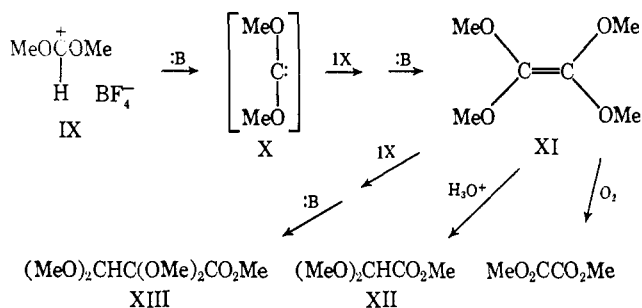
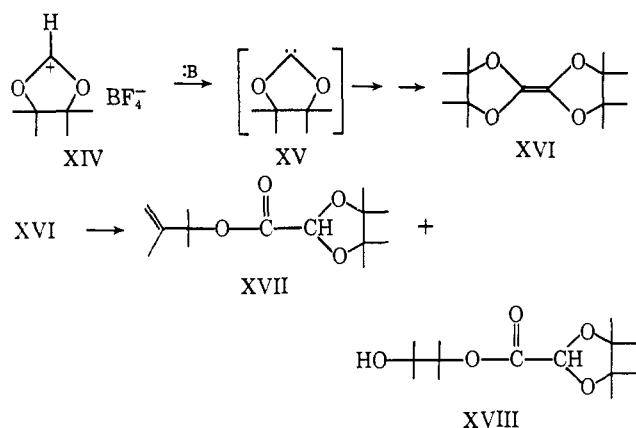


and  $\text{BF}_3 \cdot \text{Et}_2\text{O}^{6,9}$ ) affords the esters XII<sup>10</sup> and XIII<sup>11</sup> (bp 93° (5 mm)) almost certainly *via* dimethoxycarbene (X)<sup>10</sup> and the very unstable (to acid and trace water) tetramethoxyethylene (XI).<sup>10,12</sup> As expected, dimethyl oxalate is also obtained when the reaction is run under  $\text{O}_2$ .<sup>10</sup>



When the carbonium ion XIV<sup>9</sup> is used as the reaction substrate, the products are the alkenes XVI (nmr,  $\delta$  1.22) and XVII (nmr,  $\delta$  5.05 (1), 4.95 (1), 4.74 (1), 1.78 (3), 1.53 (6), 1.20 (12) in  $\text{CCl}_4$ ) and the alcohol XVIII (mp 88–91°; nmr,  $\delta$  5.00 (1) and 1.47, 1.35, 1.30, 1.25, 1.16 (total 24) in  $\text{CCl}_4$ ). This experiment was intended



as a test for a synthetic method for converting *vic*-glycols to alkenes, but it would seem that under our experimental conditions (unlike those of Corey<sup>13</sup>) the carbene XV does not spontaneously decompose to  $\text{CO}_2$  and tetramethylethylene but instead survives to be trapped by XIV.

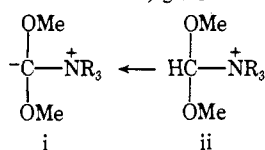
It might finally be noted that the above reactions are best carried out in chlorinated hydrocarbons or in sulfolane. Nitromethane as solvent may change the reaction

(9) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, **632**, 38 (1960).

(10) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966), and related papers; R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197, 1368 (1964).

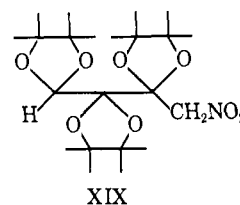
(11) Satisfactory analytical data have been obtained for all new compounds.

(12) The intervention of an ylide intermediate (i) is most unlikely considering the amine used<sup>4</sup> and the fact that ii (very unstable solution made by alkylation of amide acetal) gives other products in controls.



(13) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963). They generated the carbene XV or its equivalent by reaction of a thionocarbonate with  $(\text{RO})_3\text{P}$  at 120–160°. Unfortunately XIV decomposes thermally to pinacolone so the fate of XV when obtained from XIV at high temperature could not be determined.

course; e.g., XIV plus diisopropylethylamine in nitromethane yields a compound which we believe has structure XIX (mp 153.5–155°; nmr,  $\delta$  4.96 (1), 4.70 (2),



and 1.32, 1.20 (36) in  $\text{CCl}_4$ ). XIX could be formed by a reversible reaction of XVI with XIV followed by attack of *aci*-nitromethane on the resulting carbonium ion.

In future papers we hope to describe: (1) inverse addition experiments in which the carbonium ion is added to the base in the presence of competing carbene trapping agents, (2) extensions to the deprotonation of other carbonium ions with stronger hindered bases, and (3) new synthetic methods involving the extrusion of other electrophilic X moieties from the general cation structure II.

**Acknowledgment.** We thank the Alfred P. Sloan Foundation, the U. S. Public Health Service, and Eli Lilly and Co. for financial support.

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## Crystal and Molecular Structure of [16]Annulene<sup>1</sup>

Sir:

[16]Annulene (I) has been the subject of much recent experimental<sup>2,3</sup> and theoretical interest.<sup>4,5</sup> Several conformations have been proposed for [16]annulene,<sup>2–4</sup> and the low-temperature (–110°) nmr spectrum indicates that there are four “inner” protons and twelve “outer” protons.<sup>3</sup> At higher temperatures the protons are magnetically indistinguishable, possibly due to conformational isomerism arising from rotation about carbon–carbon bonds or valence tautomerism of the  $\pi$  bonds.<sup>3,6</sup> The results of an X-ray single-crystal structure analysis of [16]annulene, carried out at 4°, are now reported.

The deep purple crystals (mp 85–89°) belong to the monoclinic system with  $a = 8.79 \pm 0.02$ ,  $b = 8.13 \pm 0.02$ ,  $c = 18.60 \pm 0.04$  Å, and  $\beta = 109^\circ 10' \pm 10'$  at 4°. There are four molecules of  $\text{C}_{16}\text{H}_{16}$  (mol wt 208.3) in the unit cell ( $\rho_{\text{meas}} = 1.08$  g  $\text{cm}^{-3}$ ,  $\rho_{\text{calcd}} = 1.11$  g  $\text{cm}^{-3}$ ). The space group is  $\text{P2}_1/\text{c}$ . A total of 1205 independent structure amplitudes was obtained by visual estimation of equiinclination Weissenberg films taken at 4° (Cu  $\text{K}\alpha$  radiation). The structure

(1) Work supported by U. S. Public Health Service Grant GM 12470-04.

(2) F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 4863 (1961); I. C. Calder, Y. Gaoni, and F. Sondheimer, *ibid.*, **90**, 4946 (1968).

(3) G. Schröder and J. F. M. Oth, *Tetrahedron Letters*, 4083 (1966).

(4) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

(5) H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109.

(6) I. C. Calder and P. J. Garratt, *J. Chem. Soc., B*, 660 (1967).

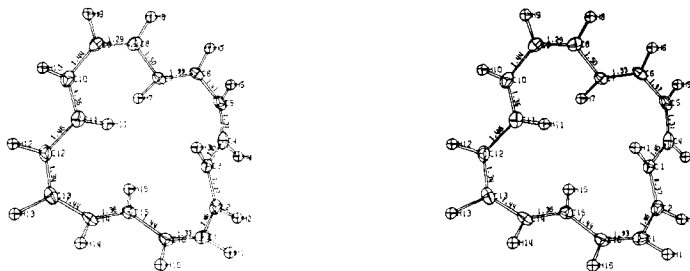


Figure 1. Stereoscopic view of the [16]annulene molecule looking along the *b* axis. Bond distances in ångströms; standard deviation of C-C bond distances lie in range 0.010–0.015 Å.

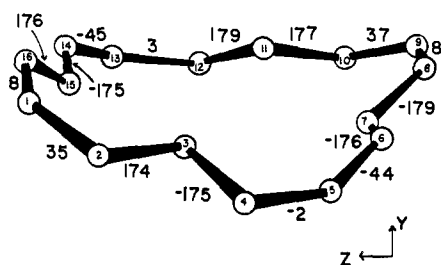


Figure 2. View of the [16]annulene molecule looking along the *a* axis. The dihedral angles along the bonds in the ring are given in degrees. The angle is taken as positive if, when viewed along the bond, the nearer substituent has to be rotated clockwise to eclipse the more distant substituent.

was solved by the symbolic addition method<sup>7</sup> and has been refined by full-matrix least-squares procedures to an *R* factor of 0.12. All 16 hydrogen atoms have been located.

Views of the molecular structure are shown in Figures 1 and 2. The [16]annulene molecule is seen to contain alternating *cis* and *trans* double bonds, thus confirming the proposals of Sondheimer<sup>2</sup> and Schröder.<sup>3</sup> The maximum distance of a carbon atom from the best plane through C(3), C(7), C(11), and C(15) is 0.57 Å, so that the nonplanarity of the molecule, although *highly significant*, is not exceptionally great. If bond alternation is a reliable indicator of the absence of aromaticity, then there is no evidence from the X-ray analysis for aromatic character in [16]annulene.<sup>8</sup> The average C(sp<sup>2</sup>)–C(sp<sup>2</sup>) distance is 1.46 Å, and the average C(sp<sup>2</sup>)=C(sp<sup>2</sup>) distance is 1.34 Å. The C–C–C bond angles (external to the ring) at C(3), C(7), C(11), and C(15) range from 120 to 123°, while the other C–C–C bond angles (internal to the ring) range from 125 to 131°. The nonplanarity of the molecule arises principally from quite large dihedral angles (Figure 2) around four of the eight single bonds ( $\tau$  35–45°). The dihedral angles at the other bonds range from 1 to 8° (or the equivalent deviation from 180°). The result of the large twists about four of the single bonds is to force two of the four “inner” protons (*i.e.*, H(3) and H(11)) to one side of the mean molecular

(7) For an authoritative review, see J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

(8) This is in marked contrast to the result of X-ray analyses on [14]annulene<sup>9</sup> and [18]annulene,<sup>10</sup> where the molecules occupy positions of site symmetry *C*<sub>1</sub>(1) in the crystal, and in the case of [18]annulene only very small differences in bond distance are observed.

(9) J. Bregman, *Nature*, **194**, 679 (1962).

(10) J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Cryst.*, **19**, 227 (1965); F. L. Hirshfeld and D. Rabinovich, *ibid.*, **19**, 235 (1965).

plane, and the other two inner protons (*i.e.*, H(7) and H(15)) to the other side of the plane, thus minimizing the internal H–H contacts. In this way, the molecule approaches *S*<sub>4</sub>(4) symmetry.

There is therefore evidence from ground-state geometry to support Longuet-Higgins' explanation<sup>5</sup> for a large paramagnetic ring current in [16]annulene to account for the differences in nmr behavior between the 4*n* and 4*n* + 2 annulenes.<sup>11</sup> At 4° there is no evidence for valence tautomerism or conformational isomerism in the crystal.

**Acknowledgment.** We thank Dr. Gerhard Schröder for kindly supplying the sample of [16]annulene used in this study.

(11) See also discussions by J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966), and by F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967).

(12) Alfred P. Sloan Foundation Fellow.

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### Bis(phosphino)silane and Tris(phosphino)silane<sup>1</sup>

*Sir:*

This communication describes the preparation of two new ternary silicon–phosphorus hydrides, bis(phosphino)silane (SiH<sub>2</sub>(PH<sub>2</sub>)<sub>2</sub>) and tris(phosphino)silane (SiH(PH<sub>2</sub>)<sub>3</sub>). Although monophosphinosilanes, *i.e.*, SiH<sub>3</sub>PH<sub>2</sub>,<sup>2,3</sup> and Si<sub>2</sub>H<sub>5</sub>PH<sub>2</sub>,<sup>4,5</sup> have been reported previously, SiH<sub>2</sub>(PH<sub>2</sub>)<sub>2</sub> and SiH(PH<sub>2</sub>)<sub>3</sub> are the first well-characterized examples of ternary hydrides containing multiple PH<sub>2</sub>-group substitution.

Bis(phosphino)silane and SiH(PH<sub>2</sub>)<sub>3</sub> were prepared by allowing stirred triglyme (1,2-bis(2-methoxyethoxy)ethane) solutions of LiAl(PH<sub>2</sub>)<sub>4</sub><sup>6</sup> to react at –30° for 15 min with SiH<sub>2</sub>Br<sub>2</sub> and SiHBr<sub>3</sub>, respectively. The reactions occur as shown below.



The reaction mixtures were separated by high-vacuum

(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) G. Fritz, *Z. Anorg. Allgem. Chem.*, **280**, 332 (1955).

(3) J. E. Drake and W. L. Jolly, *Chem. Ind.* (London), 1470 (1962).

(4) S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 1141 (1964).

(5) S. D. Gokhale and W. L. Jolly, *ibid.*, **4**, 596 (1965).

(6) The LiAl(PH<sub>2</sub>)<sub>4</sub> used in these experiments was prepared essentially as described by A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, and E. Jacobson, *ibid.*, **2**, 504 (1963).