precursor tosylhydrazone salt in monoglyme containing 9,10-diphenylisobenzofuran did indeed give an adduct of the expected formula, but it was obvious from its NMR spectra that it had not been formed by a 4 + 2 cycloaddition. The cyclohexadiene component of the isobenzofuran had not been aromatized; addition had occurred instead to one of the double bonds of this ring. This led us to use simple monoolefins as trapping agents.

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[1] For an excellent review of anti-Bredt olefins and previous references, See that of Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; pp 329–359.

[2] Wiseman, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 5966.

[3] Examples: 1-norbornene (Keese, R.; Krebs, E. P. *Angew. Chem.* **1971**, *83*, 254.); adamantene (Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637. Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R.; Maier, W. F. *J. Am. Chem. Soc.* **1979**, *101*, 7634); see ref 1 for others.

[4] Allinger, N. L. *Quantum Chemistry Program Exchange*, program MMP2(85).

[5] For a detailed review of the Bamford–Stevens reaction for the synthesis of diazo compounds, see: Maas, G.; Regitz, M. *Diazo Compounds*; Academic: New York, 1986; pp 257–272.

[6] Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962, 3157.

[7] The analytical and spectra data are in accord with expectation. Only the critical NMR data are given here (PMR at 500 MHz; CMR at 100 MHz; shifts in ppm from TMS; CDCl$_3$ solutions). Aromatic resonances are not included. **1**: PMR 4.10 (m); CMR 58.4 (s, br, weak), 51.7 (1 C, s), 49.9 (3 C, d, 155 Hz), 47.9 (1 C, d, 157.5 Hz), 45.0 (3 C, d, 157.5 Hz). **3**: PMR 3.65, 3.47, 3.26, 3.19 (2 H each, multiplets), 3.13 (2 H, q), 1.04 (3 H, t); CMR 102.0 (1 C, s), 61.1 (1 C, t, 140 Hz), 50.5 (2 C, d, 148 Hz), 44.4 (2 C, d, 151 Hz), 43.0 (2 C, d, 153 Hz), 41.1 (2 C, d, 156 Hz), 16.2 (1 C, q, 126.5). **5**: PMR 4.11 (1 H, d, 2), 3.91 (1 H, m), 3.81 (1 H, m), 3.56 (1 H, m), 3.46 (2 H, m), 3.38 (2 H, m), 3.35 and 3.47 (2 H, AB of ABX$_3$; J_{AB} 9.6, $J_{AX} = J_{BX} = 7$), 1.13 (3 H, t, 7); CMR 96.5 (1 C, d, 140), 65.5 (1 C, t, 143), 61.3 (1 C, s), 48.6 (1 C, d, 156), 48.3 (1 C, d, 157.5), 47.2 (1 C, d, 146.5), 44.85 (1 C, d, 156), 41.9 (1 C, d, 156), 41.8 (1 C, d, 156), 40.1 (1 C, d, 155), 15.7 (1 C, q, 126). **6**: PMR 3.68 (2 H, m), 3.45 (3 H, m), 3.18 (1 H, m), 3.10 (1 H, m), 0.92 (6 H, m), 0.28 (2 H, m); CMR 61.8 (1 C, s), 51.6, (1 C, s), 50.2 (2 C, d, 150), 45.7 (1 C, d, 145), 43.7 (2 C, d, 150), 42.5 (1 C, d, 154), 40.2 (1 C, d, 150), 12.2 (2 C, d, 154 to H at ∂ 0.28), 9.41 (2 C, q, 127). **7**: 3.80 (2 H, m), 3.23 (2 H, m), 3.17 (1 H, m), 3.10 (1 H, m), 2.47 (1 H, m), 0.98 (2 H, m), 0.72 (6 H, m); CMR 59.6 (1 C, s), 58.8 (1 C, d, 144), 52.3 (2 C, d, 145), 48.2 (1 C, s), 41.7 (2 C, d, 153), 40.6 (1 C, d, 157.5), 40.4 (1 C, d, 155), 16.7 (2 C, d, 153 to H at ∂ 0.98), 9.35 (2 C, q, 127). **8**: PMR 4.01 (1 H, m), 3.62 (1 H, m), 3.52 (1 H, m), 3.44 (1 H, m), 3.27 (1 H, m), 3.20 (1 H, m), 2.99 (1 H, m), 1.14 (3 H, d, 6.3), 0.63 (2 H, m), 0.48 (3 H, d, 6.3); CMR 60.3 (1 C, s), 55.0 (1 C, d, 153), 51.9 (1 C, s), 51.4 (1 C, d, 145), 47.6 (1 C, d, 149), 43.4 (2 C, d, 159), 41.1 (1 C, d, 156), 40.5 (1 C, d, 155), 21.8 (1 C, d, 154 to H at ∂ 0.63), 18.9 (1 C, d, 154 to H at ∂ 0.63), 15.6 (1 C, q, 127), 14.2 (1 C, q, 127).

[8] Solvolyses of cubylcarbinylbenzoates and the like are assisted anchimerically and occur with ring expansion (Cole, T. W., Jr. Ph.D. Thesis, The University of Chicago, 1964.). There is no evidence for solvolysis without expansion even for diphenylcubylcarbinyl derivatives (Stock, L.; Cole, T. W., Jr.; Luh, T. Y., unpublished results.).

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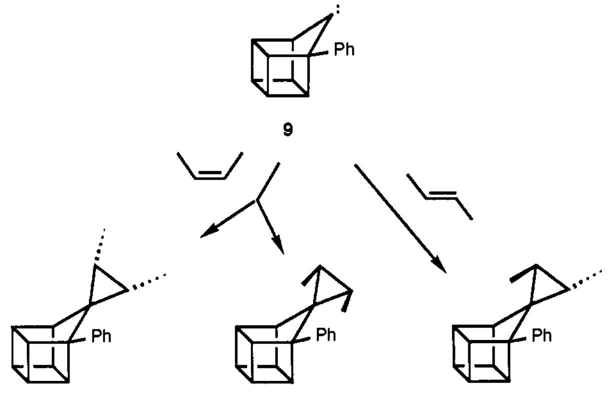
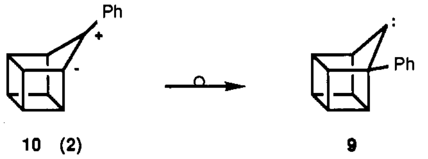
Photolysis of cubylphenyldiazomethane in neat *cis*-2-butene at -78 °C gave cleanly two adducts ($-N_2$) in the ratio of 2:1. These were separated by careful TLC on silica gel. Their NMR spectra left no doubt that both were spiro-fused cyclopropanohomocubanes, each with a single plane of symmetry. Structures **6** and **7** were assigned: **6** as the predominant isomer using (questionably) simple steric and chemical shift arguments. The NMR spectra showed that within each isomer the methyl groups are identical and hence in both isomers must be cis on the cyclopropane ring. Complementarily, irradiation of cubylphenyldiazomethane in *trans*-2-butene gave only the single adduct **8**, again a spiro-fused cyclopropanohomocubane, but now with no plane of symmetry and two methyl groups which are different and must therefore be trans to one another on the cyclopropane ring. It follows, we believe unequivocably, that cyclopropanes **6**, **7**, and **8** were formed by reaction of 1-phenyl-9-homocubylidene (**9**) with the isomeric butenes in stereospecific, singlet carbene additions.[9]



Once the carbene **9** is admitted into the reaction manifold, the formation of ether **5** upon the decomposition of cubylphenyldiazomethane in ethanol is easily understood. It is the expected product from reaction of the carbene with the O–H bond of the alcohol.[10]

Given what is known to this point, we believe that 9-phenyl-1(9)-homocubene (**2**) is formed on thermolysis or photolysis of cubylphenyldiazomethane, that it lives long enough even in refluxing ethanol to undergo intermolecular addition of solvent, and that on a similar time scale it rearranges to the carbene 1-phenyl-9-homocubylidene (**9**). Carbenes are normally of much higher energy than the isomeric olefins. However, the case here is quite special for the olefin is exceedingly strained. Indeed, MNDO calculations give similar heats of formation for **2** (201 kcal/mol) and **9** (199 kcal/mol).[11,12]

In accord with the usually large endothermic gap, the rearrangement of an olefin *to* a carbene is a rare reaction; one usually only postulated to account for certain aspects of cyclopropene chemistry[13] or olefin photochemistry.[14] Otherwise, it has been proposed by Chan and Massuda to account for the very odd chemistry they found on fluoride-induced thermolysis of a β-halosilane thought to be precursor to a bridgehead bicyclo[2.2.2]octene.[15] As such an olefin would be quite twisted, their case and ours may be related. (Interestingly, however, they observed neither simple solvent additions nor cyclopropanation reactions. The origin of this difference is not yet clear, but it could relate to a change in carbene spin state.) We, like Chan and Massuda, speculate that the rearrangement of an olefin to a carbene occurs from a zwitterionic state of the olefin. Salem has theorized that such a dipolar form might be stabilized relative to the corresponding diradical were the olefin much twisted and were its termini dissymmetrically substituted and open to pyramidalization.[16] A dipolar structure like **10** is not an unreasonable part description for 9-phenyl-1(9)-homocubene,[17] and it opens a good way to rationalize the observed chemistry; a "simple" Wagner–Meerwein shift provides for the skeletal reorganization of **2** into **9**.[18]



10 (2) **9**

As Chan and Massada noted, their case was too complex to permit a fuller exploration of the olefin-to-carbene rearrangement. Fortunately, we do not face this obstacle. Variations on **2** are easily possible, and we should be able to examine thoroughly the chemistry of cubyldiazomethanes not only by ordinary techniques but also by matrix isolation spectroscopy.

Finally, we return to the phrase in the opening paragraph "were there no pyramidalization of C-9, the p-orbitals of the "double bond" would be orthogonal to one another". Of course, rehybridization is expected, and substantial pyramidalization will occur to recover part of the π bonding energy.[19] The MNDO optimized geometry of **2** puts the phenyl carbon 12° out of the plane defined by C-9 and its two other substituents.[20] We note that pyramidalization at this carbon will diminish the conjugative interaction of its p-orbital with the attached phenyl group. Thus, spectroscopic characterization of phenylhomocubenes with various substituents on the aromatic ring should give us a new experimental probe of the pyramidalization phenomenon.

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(9) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496.

(10) Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 23.

(11) Steward, J. J. P.; Dewar, M. J. *Quantum Chemistry Program Exchange*, program MOPAC, no. 445.

(12) The phenyl substituent stabilizes the olefin. In the desphenyl series, the carbene is calculated to be 13 kcal/mol *more* stable than the olefin.

(13) For example: (a) Billups, W. E.; Lin, L. P.; Chow, W. Y. *J. Am. Chem. Soc.* **1974**, *96*, 4026. (b) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680.

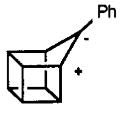
(14) For example: (a) Hixon, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 1981. (b) Fields, T. R.; Kropp, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7559.

(15) Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936.

(16) Salem, L. *Science (Washington, DC)* **1976**, *191*, 822. See, also: Brooks, B. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1979**, *101*, 307.

(17) MNDO calculation gives the net atomic charges at carbons 1 and 9 as -0.1565 and -0.0236, respectively.

(18) Instead, **9** could come about by a phenyl shift within zwitterion **11** whose polarization is opposite to that of **10**. However, here the orbital arrangement seems less attractive. The two possibilities are distinguishable by labeling experiments in progress.



11

(19) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734. For a discussion particularly germane to the case here, see: Michl, J.; Radziszewski, J. W.; Downing, J. W.; Kopecky, J.; Kaszynski, P.; Miller, R. D. *Pure Appl. Chem.*, in press.

(20) The actual dihedral angle between the rehybridized "double bond" orbitals is more difficult to obtain. Quantitative application of Haddon's π-orbital axis vector (POAV) analysis[21] is presently outside the bounds of POAV methodology as the σ frame internuclear angles in homocubenes are significantly less than 100° and provide a poor approximation of bond path angles. In due course, one expects these will be calculated[22] and incorporated appropriately.

(21) Haddon, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 2837.

(22) Cf. Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.