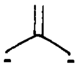
trianion was achieved by treatment with 2 equiv of benzyl chloride for 4 h at 20 °C. The sole dialkylation product (64% yield) was 1,7-diphenyl-3,5-heptanedione arising from 1,5-dialkylation. Dialkylation of the trianion with methyl iodide (2 equiv, 20 °C, 1.5 h) gave 3,5-heptanetrione in 59% yield. It can be concluded that the trianion of 2,4-pentanedione is substantially more nucleophilic than the dianion, although the dianion itself is a strong nucleophile.

The new anions described herein bear a formal relationship to the dianions of 2-methylpropene (**5**) and methylenecyclohexane (**6**) and the trianion of 2,4-dimethyl-1,3-pentadiene (**7**) which have been prepared from the hydrocarbons[12-14] by treatment with strong bases. Y-Delocalized systems, such as these anions, may possess aromatic stabilization.[14,15]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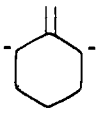
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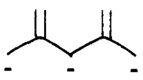
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Acknowledgement. This work was supported by the U.S. Public Health Service (Grant GM-12848).

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Received August 6, 1979

On the Prediction of Angles in Tetrahedral Complexes and Pseudotetrahedral Complexes with Stereoactive Lone Pairs

Sirs:

In a recent paper Schmiedekamp et al.[1] showed that it is possible to remove some of the apparent inconsistencies found when the VSEPR model is used to make numerical predictions of the angles in tetrahedral molecules if, rather than considering the interbond angles, one considers the space occupied by bonding and nonbonding (lone pair) electrons. Using ab initio electron density calculations they propose a method for determining the centroid of the lone pair which allows them to determine the angles between bonds and lone pairs, or between two lone pairs, in addition to the angles between bonds. They then use the triple-angle average $\langle\theta\rangle$ (average of the three angles formed by a bond or a lone pair) as a measure of the angular space occupied by the bonding or lone-pair electrons. When this is done, the triple-angle averages fall into natural groups according to bond type and geometry; for example, single S–H and S–F bonds have $\langle\theta\rangle \sim 103°$ and double S–O bonds and S–(lone-pair) orbitals have $\langle\theta\rangle \sim 114°$. They conclude that the angular space required by a particular bond depends on the central atom and whether the bond is a double or single bond, with lone pairs occupying the same angular space as a double bond.

Murray-Rust, Dunitz, and Bürgi[2] have also used the triple-angle average to study distortions found in many tetrahedral groupings of atoms in the solid state. By converting the bond lengths into Pauling-like bond numbers or bond valences,[3] they remove the effects of atomic size and bring all the tetrahedral groups to the same scale. They find that in all the cases studied the bond lengths (expressed in terms of bond valences, S) are related to the triple angle average $\langle\theta\rangle$ by

$$S/V = 2.25\cos^2\langle\theta\rangle \qquad (1)$$

where V is the valence of the central atom.

They conclude that the angles required by various ligands in tetrahedral groups are independent of the nature of the atoms forming the group and depend only on the deviations of bond valences from the average.

In an earlier paper[4] I have shown that, by fitting two limiting geometries, the regular tetrahedron ($S/V = 1/4$, $\langle\theta\rangle = 109.5°$) and the planar triangle where one ligand has been removed to infinity ($S_1/V = 1/3$, $S_2/V = 0$, $\langle\theta_{11}\rangle = 120°$, $\langle\theta_{12}\rangle = 90°$), one can derive a relationship for predicting individual bond angles (θ) using the average bond valence $\langle S\rangle$ of the two bonds defining the angle. A quadratic expression (eq 2) is the simplest relation that gives correctly the three angles found in the above two limiting geometries:

$$\theta = 109.5 + 180(\langle S\rangle/V - 1/4) - 652(\langle S\rangle/V - 1/4)^2 \quad (2)$$

This equation works well for predicting the angles in phosphates, sulfates,[5] and perchlorates[6] and can be used in reverse as an alternative method of assigning bond valences. It also works with lone-pair S(IV) complexes (SO_3^{2-}, Me_2SO) provided that the sulfur is treated as hexavalent and the lone pair is regarded as a double-bonded ligand ($S = 2.0$).[7]

This latter observation supports the conclusion of Schmiedekamp et al.[1] that the angular requirements of a lone pair are similar to those of a double-bonded oxygen and suggest that, at least for the present purposes, lone pairs can be treated as ions like oxygen having a formal charge of −2 but lacking a nucleus and core electrons. Such a view is in agreement with the findings of Galy, Meunier, Andersson, and Åström[8] that in crystals the lone pair occupies a volume comparable to an O or an F atom.

By considering the lone pair as a dibasic ligand, the neutral molecules discussed by Schmiedekamp et al.[1] can all be written in the form $A(VI)X_2Y_2$ or $A(V)XY_3$ where A is the hexa- or pentavalent central atom (S, O, P, or N), X is oxygen or a lone pair, and Y is F or H. The triple-angle averages for X and Y can be calculated from their valences (S_1) using eq 3 which has been derived by averaging eq 2 over the appropriate three angles recognizing that the sum of all four bond valences is equal to V:

$$\langle\theta\rangle = 109.5 + 60(S_1/V - 1/4) - 217.3[\langle(S/V)^2\rangle_4 - 1/16] \quad (3)$$

Here $\langle(S/V)^2\rangle_4$ is the value of $(S/V)^2$ averaged over all four bonds. Equation 3 gives the following values for $\langle\theta\rangle$ (the values

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given by Schmiedekamp et al.[9] are given in parentheses): A(VI)-X = 113.0° (111.6-114.9, average 113.8), A(VI)-Y = 103.0° (102.2-107.1, average 104.0), A(V)-X = 116.9° (113.3, 122.3), and A(V)-Y = 104.9° (103.5, 108.0). In all cases predicted angles from eq 3 lie close to the mean values given by Schmiedekamp et al.[9]

Calculating the angles in the charged species NH_2^- and NF_2^- is not quite as straightforward since one must make assumptions about the distribution of net charge. Assuming that the lone pairs and the ligands carry an equal charge, that is, they each use 0.25 valence units to form external bonds, the bond valences will be 1.75 for the lone pairs and 0.75 for the ligands. This leads to $\langle\theta\rangle$ = 113.3 and 101.3°, respectively, compared with the values of 115.0, 113.8 and 102.0, 103.8 calculated by Schmiedekamp et al.[9] In a solid-state complex the valences of the bonds to the ligands (including the lone pairs) will be affected by whether the nitrogen or the ligands form the stronger external bonds and in that case the observed angles may well be different.

The conclusions that can be drawn from the above discussion are that for certain purposes it is convenient to treat a stereoactive lone pair of electrons as a divalent base. The atom that it belongs to must then be treated as if it were in its highest oxidation state; thus S(IV) is treated as the complex S(VI)-(lone pair). An incidental advantage of this approach is that it separates the Lewis acid and base functions of S(IV) into an acid function (S(VI)) and a base function (lone pair), a concept that is particularly helpful when the lone pair also forms a coordinate bond to a metal or other Lewis acid. Using this formalism the angular space occupied by a ligand or a lone pair can be predicted from simple geometric considerations if the strength (valence) of the bond that it forms with the central atom is known. In the case of isolated neutral molecules, such as those treated by Schmiedekamp et al.,[1] the bond valence is the same as the bond order and can be assigned by inspection, but in the solid state nonintegral bond valences will result from the bonding between the tetrahedral group and adjacent ions and thus the geometry of the group will depend in a predictable way on the environment.[4]

Acknowledgment. I thank the National Research Council of Canada for financial support.

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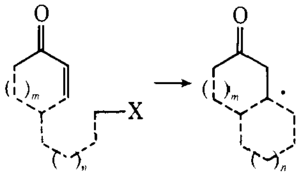
Received October 25, 1979

Alkyltin(IV)-Mediated Carbocyclization

Sir:

The synthesis of complex organic molecules requires methods for the formation of carbocyclic rings.[1,2] Although a number of carbocyclization methods have been developed which employ concerted, ionic, or radical processes, conjugate addition to α,β-enones, a central reaction type in intermolecular carbon–carbon bond formation, has witnessed limited utility in carbocyclization (e.g., **1** → **2**).[3] This approach to cyclization has been constrained by the substantial stabilization of the carbanionic nucleophile required for effective intramolecular anionic enone addition[3a,b] and by the effective competition of α,β-enone polymerization with desired cyclization in radicaloid processes. The internal addition of an unactivated, carbanionic nucleophile to the electrophilic β site of an enone is the vinylogous counterpart of the halocarbonyl reductive cyclization.[4]



1 **2**

We report here a method for effecting intramolecular conjugate addition to 2-cyclohexenones of unactivated carbon nucleophiles which proceeds through the mediation of novel alkyltin(IV) chemistry. This method of carbocyclization illustrates the use of the carbon–tin σ bond as a latent carbanionic nucleophile in internal carbon–carbon bond formation.[5] As illustrated here, the overall sequence corresponds to the annulation of variable-sized rings onto a preexisting cyclohexanone ring system.

The cyclization method employs activation of the α,β-enone moiety with Lewis acids to engender a β-electrophilic site (e.g., **4**) which is sufficiently potent to react with a stereoproximate carbon–tin σ bond. A synthetically useful feature of this approach to carbocyclization is that the weakly polarized nature of the carbon–tin σ bond ($C^{\delta-}$–$Sn^{\delta+}$) ensures compatibility of the α-enone and tetraalkyltin moieties until electrophilic activation. Thus a model 2-cyclohexenone substrate **3**[6] yields a mixture of 2-decalone isomers **5** and **6**[6a] upon treatment with Lewis acids (Scheme I). When the cyclization is conducted in methylene chloride with titanium tetrachloride as acid catalyst, a temperature dependence of 2-decalone isomer distribution is observed. The ratio of *cis*-2-decalone (**5**) to *trans*-2-decalone (**6**) varied from 93:7 at 40 °C (2-min reaction period) to 33:67 at −78 °C (30 min). The formation of products was established to be kinetic and not reversible and could be a consequence in part of the distribution of pseudoaxial:pseudoequatorial (4′-trimethylstannyl)butyl side-chain conformers.[7] The preparation of 4-(4′-trimethylstannyl)butyl-2-cyclohexenone (**3**) was effected by the method of Stork and Danheiser[8] through alkylation of the kinetic enolate of 3-ethoxy-2-cyclohexenone (**7**) with 1-iodo-4-(trimethylstannyl)butane[9] followed by reduction and acid-catalyzed hydrolysis.

The 3-methyl-2-cyclohexenone derivative **9**,[6] in which the preferred conformation has the (4′-trimethylstannyl)butyl side chain in a pseudoaxial position, did not undergo the expected carbocyclization. Instead, transfer of a hydride β to the trimethyltin moiety occurred generating a single, stereoisomeric cyclohexenone **11** (Scheme II).[6b] The lack of carbon–carbon bond formation is presumably a consequence of the substantial steric interactions which occur in the six-membered transition state for coupling of the encumbered, trimethylstannyl-bound carbon nucleophile to the electrophilic, disubstituted β-enone position. The hydride transfer process is facilitated by the ca-

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