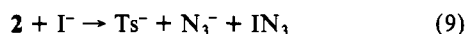


nitrene intermediate. However, irradiation of 1-1,3-¹⁵N₁ in dichloromethane in the presence of 18-crown-6 under conditions in which dinitrogen is formed, presumably by way of the nitrene, gave no evidence for formation of 1-2-¹⁵N. Similar results were obtained by irradiation of 1-3-¹⁵N in toluene where formation of the nitrene was indicated by *p*-toluenesulfonylamido insertion products resulting from attack of the nitrene on the solvent.

Interestingly, addition of 1 equiv of potassium iodide to a solution of **1**, potassium azide-1-¹⁵N, and 18-crown-6 in dichloromethane inhibits formation of 1-2-¹⁵N. The iodide ion appears to intercept **2** causing decomposition to *p*-toluenesulfinate ion, azide ion, and iodoazide (eq 9), before cyclization or other



reactions occur. Dinitrogen and iodine, products of the reaction of iodoazide¹¹ with iodide and azide ion, are in fact observed.¹²

The reaction of **1** with azide ion is strongly solvent dependent. In dimethyl sulfoxide, although **2** is probably formed,² decomposition to dinitrogen and *p*-toluenesulfinate is rapid. In dichloromethane, the major reaction in dimethyl sulfoxide is depressed, and eq 3 is dominant. In toluene with 18-crown-6 present, the reactions of eq 1 and 3 occur simultaneously. The origin of solvent effects is not clear, and research on the mechanism of these nitrogen scrambling reactions is under way.

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Semibullvalenes. 1. Synthesis and Crystal Structure of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene—A Donor-Acceptor-Substituted Semibullvalene

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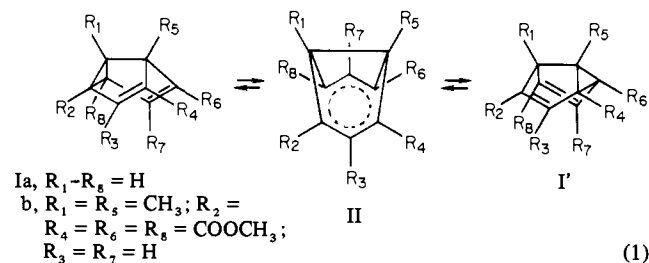
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Semibullvalenes undergo a facile Cope rearrangement ($\text{I} \rightleftharpoons \text{I}'$) whose energy barrier is the lowest known to date^{1,2} (eq 1). This barrier has been calculated¹ to be 3.6 kcal/mol and found experimentally² to be 5.5 kcal/mol for the unsubstituted compound (**Ia**). Both extended Hückel³ and MINDO-2¹ calculations have been used to assess the effects of ring substituents on the energy barrier for this rearrangement. On these bases, π -electron donors on positions 1 and 5 and π -electron acceptors on positions 2, 4, 6, and 8 of **I** are expected to lower the activation energy for Cope rearrangement and, perhaps, to yield a species with a stabilized transition state, i.e., a "bishomobenzene"-type structure (**II**).



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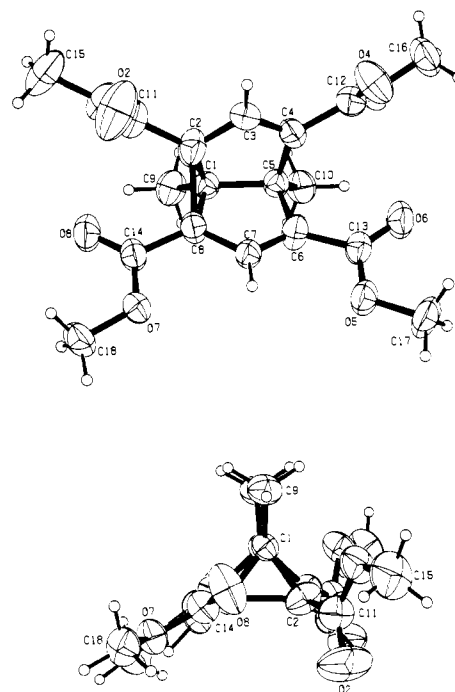


Figure 1. Structure of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**Ib**), showing the 50% thermal ellipsoids. Hydrogen atoms are not labeled.

We wish to report the synthesis and X-ray structure determination of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**Ib**). The new synthetic route is outlined in Scheme I.⁴ Enol **1**⁵ was converted into the tetracyclic ketone **3**⁶ by successive bromination and cyclizing dehydrobromination. Diketone **3** was stereospecifically reduced to *exo*-diol **4**⁶ by using (*i*-Bu)₃Al.⁷ The corresponding dimesyl derivative **5**⁶ was refluxed with an excess of sodium iodide in acetone in order to form **Ib** through a conjugate 1,4-elimination reaction.⁸ After 1 h a white solid could be isolated whose spectra were consistent with the monoiodomomesyl compound **6**.⁹ After several hours of reflux a new yellow compound (**Ib**)⁶ was isolated. Longer reflux produced a side product whose structure is currently being elucidated.¹⁰ Crystals of **Ib** suitable for X-ray crystallography were obtained by recrystallization from CH₃OH.

Compound **Ib** is a bright yellow crystalline solid which melts at 102.5-103 °C. Spectral characteristics¹¹ are as follows: IR (CHCl₃) 3010, 2950, 1725, 1595, 1435, 1335, 1200-1250, 1055, 1040 cm⁻¹; UV λ_{max} (EtOH) 232 nm (ε 12400); ¹H NMR¹¹ 1.45 (s, 6 H, CH₃), 3.67 (s, 12 H, OCH₃), 6.18 (br s, 2 H, H_{3,7}); ¹³C NMR¹¹ 11.02 (C_{9,10}), 52.09 (OCH₃), 68.67 (C_{1,5}), 104.07 (C_{2,4,6,8}), 131.23 (C_{3,7}), 165.47 (C=O).

The ¹H and ¹³C NMR spectra both clearly show averaged signals for carbons 1 and 5, carbons 2, 4, 6, and 8, and for the proton-bearing groups attached to these carbons. The 270-MHz

(4) Complete experimental details will be published in a subsequent paper.

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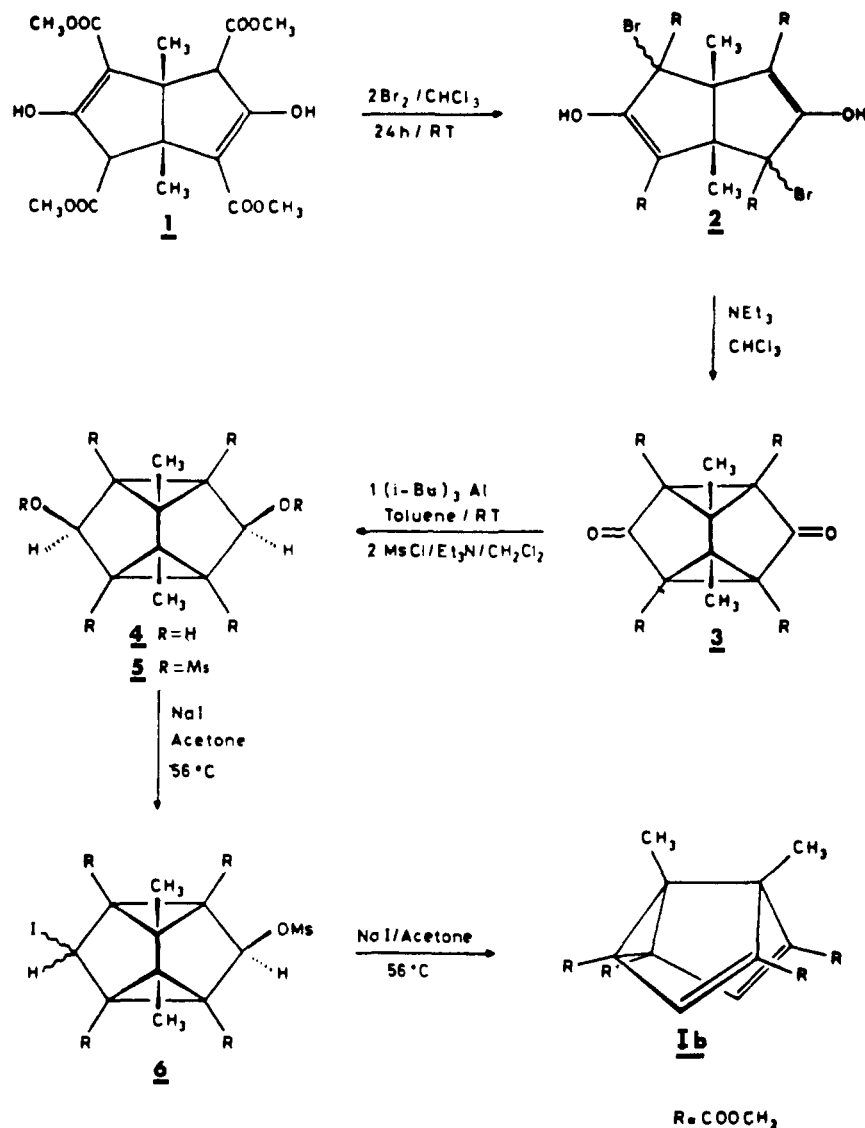
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(9) Compounds **6**: ¹H NMR (CDCl₃) 1.53 (s, 6 H), 2.91 (s, 3 H), 3.63, 3.65 (2s, 12 H), 5.38 (s, 1 H), 6.06 (s, 1 H) ppm. Upon reheating with sodium iodide in acetone, **6** reacted further to form **Ib**.

(10) **Ib** isomerizes to this compound upon heating or prolonged standing in solution.

(11) ¹H NMR spectra were measured in CDCl₃ on a Varian A-60 spectrometer, ¹³C NMR were measured in CDCl₃ on a JEOL-PFT100 instrument. All signals are reported in ppm downfield from Me₄Si. IR spectra were recorded in CHCl₃.

Scheme I



¹H NMR spectrum shows no change at -120 °C. Lower temperature ¹H NMR and ¹³C NMR studies are in progress which should clarify the solution dynamics of Ib.¹²

The crystal structure¹³ of Ib is shown in Figure 1. Pertinent structural parameters are summarized in Table I. The geometry of the cyclopropane ring is particularly unusual. There is a striking lack of symmetry in the molecule. The C2-C8 bond is very long (1.782 Å) while the C1-C2 bond is shortened (1.480 Å). Also, the C1-C8 bond is somewhat longer (1.530 Å) than an average cyclopropane bond (1.51 Å).¹⁴ The bonds adjacent to the cyclopropane ring (C2-C3 = 1.430, C7-C8 = 1.419 Å) are shorter than normal C_{sp²}-C_{sp²} bonds (1.48 Å).¹⁵ The nonbonded distance

Table I. Selected Geometric Features of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene (Ib)^a

Distance, Å			
C1-C5	1.581 (4)	C6-C7	1.349 (4)
C1-C2	1.483 (5)	C4-C5	1.511 (5)
C1-C8	1.530 (4)	C5-C6	1.532 (4)
C2-C8	1.782 (5)	C1-C9	1.504 (5)
C2-C3	1.430 (5)	C5-C10	1.511 (4)
C7-C8	1.413 (4)	C4-C6	2.21
C3-C4	1.341 (4)	C3-C7	3.05
Angle, deg			
C2-C1-C8	72.5 (2)	C1-C8-C7	109.7 (2)
C1-C8-C2	52.5 (2)	C5-C4-C3	111.1 (3)
C8-C2-C1	55.0 (2)	C5-C6-C7	112.0 (3)
C4-C5-C6	93.1 (2)	C2-C3-C4	111.3 (3)
C1-C2-C3	109.5 (3)	C6-C7-C8	111.4 (3)
Torsional Angle, deg			
O2-C11-C2-C1	147.52	O4-C12-C4-C5	-143.52
O2-C11-C2-C8	82.96	O4-C12-C4-C6	-92.90
O8-C14-C8-C1	-26.42	O6-C13-C6-C5	8.83
O8-C14-C8-C2	32.32	O6-C13-C6-C4	-35.00

^a Atoms labeled as in Figure 1.

at the open end of the molecule (C4-C6) is 2.21 Å, and the C4-C5-C6 bond angle is 93°. These parameters are both smaller than those observed for unsubstituted semibullvalene Ia (2.261 Å and 95.2°)¹⁶ and for 1-cyanosemibullvalene (2.35 Å and 101°).¹⁷

(12) Miller, L. S.; Grohmann, K., unpublished results.

(13) X-ray analysis: The crystals were orthorhombic, space group *P2₁2₁2₁* with *a* = 6.633 (1), *b* = 10.841 (2), *c* = 24.658 (2) Å, *d*_{calcd} 1.364 g/cm³, *d*_{obsd} 1.361 g/cm³ for *Z* = 4. The intensity data were measured on a Hilger-Watts diffractometer (Ni filtered Cu Kα radiation, θ-2θ scans, pulse height discrimination). A total of 1415 reflections were measured for θ < 57°, of which 1369 were considered to be observed [*I* > 2.5σ(*I*)]. The structure was solved by a multiple solution procedure (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, *A27*, 368) and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indexes are *R* = 0.037 and *wR* = 0.048. The final difference map has no peaks greater than ±0.2 eÅ⁻³.

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The cyclopropane ring asymmetry is consistent with the orientation of the carbomethoxy groups about this ring. π -Electron acceptors are known to affect the geometry of cyclopropanes because of the interaction between the LUMO of the electron acceptor system and the cyclopropane HOMO of the correct symmetry ($3e'$).^{3,14} The resultant transfer of electron density from the cyclopropane to the π -electron acceptor system weakens those bonds for which the $3e'$ orbital is bonding (the vicinal bonds) and strengthens the distal bond (for which the $3e'$ orbital is antibonding). The extent of this interaction is dependent on the geometric relationship of the two orbital systems. It can be assessed by measuring the dihedral angle between the carbonyl oxygen and the midpoint of the distal cyclopropane bond (e.g., O8-C14-C8-midpoint C1-C2); at 0° maximum overlap occurs, while at 90° there is no overlap.¹⁴ The data from Table I can be used to calculate the relevant dihedral angles for compound Ib. These angles are 2.95° for the C=O bond to C8 and 115° for the C=O bond to C2. The carbonyl group bound to C2 is twisted almost completely out of conjugation with the Walsh orbitals, while that attached to C8 adopts the most favorable conformation for orbital overlap. Therefore, the C1-C8 bond is lengthened because of the vicinal, interacting carbomethoxy substituent and is not competitively shortened by the C2 carbomethoxy group. Conversely, the C1-C2 bond is shortened as it is distal to the C8 substituent.

Applying this theory to the C2-C8 bond, one would expect a bond length similar to that of C1-C8. A study of a series of substituted cyclopropanes has shown that the bond lengthening induced by a π -electron acceptor need not be equal for both vicinal bonds.¹⁴ However, the effects of these substituents is nowhere near as large as is seen here for the C2-C8 distance. While molecules containing a cyclopropane ring with one long C-C bond are known,^{14,18} there are very few in which the bond distance is greater than 1.6 \AA .¹⁹ The C2-C8 bond length of semibullvalene (Ia) is 1.6 \AA .¹⁶ A steric effect caused by the adjacent carbomethoxy groups might influence the C2-C8 bond length. This is unlikely as identical substitution at the open end of Ib does not increase the C4-C6 distance with respect to the unsubstituted compounds.^{16,17}

It is not possible to draw exact parallels between the crystal and solution structures of Ib since crystal packing may affect the former. However, it appears that the pattern of substitution in Ib has led to a substantial electronic rearrangement as manifested by the unusual crystal structure. The observed geometry is consistent with a structure that is approaching the transition state for Cope rearrangement (IIB). In addition to the extremely long C2-C8 bond, the short nonbonded C4-C6 distance and the long C1-C5 bond (1.581 \AA), the C2-C3 and C7-C8 bonds are significantly shorter than average. Theoretical calculations assessing the effects of both geometry and substituents on the reaction pathway for this Cope rearrangement are in progress.²⁰ These results will be used as guidelines for further synthetic work.

Acknowledgment. We acknowledge the help of Drs. M. Uskokovic and J. F. Blount at Hofmann-La Roche, Inc., Nutley, NJ, as well as Drs. R. Lichter, D. K. Lavalley, and J. K. Barton at Hunter College. This research was supported in part by a C.U.N.Y. PSC-BHE grant (RF-13341).

Supplementary Material Available: Atomic position and thermal parameters for Ib (4 pages). Ordering information is given on any current masthead page.

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α -Silyl Aldehydes: Preparation and Use as Stereoselective Vinyl Cation Equivalents¹

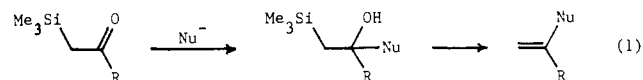
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Efficient methods for the introduction of a vinyl group α to carbonyl would be very desirable not only for the synthesis of biologically important α -vinylcarbonyl compounds but also for the preparation of synthetic intermediates, e.g., substrates for Cope and Claisen rearrangements. A number of vinyl cation equivalents have been recently reported,²⁻⁴ but few have been used with simple ketone enolates.³ We have previously reported the use of α,β -epoxysilanes as stereospecific vinyl cation equivalents for the synthesis of olefins⁵ and heteroatom-substituted olefins.⁶ Attempts to use α,β -epoxysilanes for the preparation of α -vinylcarbonyl compounds, however, have so far been unsuccessful.⁷ We have therefore become interested in the possibility of using α -silyl aldehydes as vinyl cation equivalents.

A number of years ago we⁸ and others⁹ demonstrated that α -trimethylsilyl ketones (β -ketosilanes) could serve as (secondary) vinyl cation equivalents according to eq 1 ($R \neq H$). The pos-



sibility of using α -silyl aldehydes as (primary) vinyl cation equivalents in a similar process (eq 1, $R = H$) was stymied by the lack of methods for preparing α -silyl aldehydes. Our attempts to prepare and isolate simple α -trimethylsilyl aldehydes have been unsuccessful, indicating they are quite sensitive, easily losing silicon (by hydrolysis) or isomerizing to silyl enol ethers,¹⁰ although we¹¹

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