

and biphenyls can be reduced in the 0 to -3 V range, but trifluoroethoxy, phenoxy, *o*-dioxypheyl, and methoxy units cannot. Benzene cannot be reduced in the 0 to -3 V range but, when a phenyl group is bonded directly to phosphorus in I or II, the reduction potential is lowered until it is comparable to that of free naphthalene. This result is consistent with observations reported by Santhanam and Bard for triphenylphosphine and triphenylphosphine oxide reductions.¹⁵ Thus, it appears that the reducibility of the phenylcyclophosphazenes I and II results from delocalization effects involving the phenyl groups and the skeleton.

This interpretation is confirmed by the esr data. The spectra derived from III, IV, and V can be rationalized in terms of hyperfine splittings within each discrete side group unit only. For example, the spectra are similar to those of *p*-nitroanisole, or the appropriate disubstituted naphthalenes. Presumably the oxygen atoms effectively insulate the reduced organic aromatic component from the phosphazene ring. This is further confirmed by the nonreducibility of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ and $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ below -3 V.

However, the esr singlet obtained from I and II must indicate delocalization of the unpaired electron either within a $\text{C}_6\text{H}_5\text{-P-C}_6\text{H}_5$ unit or into the phosphazene skeleton as a whole. Interaction within a $\text{C}_6\text{H}_5\text{-P-C}_6\text{H}_5$ segment could give rise to as many as 150 lines (648 lines if the phenyl groups are nonequivalent), and this is probably beyond the resolution limit for this system. Delocalization involving the whole skeleton²⁻⁴ is also possible, but the failure of the skeleton to reduce when aliphatic substituents are present, coupled with the almost identical results obtained from $[\text{NP}(\text{C}_6\text{H}_5)_2]_3$ and $[\text{NP}(\text{C}_6\text{H}_5)_2]_4$, and the inability of long-chain species such as $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ and $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ to stabilize an unpaired electron, force us to the view that extensive skeletal delocalization does not occur under these conditions. It appears more likely that in phenylphosphazenes an unpaired electron can be delocalized within a $\text{C}_6\text{H}_5\text{-P-C}_6\text{H}_5$ unit or, at the most, into a very short adjacent skeletal segment.^{1,8}

A more detailed discussion of these results and of additional work now in progress will be given in a subsequent publication.

Acknowledgment. We are indebted to Dr. M. D. Morris for his suggestions concerning the polarographic technique.

(15) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 1118 (1968).

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Steric Effects in *ortho*-Substituted Triarylmethanes

Sir:

Triarylmethane derivatives in which all *ortho* positions have bulky substituents reflect¹⁻³ in their chemical

(1) J. C. Martin, *J. Chem. Educ.*, **38**, 286 (1961); J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, **86**, 2252 (1964); M. J. Sabacky, C. S. Johnson, Jr., R. G. Smith, H. S. Gutowsky, and J. C. Martin, *ibid.*, **89**, 2054 (1967).

(2) F. A. Carey and H. S. Tremper, *ibid.*, **90**, 2578 (1968).

(3) N. Kessler, A. Moosmayer, and A. Rieker, *Tetrahedron*, **25**, 287 (1969).

and physical properties the effects of the large nonbonded interactions between *ortho* substituents. Compound **1** (Figure 1), mp $156\text{--}157^\circ$, was prepared from dimesitylcarbinol and 1,3,5-trimethoxybenzene by treatment with sulfuric acid in acetic acid. It shows unprecedentedly large interactions of this sort (a) in nmr evidence for hindered rotation, (b) in $J_{\text{H-C-H}}$ for the methane proton, and (c) in a structure determined by X-ray crystallography.

Below -30° compound **1** shows three peaks (with areas 3:6:3, separated by about 12 Hz at 60 MHz) for four nonequivalent *o*-methyls and two peaks (of area 3 and separated by 20 Hz) for two *o*-methoxys. The methyl peaks coalesce to a single peak near -20° , but the methoxyl peaks require a much higher temperature, near 145° . Line-shape analyses⁴ over the temperature range $118\text{--}176^\circ$ for the nmr signals for the *o*-methoxyl groups show $\Delta H^* = 17.7 \pm 0.4$ kcal/mol and $\Delta S^* = -9.8 \pm 1.0$ eu for the process interconverting *exo*- and *endo*-methoxyl groups. These data suggest the importance in solution of a distorted propeller conformation similar to that established by X-ray analysis for crystalline **1**. The higher energy barrier for the position exchange of methoxyl groups than for methyl groups in **1** is in accord with the order of size ($\text{CH}_3 > \text{OCH}_3$) established from rate data for biphenyl racemization⁵ and from consideration of the relative van der Waals radii of oxygen and methyl groups⁶ if the detailed mechanism for rotation about the $\text{C}_\alpha\text{-aryl}$ bond is considered. Individual steps in this rotation must involve a reversal of the pitch of the propeller, with simultaneous 90° rotations of each ring about the $\text{C}_\alpha\text{-aryl}$ bond.

The pictured process moves *exo*-methyl group Z_1 (in **1a**) to an *endo* position (in **1b**) and moves Z_2 *endo* to *exo*. No *exo-endo* interconversion of methoxyl groups is effected by this process. It involves a "gear-meshing" correlation of the rotations of rings A and C and of rings B and C.⁷ The "gear-clashing" correlation of rotation of rings A and B which is necessary in this mechanism provides the largest steric interaction in the transition state, that between *endo* substituents X_2 (OCH_3) and Y_2 (CH_3).

The related processes which would interconvert *exo*- and *endo*-methoxys in **1a** would involve rings B and C in a "gear-clashing" counterrotation with a resulting large nonbonded transition-state interaction between juxtaposed *endo*-methyls (e.g., Y_2 and Z_2) in the transition state. This interaction would be expected to be less favorable than the methyl-methoxyl interaction in the pictured process (**1a** \rightarrow **1b**) which exchanges methyls.

As expected, the rotation of the methoxylated rings in **2**, which involves only the much smaller methoxyl-methoxyl interactions, is much faster, $\Delta H^* = 8 \pm 1$ kcal/mol and $\Delta S^* = -10 \pm 5$ eu (over the range -69 to -81°)⁸ as established by the line-shape analysis of the

(4) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(5) R. Adams and H. C. Yuan, *Chem. Rev.*, **12**, 261 (1933).

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 3rd ed, Ithaca, N. Y., 1960, pp 257-264.

(7) For a discussion of such rotation in triphenylmethyl cations see A. K. Colter, I. I. Schuster, and R. J. Kurland, *J. Am. Chem. Soc.*, **87**, 2278 (1965); in diarylmethanes see H. Kwart and S. Alekman, *ibid.*, **90**, 4482 (1968).

(8) In ref 3 the coalescence temperature for **2** was recently reported to

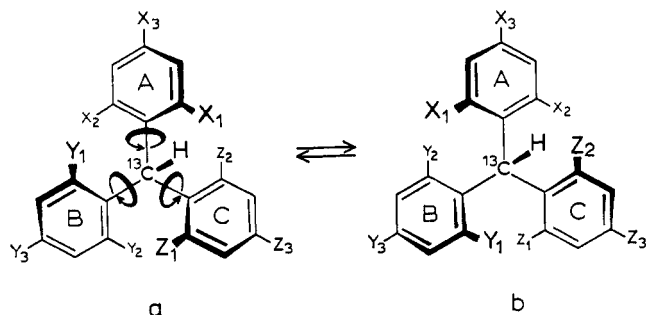


Figure 1. A mechanism for the conformational change involving *exo-endo* exchange of groups Z_1 and Z_2 for compounds **1** ($X = \text{OCH}_3$; $Y = Z = \text{CH}_3$) and **2** ($X_1 = X_2 = Y_1 = Y_2 = Z_1 = Z_2 = \text{OCH}_3$; $X_3 = Y_3 = Z_3 = \text{H}$).

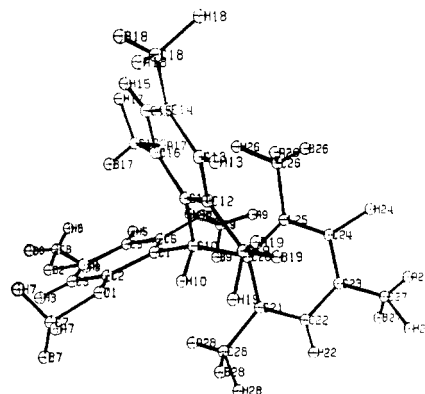
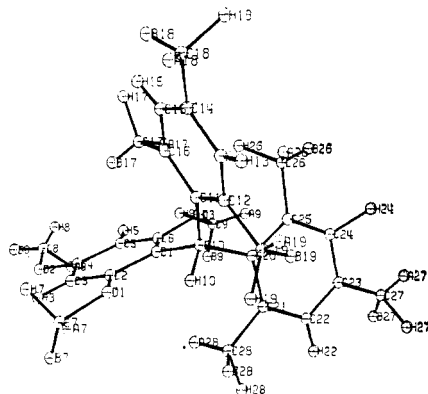


Figure 2. Stereoscopic drawing of **1** viewed along the b axis. The spheres depicting the atoms in the molecule are of uniform size and do not represent the magnitude of the thermal vibrations of the various atoms.

methoxyl signals (which are separated by 21 Hz at -90°).

The expected opening out of the central C-C-C bond angles, to relieve these large nonbonded interactions, should reduce the s character in the methine C-H bond and hence reduce $J_{\text{H-C}}$.⁹ This is seen in values measured on samples of triarylmethanes enriched (*ca.* 65%) in carbon-13 at the central position: triphenylmethane, 126 Hz; **2**, 126 Hz; and **1**, 119.5 Hz. The less strained members of the series show the same $J_{\text{H-C}}$ as does methane, but **1** has a value comparable with that seen^{9b} for cyclodecane (119 Hz), where the average C-C-C bond angle is 116.5° .¹⁰

Crystals of **1** belong to the monoclinic system, with $a = 15.72$ (4), $b = 8.36$ (2), $c = 20.25$ (5) Å, and $\beta = 116^\circ 0'$ (20'), as determined on a precession camera with Mo K α radiation (λ 0.7107 Å). The space group is $P2_1/c$ and there are four molecules of **1** in the unit cell. A total of 3445 independent structure amplitudes was obtained by visual estimates of equiinclination Weissenberg photographs at 4° (Cu K α radiation). The structure was solved by the symbolic addition procedure¹¹ and has been refined including hydrogen atoms to an R factor of 0.10 on all observed reflections

(see Figure 2). The average esd in C-C bond lengths is ± 0.007 Å, and in C-C-C angles is 0.3° .

Methyl groups C(17) and C(26) and methoxyl group O(3) are *endo* in Figure 2. The three C-C-C angles around the central carbon atom, while all being greater than tetrahedral, are substantially unequal: C(1)-C(10)-C(11) is 116.1° , C(11)-C(10)-C(20) is 117.8° , and C(1)-C(10)-C(20) is 112.1° . The central carbon atom, C(10), is 0.333 Å from the plane defined by C(1), C(11), and C(20); this distance compares with 0.51 Å to be expected if the C-C-C angles were tetrahedral and the C-C distances were 1.53 Å. The C(aromatic)-CH₃ (*endo*) intramolecular contacts bespeak of significant repulsions, with the C(1)-C(17) and C(11)-C(26) dis-

tances being 2.927 (7) and 2.966 (8) Å, respectively, compared to the sum of the appropriate van der Waals radii of 3.70 Å;⁶ the C(20)-O(3) contact is 2.762 (6) Å, which is 0.36 Å less than the sum of the van der Waals radii. The greater steric interference involving the aromatic ring and the *endo*-methyl groups is responsible for the greater opening out of the C(1)C(10)C(11) and C(11)C(10)C(20) angles when compared to the C(1)-C(10)C(20) angle which is forced apart by the somewhat lesser aromatic-*endo*-methoxyl interaction. Another result of these steric interactions is the increase in *endo*-C-C-C angles external to the ring (average 125.7°) involving C(10) over the corresponding *exo*-C-C-C angles (average 117.4°). The latter distortions imply the action of a torque at C(1), C(11), and C(20) which should accentuate bond bending in the C-C bonds about C(10). While the X-ray data point up the inappropriateness of the various high-symmetry models^{9a} relating $J_{\text{H-C}}$ to bond angles, if one simply takes the average of the three central C-C-C angles (115.3°) and applies Mislow's equations for C_{3v} symmetry,^{9a} the calculated interorbital angle is $110^\circ 17'$ corresponding to a $J_{\text{H-C}}$ of 113.9 Hz. The inverse calculation, starting with the observed $J_{\text{H-C}}$ (119.5 Hz), gives an interorbital angle of $109^\circ 52'$ and an internuclear angle of $112^\circ 14'$. The amount of bond bending in this molecule appears to be substantially greater than predicted^{9a} by a correlation fitting numerous other data.

The bending of the central C-H bond may also be important in reducing $J_{\text{H-C}}$. The C(10)-H(10) vector is not perpendicular to the C(1), C(11), C(20) plane. The C(1)C(10)H(10) angle is 92 (3) $^\circ$, indicating that

give $\Delta G^\circ_{-37^\circ} = 11.1$ kcal/mol, in reasonable agreement with these results.

(9) (a) K. Mislow, *Tetrahedron Lett.*, 1415 (1964); (b) C. S. Foote, *ibid.*, 579 (1963); (c) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768 (1959).

(10) J. D. Dunitz in "Perspectives in Structural Chemistry," Vol. 2, J. D. Dunitz and J. A. Ibers, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, pp 21-35.

(11) J. Karle and I. L. Karle, *Acta Cryst.*, 21, 849 (1966).

the hydrogen is forced away from the C(19) and C(28) methyl groups toward the O(1) methoxyl group; the O(1)–H(10) contact is 2.10 (6) Å, while the sum of the van der Waals radii is 2.60 Å.^{6,12}

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(12) While some of the hydrogen atoms in the difference map were not very well defined, H(10) had a height of 0.4 electron/Å³ and had a well-resolved peak. Refinement of the thermal parameters of all the hydrogen atoms gave B_{00} values ranging from -1.8 (that for H(10)) to $+12.0$ Å². While these values are clearly not quantitatively significant, the relatively low B_{00} values for H(10) and for many of the other hydrogen atoms involved in close contacts in the *endo* region of the molecule give us confidence in their location.

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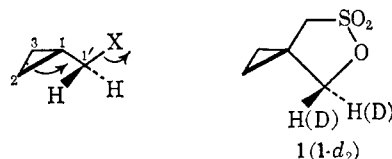
Solvolysis of 1-Hydroxymethylcyclopropanemethanesulfonic Acid Sultone, a Cyclopropylcarbinyl Derivative with an Oriented Leaving Group

Sir:

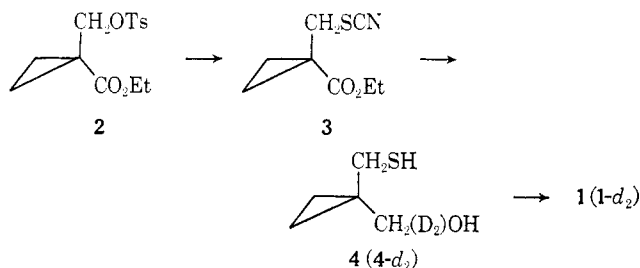
Despite the extensive investigations on the carbocation ion reactions and rearrangements of cyclopropylcarbinyl compounds,¹ it has not been possible to define precisely the character of the solvolytic transition state(s) or the structure of the product-forming intermediate(s).² Recent studies have been concerned with structurally rigid precursors of various designs^{1b,3} and the mechanism of the cyclopropylcarbinyl to cyclopropylcarbinyl rearrangement.^{4,5}

Although the 1,2 bond of the cyclopropane ring clearly participates in rearrangements leading to cyclobutyl and allylcarbinyl products, the 2,3 bond becomes involved in the overall cyclopropylcarbinyl-cyclopropylcarbinyl isomerization process. In order to examine the possibility of direct participation by the 2,3 bond,⁶ we have prepared the cyclopropylcarbinyl sultone **1**. In this structure, the sulfonate leaving group is fixed in an orientation which would seem most favorable for involvement of the electron pair of the 2,3 bond in the ionization process. The 1,2 bond is, however, considerably skewed from the apparently optimal geometry for concerted participation. For example, ionization of **1** without bond rotation would give an "in-plane" cyclopropylmethyl cation⁷ (or possibly a tricyclonium ion⁸). In order to attain the "bi-

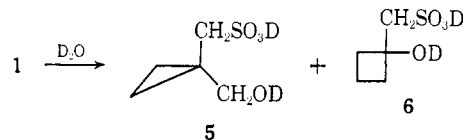
sected"⁹ (out of plane⁷) conformation, the 1,1' bond must rotate through an angle of 90°.¹⁰



1-Hydroxymethylmethanesulfonic acid sultone (**1**) was synthesized by the route outlined below. The tosylate **2**¹² was converted to the thiocyanate **3** (82%, ν_{\max} 2140 cm⁻¹)¹³ by reaction with sodium thiocyanate in refluxing 90% ethanol. Reduction with lithium aluminum hydride (or deuteride) in ether affords 1-mercaptomethylcyclopropanemethanol (**4** or **4-d₂**) in 73% yield. The sultone **1** or **1-d₂** is obtained by direct oxidation with 4 equiv of *m*-chloroperbenzoic acid in methylene chloride [yield 56%; mp 36.5–38°; ν_{\max} 1340, 1160 cm⁻¹; δ_{CDCl_3} 0.90 and 0.97 (2 m, 4 H), 3.26 (s, 2 H), 4.28 (s, 2 H)].¹⁴



Hydrolysis of sultone **1** (*ca.* 1 M) in 7:3 v/v acetone-*d*₆-deuterium oxide at 50° produces a mixture of two sulfonic acids, **5** [40%; δ 0.62 and 0.70 (2 t, J = 1.5 Hz; 4 H), 2.93 (s, 2 H), 3.57 (s, 2 H)] and **6** [60%; δ 1.5–2.5 (m, 6 H), 3.16 (s, 2 H)], which could be isolated as a mixed phenylhydrazine salt (80%; mp 156–163°). The ratio **5**:**6** remains constant throughout the hydrolysis and is unchanged by the presence of an equivalent amount of urea. Hydrolysis in the presence of 1.1–1.2 equiv of sodium hydroxide affords the cyclopropyl product exclusively (phenylhydrazine salt, 66%; mp 147–148°).



The deuterated sultone **1-d₂** hydrolyzes to 60% **6-d₂** (not possible to locate the deuterium) and **5-d₂** with the label in both the carbinyl position (29%) and in the cy-

(1) For references to the earlier literature see (a) P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); (b) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303, 4311 (1968).

(2) W. B. Kover and J. D. Roberts, *ibid.*, **91**, 3687 (1969).

(3) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969).

(4) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968).

(5) C. D. Poulter and S. Weinstein, *ibid.*, **91**, 3649, 3650 (1969).

(6) In certain structures, homocyclopropylcarbinyl participation can give rise to very large rate enhancements: H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); R. M. Coates and J. L. Kirkpatrick, *ibid.*, **90**, 4162 (1968); J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(7) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(8) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S.

Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

(9) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 150 (1964).

(10) Theoretical calculations^{1b,7,11} seem to be in general agreement, predicting that both the in-plane and pyramidal configurations for the cyclopropylmethyl cation should be less stable than the out-of-plane conformation.

(11) C. Trindle and O. Sinanoglu, *J. Am. Chem. Soc.*, **91**, 4054 (1969); R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968).

(12) H. Najer, R. Giudicelli, and J. Sette, *Bull. Soc. Chim. France*, 2118 (1965).

(13) All new compounds gave satisfactory elemental analyses and infrared and nmr spectra consistent with the indicated structures.

(14) This reaction represents a new and especially mild means for preparing sultones. The cyclic sulfinate is evidently an intermediate and is more slowly oxidized to the sulfonate stage. The oxidation of sulfonates to sultones under these conditions has recently been reported: R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).