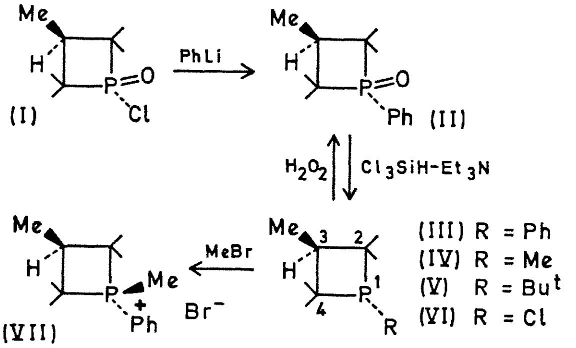
Stereochemical Assignments in Phosphetane Compounds

By SHELDON E. CREMER

(*Department of Chemistry, Marquette University, Milwaukee, Wisconsin* 53233)

Summary Revised stereochemical assignments have been made for the *cis*- and *trans*-isomers of 1-substituted-2,2,3,4,4-pentamethylphosphetanes and related derivatives.

IN previous reports from our laboratory we stated that the *cis versus trans* relation of the 1-phenyl and 3-methyl substituents in (II), (III), and (VII) was a tentative assignment.[1a,b] Although the structure and stereochemistry of (II)[2] and (VII)[3] have been determined by *X*-ray analysis, no m.p. or other data were provided which would enable other investigators to associate a given geometrical isomer with its allied physical or spectral properties. The present communication clarifies the stereochemical assignments in these systems.



The stereochemical assignments and relation of the acid chloride (I) to the oxide (II) have been established.[4] Reduction of the *trans*-oxide (II), m.p. 126—127°, with Cl_3SiH–Et_3N was concluded [1a] to proceed with retention of configuration to give the *trans*-phosphetane (III). Proof for the *trans* relation of the 1-phenyl and 3-methyl groups in (III) comes from its quaternization[5] to give (VII), m.p. 224—228°, which was submitted for *X*-ray[3] analysis. The sample of (VII) used contained about 5% of the isomeric *cis*-3-methyl-1-phenyl salt, m.p. 230—234°; a single crystal of this minor component is invariably selected (from a mixture) by the crystallographer because of its more suitable crystalline form. The major isomer (*trans*) gives only poor or mediocre crystals. Thus, the *X*-ray analysis by Trefonas[3] was inadvertently performed on the minor isomer (*cis*) taken from a batch of crystals which were mostly *trans*-(VII).†

The reassignment of geometrical isomers in this series does not change the conclusions or arguments in previous papers from this laboratory[1] or those of Mislow[6] or Trippett.[7] The stereochemical assignment must be reversed for the t-butyl derivative (V)[1b,c] as well as for other 1-substituted compounds.[7] Both ^1H and ^{31}P n.m.r. provide a convenient way of distinguishing between the *cis*- and *trans*-isomers of (III)—(VI). The chemical shift of the 3-H in the *trans*-isomer is about 0·4—0·7 p.p.m. downfield from that of the *cis*-isomer.[1a,8] Also the ^{31}P chemical shifts for the *cis*-compounds are about 20—30 p.p.m. to higher field of the *trans*-isomer.[8]

I thank the P.H.S. (National Cancer Institute) for a grant.

(*Received, March 24th*, 1970; *Com.* 426.)

---

† Prof. Trefonas has rechecked the m.p. and corresponding cell dimensions of both the *cis*- and *trans*-isomers; personal communication.

[1] (a) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066; (b) S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Letters*, 1968, 5799; (c) S. E. Cremer and C. H. Chang, *Chem. Comm.*, 1969, 1456.

[2] M. Haque and C. N. Caughlan, *Chem. Comm.*, 1968, 1228. Note that the isomer reported by these workers is *trans* as indicated by their Figure and not *cis* as stated in the last paragraph.

[3] C. Moret and L. M. Trefonas *J. Amer. Chem. Soc.*, 1969, **91**, 2255.

[4] S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200, ref. 3 and 9; M. Haque, *J. Chem. Soc.* (*B*), in the press.

[5] Quaternization reactions are considered to go with retention of configuration; L. Horner, *Pure Appl. Chem.*, 1964, **9**, 225.

[6] P. D. Henson, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 5645; K. E. Debruin, G. Zon, K. Naumann, and K. Mislow, *ibid.*, p. 7027; see also K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, p. 7031.

[7] J. R. Corfield, J. R. Shutt, and S. Trippett, *Chem. Comm.*, 1969, 789; D. J. H. Smith and S. Trippett, *ibid.*, p. 855; W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465.

[8] Unpublished data.