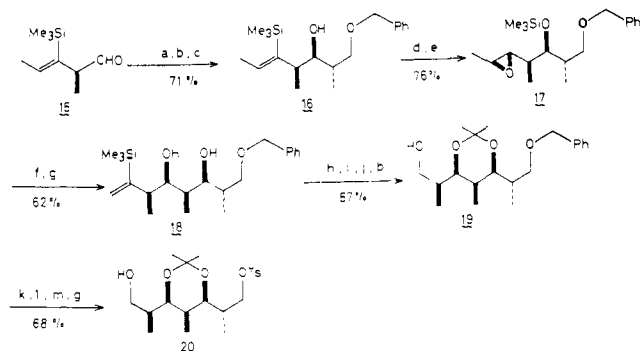


Table I. Epoxidation of Homoallyl Alcohols and Their Esters

entry	substrate ^a	reagent	yield, %	major product ^b	selectivity ^c
1		TBHP ^d	88		>99:1
2	1a	mCPBA ^e	90	3a	4:1
3		TBHP ^d	91		>99:1
4 ^f	1b	TBHP ^d	91	3b	2:1
5 ^f	2a	mCPBA ^e	88	5a	3:1
6		mCPBA ^e	96		6:1
7		mCPBA ^e	100		5:1
8 ^g	8	mCPBA ^e	89	10	3:1

^a Diastereoisomerically homogeneous (>99% pure) racemic substrates were used for each reaction. ^b The stereochemistry of the epoxides was unambiguously established (see supplementary data). ^c Determined by ¹H and ¹³C NMR spectroscopy. ^d The reaction was carried out using TBHP in CH₂Cl₂ at 0 °C. ^e The reaction was carried out by using mCPBA in CH₂Cl₂ at 0 °C → room temperature. ^f The anti alcohol 2b gave a mixture of 5b and 4b in a ratio of 2:1. ^g The corresponding acetate gave a similar result.

Scheme I^a

^a (a) CH₃CH₂COOBHT, LDA; (b) LiAlH₄; (c) PhCH₂Br, NaH; (d) TBHP, VO(acac)₂; (e) *t*-BuOK, THF; (f) CH₂=C(SiMe₃)MgBr, CuI, THF; (g) *n*-Bu₄NF; (h) KH, HMPA; (i) Me₂C(OMe)₂, PPTS, CH₂Cl₂; (j) O₃, MeOH; (k) TBSCl, DMAP; (l) H₂, Pd/C; (m) TSCl, C₅H₅N.

all respects with data kindly provided by I. Paterson.

Acknowledgment. We are grateful to Dr. Ian Paterson of University Chemical Laboratory, England, for providing us data (¹H and ¹³C NMR and [α]_D) of 20.

Supplementary Material Available: Assignment of the stereochemistry of the epoxides prepared in text and listing of optical rotations and spectral data (8 pages). Ordering information is given on any current masthead page.

Chemistry and Structure of the First 10-Sb-3 Species¹

Constantine A. Stewart, Richard L. Harlow, and
Anthony J. Arduengo III*

Contribution No. 3778, Central Research &
Development Department, Experimental Station
E. I. du Pont de Nemours & Company
Wilmington, Delaware 19898

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We report the chemistry and structure of 5-aza-2,8-dioxo-3,7-di-*tert*-butyl-1-stibabicyclo[3.3.0]octa-3,6-diene (ADSbO). ADSbO is the first molecule to contain the 10-Sb-3 bonding system. In spite of the large size of the antimony center, 10-Sb-3 ADSbO exhibits a planar geometry analogous to the previously reported 10-P-3 and 10-As-3 systems.^{2,3} The formation of 10-Sb-3 ADSbO is in stark contrast to the formation of a 20-Bi-9 system when the central atom is a bismuth.⁴

As with the similar phosphorus and arsenic systems, ADSbO shows no evidence for the presence of the 8-Sb-3 electromorph;³ however, there is a marked thermochromism at the melting point (116 °C). Solid 10-Sb-3 is a light yellow-green color which turns dark red on melting and back to yellow-green on freezing. Solutions of ADSbO are red in color with the intensity dependent upon temperature and solvent polarity. The solution and solid-state ¹³C NMR spectra of ADSbO are identical and consistent with the 10-Sb-3 structure.⁵ The ¹H NMR (CD₂Cl₂) exhibits resonances at δ 1.39 (s, 18 H) and 8.46 (s, 2 H). The ring proton resonance at δ 8.46 confirms the trend observed earlier in the ADPO and ADAso systems.³ This observation suggests the importance of positive charge delocalization in the ligand backbone and discounts ring current effects for these 10-Pn-3 systems.

ADSbO is prepared by a route analogous to the previously reported 10-Pn-3 systems.^{2,3} While ADSbO is thermally stable it is sensitive to both water and oxygen. The structure (Figure 1) of ADSbO was verified by single-crystal X-ray diffraction. Table I gives the bond lengths and angles in ADSbO. It is interesting to note the Sb-O and Sb-N bonds in ADSbO are 17 and 22 pm longer than the corresponding bonds in ADAso. This correlates well with the 20-pm increase in covalent radius on going from arsenic to antimony. The central pnictogen-nitrogen bond is increasing at a faster rate than the pnictogen-oxygen bond as one goes down the family from phosphorus to antimony. This is consistent with a bonding scheme which forces the stabilization of the pnictogen lone pairs at the 10-Pn-3 center by mixing more s character into the lone pair orbitals. This results in decreased s participation in the Pn-N bond. Thus this bond is lengthened.

Another consequence of the larger atomic radius is the extension of the pnictogen center out of the ligand mandible. This extension can be seen in the decrease of the O-Pn-O bond angles of the ADPnO series. This results in the availability of a large antimony surface in ADSbO.

(1) The *N-X-L* system has previously been described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.*, **1980**, *102*, 7753). *N* valence electrons about a central atom X, with *L* ligands.

(2) Culley, S. A.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1984**, *106*, 1164.

(3) Culley, S. A.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1985**, *107*, 1089.

(4) Stewart, C. A.; Calabrese, J. C.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1985**, *107*, 3397.

(5) ¹³C(¹H) NMR spectra of 10-Sb-3 ADSbO consists of the following resonances: δ 28.8 (CH₃), 38.0 (C(CH₃)), 117.8 (CH), 176.7 (CO). The solid-state ¹³C NMR spectra was analogous to the solution spectrum. ¹⁷O δ 305; ¹⁵N δ -90 (¹⁷O and ¹⁵N spectra relative to H₂¹⁷O and NH₄¹⁵NO₃, respectively). All solution NMR spectra were run in CD₂Cl₂, satisfactory analysis (CHN) were obtained for ADSbO.

(6) This perspective drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear 50-pm grids and the lighting source is at infinity so that the shadow size is meaningful.

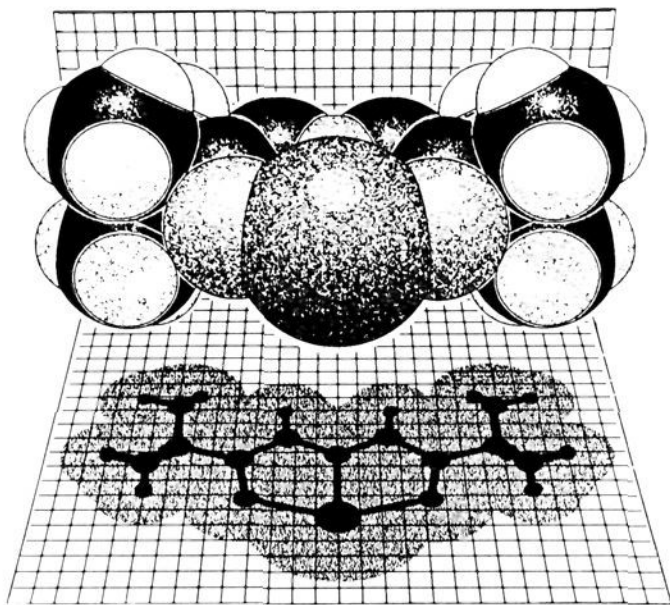
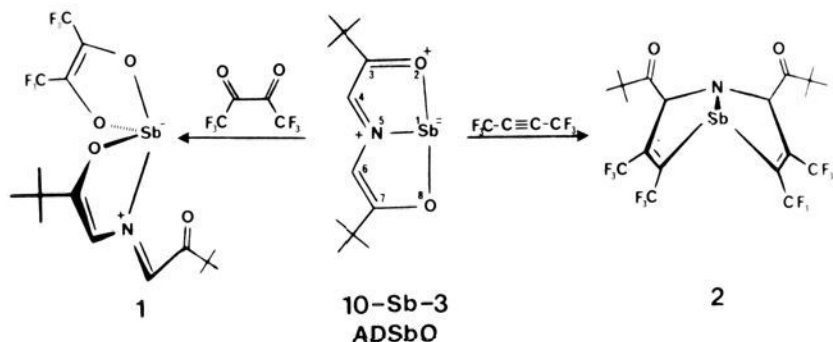


Figure 1. KANVAS⁶ drawing of 10-Sb-3 ADSbO.

Table I. Selected Bond Lengths and Angles in 10-Sb-3 ADSbO

bond lengths, pm		bond angles, deg	
Sb-O	214.4 (3), 216.5 (3)	O-Sb-O	149.6 (1)
Sb-N	206.4 (3)	N-Sb-O	74.7 (1), 74.9 (1)
C-O	132.5 (6), 131.5 (6)	C-O-Sb	115.0 (3), 114.4 (3)
C-C _{ring}	137.0 (7), 137.6 (7)	C-N-Sb	117.3 (3), 117.6 (3)
C-N	133.8 (6), 136.2 (6)	C-C-N	116.4 (4), 115.2 (4)
		C-C-O	116.4 (4), 117.9 (4)

Hexafluorobiacetyl reacts with 10-Sb-3 ADSbO to give a 1:1 adduct **1**.⁷ The solid-state geometry of **1** was determined by



single-crystal X-ray diffraction. The structure can best be described as a four-coordinate stiborane (10-Sb-4) with one loosely coordinated carbonyl of the diketo amine ligand (Sb-O 302 pm). However, in solution at room temperature the ¹H NMR spectrum of **1** reveals only two resonances; δ 1.25 (s, 18 H) and 7.72 (s, 2 H). In addition, the ¹⁹F NMR spectrum shows only a singlet, δ -63.9, at ambient temperature. These observations indicate a rapidly equilibrating system.

The reaction of ADSbO with hexafluoro-2-butyne affords **2** in good yields.⁸ The structure **2** was determined by multinuclear NMR (¹H, ¹³C, and ¹⁹F) and confirmed by an X-ray structure determination. Particularly noteworthy is the large upfield shift in the resonance for carbon 4(6) (δ 79.7) indicating an sp³ hybridization. At present it is not known whether the addition of the acetylene across the antimony and C-4 centers occurs in a concerted or stepwise fashion. This reaction represents an un-

precedented mode of addition of an acetylene to a hypervalent species.

Acknowledgment is made to Dr. D. Ovenall, F. Davidson, and Dr. R. Farlee for the work on the ¹⁷O, ¹⁵N, and solid-state ¹³C spectra, respectively.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determinations including experimental procedures, tables of data, and stereodrawings (51 pages). Ordering information is given on any current masthead page.

Efficient Triple Coupling Reaction To Produce a Self-Adjusting Molecular Cage

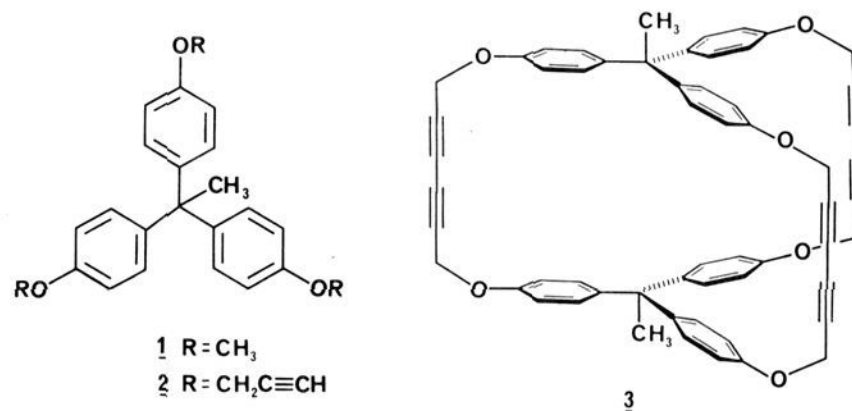
David O'Krongly, Samuel R. Denmeade, Michael Y. Chiang, and Ronald Breslow*

Department of Chemistry, Columbia University
New York, New York 10027

Received May 28, 1985

There has recently been great interest in synthetic hydrophobic cage molecules that could be used as binding groups in artificial enzymes and other biomimetic systems.¹ For instance, we have shown² that a two-dimensional Koga cyclophane³ can be covalently linked to pyridoxamine, affording an artificial transaminase with good substrate selectivity. Three-dimensional cages are of potentially greater interest. The geometry of the binding site should be better defined, and substrates that efficiently fill the entire three-dimensional space should be particularly well bound. However, to permit entry into and exit from the cage, it is probably desirable that there be an open conformation that closes up around the substrate after it enters. We wish to describe the synthesis of a cage system that seems to have many of these desirable properties. Furthermore, the synthesis is remarkably efficient: the two half-cages are joined by three links in a one-pot triple-coupling reaction.

For the components of our cage, we selected two 1,1,1-triphenylethane units, to be joined by three diacetylene linkages. The 1,1,1-triphenylethane **1**, prepared from tri-*p*-anisylcarbinol and



trimethylaluminum,⁴ was converted to the tripropargyl ether **2** by O-demethylation with NaSEt in DMF⁵ and then alkylation with propargyl bromide in K₂CO₃/DMF. The sequence gave **2**

(7) Compound **1** can be crystallized from CH₂Cl₂ (-35 °C) in good yield (>80%) as a yellow-orange solid, mp 132-134 °C. ¹H NMR δ 1.27 (s, 18 H), 7.73 (s, 2 H); ¹³C{¹H} NMR δ 26.6 (CH₃), 40.5 (C(CH₃)₃), 122.7 (CF₃) (q, ¹J_{CF} = 270 Hz), 123.0 (CH), 133.6 (CCF₃) (q, ²J_{CF} = 44.5 Hz), 196.2 (CO); ¹⁹F{¹H} NMR δ -63.9 (reference CFCl₃). All NMR spectra were run in CD₂Cl₂. Satisfactory analysis were obtained (CHN).

(8) Compound **2** can be crystallized from pentane as a colorless solid (moderate yield), mp 110-112 °C. ¹H NMR δ 1.22 (s, 18 H), 6.17 (s, 2 H); ¹³C{¹H} NMR δ 27.1 (CH₃), 44.5 (C(CH₃)₃), 79.7 (CH), 121.8 (CF₃, q, ¹J_{CF} = 277 Hz), 124.9 (CF₃, q, ¹J_{CF₂} = 272 Hz), 145.2 (CCF₃, q, ²J_{CF} = 27 Hz), 161.2 (CCF₃, q, ²J_{CF} = 39 Hz), 211.6 (CO); ¹⁹F{¹H} NMR δ -52.2 (q, J_{FF} = 10 Hz), -59.6 (q, J_{FF} = 10 Hz); ¹⁵N NMR δ -318.7. All spectra were run in CD₂Cl₂; ¹⁹F and ¹⁵N NMR resonances were referenced to CFCl₃ and NH₄¹⁵NO₃, respectively. Satisfactory analysis were obtained (CHN).

(1) (a) Description of a cage system related to **3**: Franke, J.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 219. (b) Diederich, F.; Dick, K. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 810. (c) Miller, S. P.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1492. (d) Report of a one-pot multiple-Wittig construction of a cage and discussion of the effect of twist angle on cage size: Höbger, H.-K.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 661.

(2) Winkler, J.; Coutouli-Argyropoulou, E.; Leppkes, R.; Breslow, R. *J. Am. Chem. Soc.* **1983**, *105*, 7198.

(3) (a) Soga, T.; Odashima, K.; Koga, K. *Tetrahedron Lett.* **1980**, 4351. (b) Odashima, K.; Itai, A.; Yitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504.

(4) Harney, D. W.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1639.

(5) Feutrill, G. I.; Mirrington, R. N. *Aust. J. Chem.* **1972**, *25*, 1719.