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CONFORMATIONS OF TETRASUBSTITUTED ETHANES; REASONS FOR TRANS VICINAL HYDROGENS

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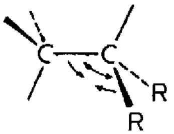
In tetrasubstituted ethanes, a marked conformational preference for trans vicinal hydrogens is frequently observed.[1] This is especially common in phenyl or carbonyl substituted ethanes having other electronegative substituents and lacking multiple alkyl substituents. In order to obtain more accurate data on the intramolecular changes that give rise to this conformational preference, an x-ray crystallographic structure was determined for the phosphine oxide 7 (cf. previous communication). A perspective drawing taken directly from the ORTEP plot is shown in Fig. 1.

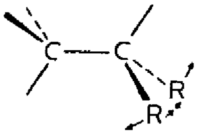
The nmr data for 7 show that the same gross conformation is preferred in solution (structure 14, previous communication) as in the solid phase (Fig. 2). The dihedral angle between vicinal protons (153°) is consistent with the rather low nmr $J_{H(1)-H(2)} = 8.5$ Hz. Accurate values of dihedral angles for the erythro isomers 4, 5, and 8 (cf. previous communication) are not known but the nmr data suggest that the dihedral angles are closer to the idealized values of 60° or 180°. Thus for 4, 5, and 8, $J_{H(1)-H(2)}$ is near maximum.[2] In 7, the dihedral angle between H(2) and P is 40°. This angle is consistent with the higher $^3J_{P-H(2)} = 11$ Hz than observed for the erythro isomers (ca. 6 Hz). However, in solution other conformers may also be partially occupied, and their contribution also affects ^3J.

Other crystallographic results[3] suggest that conformation is affected by the interplay of three types of variation in molecular geometry by which the molecule seeks the most comfortable fit of groups: (1) Rotational changes about the ethanic bond (and other bonds).[1,4] (2) Changes in bond angle between substituents and ethanic carbons[4,5] (e.g. 1). (3) Changes in bond angle between geminal substituents[4,6] (e.g. 2). Deformation of bond lengths requires high energy,[7] and the bond lengths in 7, as in other cases,[3] were close to literature values.

1



2



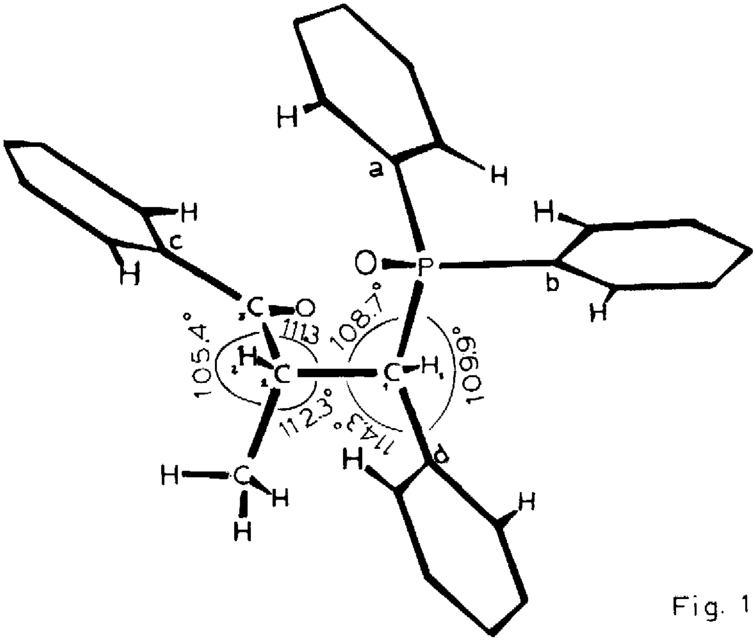

H
a
H
H
c
H
O
P
H
b
H
C
O
111.3
108.7°
105.4°
H
C
C
H
109.9°
112.3°
114.3°
H
d
H
H
C
H
H

Fig. 1

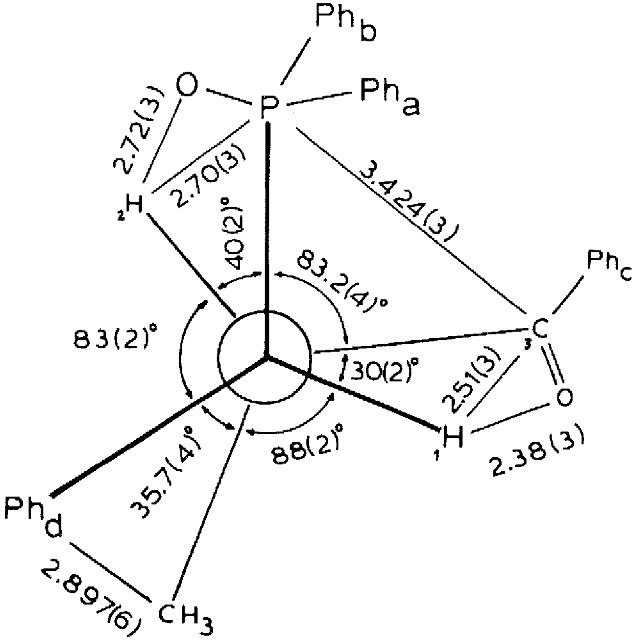

Ph$_b$
O
P
Ph$_a$
2.72(3)
2.70(3)
H$_2$
3.424(3)
40(2)°
83.2(4)°
Ph$_c$
83(2)°
C$_3$
30(2)°
2.51(3)
O
H$_1$
88(2)°
2.38(3)
35.7(4)°
Ph$_d$
2.897(6)
CH$_3$

Fig. 2

In 7, the most severe interactions occur between two sets of nearly planar atoms. Thus, CO-Ph_c approaches PO-Ph_a closely. Observed separations of 3.424(3) Å for P··C_3 and 3.123(4) Å for C_3··C_{a1} (the substituted carbon of Ph_a) are significantly less than the van der Waal's values of ~3.6 and 3.4 Å, respectively.[8a] The dihedral angle between CO and P (83.2°) is very large, and represents an adjustment by the molecule to minimize these repulsive interactions. However, bond angles are close to normal tetrahedral values. The P-C_1-C_2 angle (108.7(2)°) is rather small in view of the size of $POPh_2$.

The second severe interaction occurs between Ph_d and CH_3, which are separated by 2.897(3) Å at the point of closest approach (van der Waal's value > 3.4 Å). The dihedral angle between these groups is only 35.7°. To minimize the interaction, bond angle spreading has occurred resulting in a CH_3-C_2-C_1 angle of 112.3(3)° and a C_2-C_1-Ph_d angle of 114.3(3)°. *These angles move Ph_d and CH_3 away from one another in a manner not represented in Fig. 2.* Other less severe contacts include P··H_2 (2.70(3) Å) and C_3··H_1 (2.51(3) Å) which are smaller than the van der Waal's distances of ~3.1 and ~2.9 Å.

The question arises, then, as to why the molecule tolerates five close contacts when a simple rotation toward normal 60° dihedral angles would improve three of the interactions and worsen only the P··C_3 interactions. We suggest that two other interactions P$\underline{O}$··H_2, and $C_3\underline{O}$··H_1 may be attractive. These hydrogens could be polarized by the neighboring electronegative group (H_1 by PO and H_2 by CO) and carry a substantial partial positive charge. This partial charge would interact in an attractive manner[8b] with the partially negatively charged oxygen of the vicinal group. In the erythro isomers, 4, 5, and 8, a rotation that brings CO near H_1, separates PO and H_2, and vice versa. Thus, skewed dihedral angles in the erythro isomers increase repulsions without enhancing attractive interactions. Attempts to measure the relative stability of 7 and 8 by equilibration were complicated by side reactions, i.e. elimination to the alkene. However, in the reaction mixture, 8 was the surviving reactant. In equilibration of other erythro-threo isomers, i.e. $3 \rightleftharpoons 4$, approximately equal stability was indicated.

The decrease in geminal dihedral angle, as in 2, previously postulated as a reason for trans vicinal hydrogens is found at one ethanic carbon (CO-C_2-CH_3, 117.9(4)°), but not at the other ($PO-C_1-Ph_d$, 123.1(4)°).[9] An alternate postulate, which concerns the orientation of Ph, does find some support. As Fig. 1 indicates, the planar Ph_d ring is so oriented that one ortho hydrogen is eclipsed with H_1. The other ortho hydrogen lies nearest PO and H_2, two comparatively small groups. The result of the preference of the Ph_d ortho hydrogens to be eclipsed with, or lie near hydrogens substituted on the ethanic skeleton would favor trans vicinal hydrogens.

Data: $C_{28}H_{25}O_2P$, monoclinic, space group $P_{2_{1/n}}$ (alternate setting of $P_{2_{1/c}}-C^5_{2h}$) with four molecules per unit cell, a = 12.045 ± 0.002Å, b = 16.890 ± 0.002 Å, c = 11.522 ± 0.001 Å and β = 91.28 ± 0.01°. A total of 5365 independent reflections having $2\theta(\text{MoK}\bar{\alpha}) \leq 55°$ (the equivalent of 1.0 limiting $\text{CuK}\bar{\alpha}$ sphere) were collected on a computer controlled Syntex $P_{\bar{1}}$. Autodiffractometer using full (1.0° width) ω scans and graphite monochromated $\text{MoK}\bar{\alpha}$ radiation. The structure was solved using direct methods. Full-matrix least-squares refinement using an empirical weighting scheme, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms resulted in a conventional unweighted residual, R = 0.047 for those 2621 independent reflections having $2\theta(\text{MoK}\bar{\alpha}) \leq 55°$ and $I > 3\sigma(I)$.

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(9) The bond angle is a more basic quantity than dihedral angle; for $P-C_1-Ph_d$, the bond angle is 109.9(2)°; for $CO-C_2-CH_3$, the angle is 105.4(3)°, significantly less than tetrahedral.