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SYNTHESIS AND MOLECULAR STRUCTURE OF A TETRA-t-BUTYLETHYLENE DERIVATIVE OBTAINED FROM A PROPELLANIC CARBENOID.[1]

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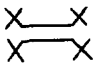
Abstract: The carbenic dimers of some tricyclic cyclopropylidenoids have been isolated. The X-ray structure of one (12) has been determined. These are derivatives of tetra-t-butylethylene (1).

Although tetra-t-butylethylene (1) remains unsynthesized, a number of its highly crowded relatives are now known (e.g., 2[3], 3[4], 4[5]). The synthetic procedures utilized have been "double extrusion" methods,[3-5] low valent Ti coupling of ketones,[6] and carbene or carbenoid dimerizations.[7] With respect to the last approach, it is known that 5 gives appreciable



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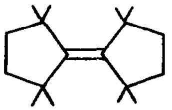

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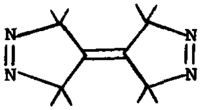

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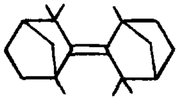

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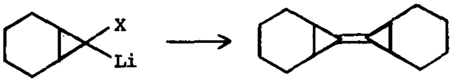

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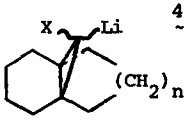
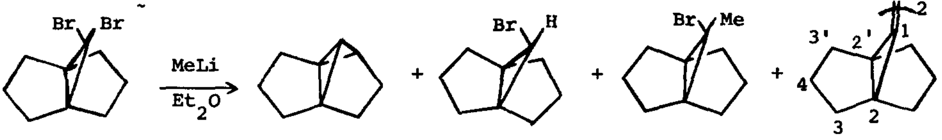


7

a, n=1
b, n=2

amounts of 6,[9] but the several reports[10] of the chemistry of 7 make no mention of a dimer analogous to 6. We now report several such dimers, all of which are derivatives of 1.

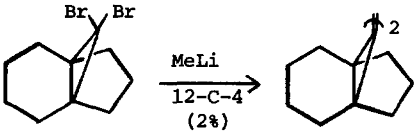


8 9 10 11 12

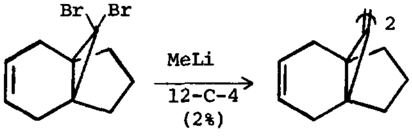
When 8[11] (140 mg) was treated with 4 eq. MeLi in 15 ml ether for 0.5 h at room temperature, 69 mg crude product was isolated. Analysis (gc-ms) showed 8 components, the first five of which had parent ions at m/e 120 and presumably corresponded to rearrangement products from 9; peaks 6 and 7 showed the appropriate parent ions at m/e 200, 202 (10) and m/e 214,216 (11), while the last peak generated a parent ion at m/e 240 (12). The (uncorrected) ratio of the peaks was 15.5 (sum of first five): 3.6: 80.3: 0.7. The major product (11) was isolated (33%) by TLC and fully characterized.[12] Similar reaction of 8 at -78° led to the isolation of 12 (mp 202-204°) in ca. 6% yield [^{13}C NMR: δ 128.0 (s,C_1), 41.2 (s, C_2), 33.2 (t, C$_3$), 30.9 (t, C$_4$)]. Single crystal X-ray analysis[13] served to define the structure of **12** (see Figure 1). The apparently short double bond (r$_{1,1'}$ = 1.307(3)Å)[15] may be relatively normal for methylenecyclopropanes, as Dewar[16] has calculated a double bond length of 1.317Å for the parent system.[17] There appear to be no severe non-bonded repulsions in **12**,[19] and the "bicyclohexane" subunits all remain in the (favored) boat conformation.[20]

Because of the crystallographically imposed symmetry, the double bond of **12** retains planarity, whereas that of **4** is twisted 11.8°[5]. However, the vibrational spectra of **12** are at once enlightening and puzzling. As expected, the IR showed no absorptions above 3000 cm^{-1} and no ordinary C=C peaks; the "fingerprint" absorptions appeared at 1460, 1445, 1385, 1319(w), 1290, 1244, 1210, 1175, 1070, 1055 and 1021 cm^{-1}. Surprisingly, however, the Raman was also devoid of ordinary C=C peaks, but showed a strong absorption at 1450 cm^{-1}; other "fingerprint" absorptions were at 1319, 1295, 1244, 1211, 1187, 1175, 1133, 1100, 1070 and 1021 cm^{-1}. If the 1450 cm^{-1} peak is a double bond stretch, then it is 90 cm^{-1} lower in energy than the previous "record low" (*i.e.*, that for **2**).[3] Regardless of the explanation to be attached to these spectra, it is noteworthy that the Raman spectrum was the same for a single crystal of **12** as for a CCl$_4$ solution of **12**.[21] This implies that the structure of **12** does not change appreciably upon dissolution, and the double bond is inherently planar.

Dimer formation could also be detected from the reactions of **13** and **15** with MeLi (room temperature) **in the presence of 12-C-4**; **14** and **16** were each isolated (TLC) in 2% yield. While **14** is presumably a stereoisomeric (E,Z) mixture, **16** most certainly is, as determined by the 2.7:1 ratio of olefinic peaks in the ^{1}H NMR. Further studies of these dimers are in progress.



13 **14**



15 **16**

REFERENCES AND NOTES

1. This work was partially supported by the NSF(CHE-7618701); the gc-ms facility was funded by the NSF; computing was financed by Iowa State University.

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6. For example, see D. Lenoir and R. Frank, *Tetrahedron Lett.*, 53 (1978).

7. This approach has yielded formal derivatives of tetra-*iso*-propylethylene (such as adamantylideneadamantane[8a] and 7,7'-norbornylidenenorbornane[8b]), but until now, not of **1**.

8. (a) H. W. Geluk, *Synthesis*, 652 (1970); (b) A. Mugnoli and M. Simonetta, *J.C.S. Perkin II*, 1831 (1976).

9. (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) G. Köbrich and W. Goyert, *Tetrahedron*, **24**, 4327 (1968); (c) Y. Fukuda, Y. Yamamoto, K. Kimura and Y. Odaira, *Tetrahedron Lett.*, 877 (1979).

10. (a) R. Vaidyanthasawamy and D. Devaprabhakara, *Chem. and Ind. (London)*, 515 (1968); (b) W. R. Moore, S. S. Hall and C. Largman, *Tetrahedron Lett.*, 4353 (1969); (c) N. L. Boardway, Ph.D. Dissertation, Massachusetts Institute of Technology, 1970; (d) L. A. Paquette, E. Chamot and A. R. Browne, *J. Am. Chem. Soc.*, **102**, 637 (1980).

11. (a) P. Warner, R. LaRose and T. Schleis, *Tetrahedron Lett.*, 1409 (1974); (b) P. Warner and S. Lu, *J. Am. Chem. Soc.*, **98**, 6752 (1976).

12. Products **9**-**11** have ample precedence in related systems.[10]

13. Crystallographic data: space group: Pcab; cell constants: a = 10.883(2)Å, b = 12.242(2)Å, c = 10.572(1)Å; radiation used: Mo, λ = 0.71002Å; number of data ($F>3\sigma_F$): 1069; solved by: MULTAN[14]; refined by: full matrix least squares; final R: 0.066; R_w: 0.075.

14. P. M. Main, M. M. Woolfson and G. Germain, "MULTAN: A Computer Program for the Automatic Determination of Crystal Structures," Department of Physics, University of York, York, England, 1971.

15. Other key dimensions of **12**: $r_{1,2}$ = 1.470(3); $r_{2,2'}$ = 1.549(3); $r_{2,3}$ = 1.512(3); $r_{3,4}$ = 1.538(4)Å; ∡ 2,1,2′ = 63.6(2)°; ∡ 1,2,2′ = 58.2(1)°; ∡ 1,2,3 = 117.8(2)°; ∡ 2,3,4 = 104.6(2)°; ∡ 3,4,3′ = 106.0(2)°.

16. R. C. Bingham, M.J.S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294(1975). The only noticeable difference between the gross structure of **12** and that calculated for methylenecyclopropane is the ratio of the length of the ring bond adjacent to that opposite from the sp^2 center (> 1 for **12**, < 1 for methylenecyclopropane). This difference may be due to the propellanic nature of **12**.

17. A number of systems structurally similar to **12**,[9,18] including the parent,[18a,b] are known, but we know of no structural data.

18. (a) P. Le Perchec and J. M. Conia, *Tetrahedron Lett.*, 1587 (1970); (b) A. J. Schipperijn, *Rec. Trav. Chim. Pays-Bas*, 90, 1110 (1971); (c) G. Köbrich, H. Heinemann and W. Zündorf, *Tetrahedron*, **23**, 565 (1967).

19. However, even nonbonded H-H interaction well within Van Der Waal's radii did not lead to distortion of the adamantylideneadamantane structure [S. C. Swen-Walstra and G. J. Visser, *J.C.S. Chem. Comm.*, 82 (1971)].

20. C_4 lies *ca.* 0.5Å out of the plane formed by $C_2C_3C_{3'}C_{2'}$, and toward C_1.

21. Attempts to chemically modify **12** in order to further investigate the Raman spectral question were unsuccessful. Thus hydrogenation at 70° and 50 psi H_2 (Pt/C) led to no reaction; bromination gave intractable materials; attempted carbene additions also led to no reaction.

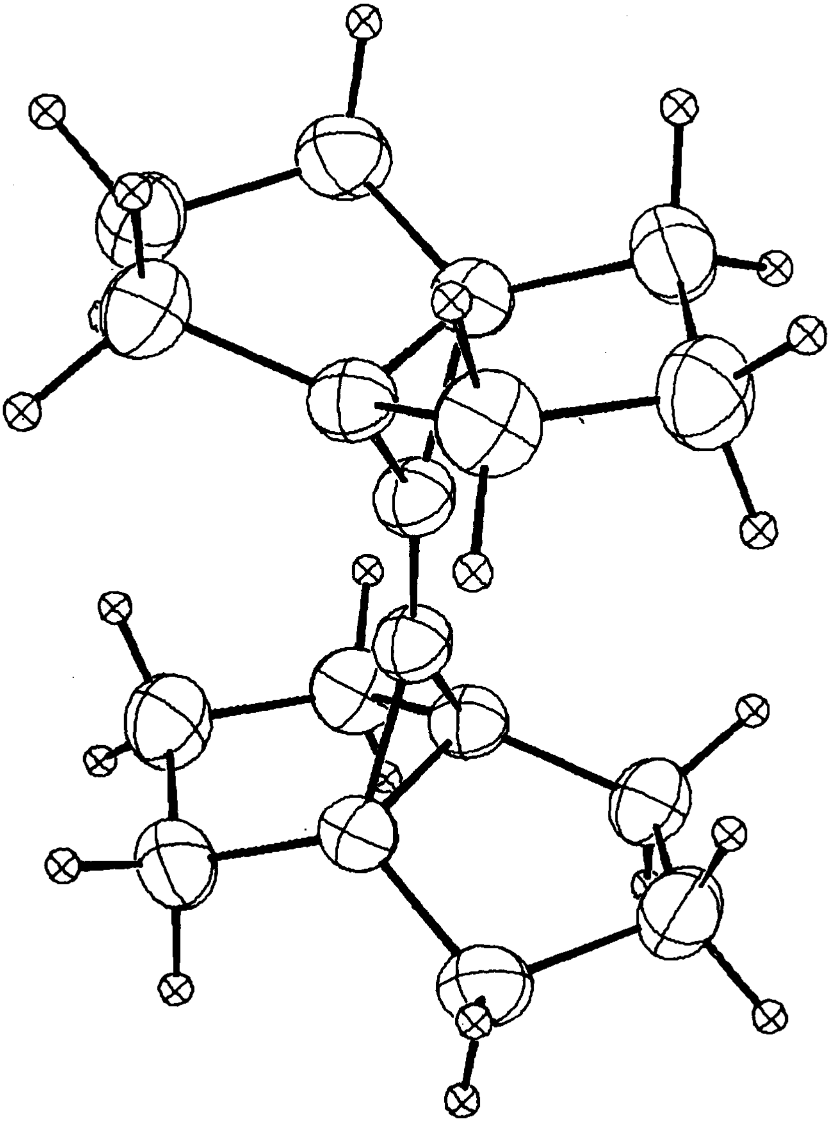

Figure 1. Computer generated perspective drawing of 12.

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