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STEREOSPECIFIC ^{13}C-^{31}P COUPLING CONSTANTS IN PHOSPHETANE OXIDES AND PHOSPHETANIUM SALTS

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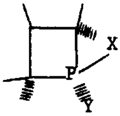
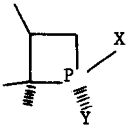
As a part of a systematic investigation of organophosphorus compounds using ^{13}C nmr we have been interested in the potential offered by the four-membered phosphorus heterocycles, the phosphetanes. The observed chemical shifts and spin couplings provide severe restraints on any attempted prescription for the electronic structure and can also contribute significant information concerning molecular structure. As indication of the latter we now report the stereospecific nature of two ^{13}C-^{31}P nuclear spin couplings in phosphetane oxide and phosphetanium salt cis and trans pairs.

Overall, the stereospecificity in one-bond coupling is fairly independent of the nature of the other exocyclic phosphorus substituent , for both aliphatic and aromatic carbons. The only case to exhibit different behavior is that for the coupling to the phenyl carbon in ⑫/⑬. Note that ⑦ has identical phosphorus substituents but different one-bond ^{13}C-^{31}P couplings. These methyl groups are rendered chemically non-equivalent in a formal sense by the cis-trans nature with respect to the 3-methyl group. However, it is the nonplanarity of the phosphetane ring which confers pseudoxial or pseudoequatorial properties and produces unequal chemical shifts due to the different steric interactions with the 2- and 4-carbon methyl groups. Either this disparity in steric interaction causes enough difference in the electronic nature of the methyl carbon sufficient to cause the difference in coupling, or the phosphorus contribution to the two bonding orbitals to the exocyclic methyls must be different. The overall uniformity in the stereospecificity of the one-bond couplings tends to rule out differential steric effects as the sole cause of the stereospecificity.

Analogous stereospecificities have been noted for ^{13}C-^{1}H couplings in bicyclobutane (1)

Table I. ^{13}C-^{31}P Nuclear Spin Coupling Constants[a]

X, Y	$^{1}J_{CP}$ [b]	ΔJ	$^{3}J_{CP}$ [c]	ΔJ	$^{1}J_{CP}$ [b]	ΔJ	$^{3}J_{CP}$ [c]	ΔJ
								
① CH_3, O	36.9	4.0	12.6	10.4				
② O, CH_3	40.9		23.0					
③ Ph, O	54.5	5.1	16.9	6.2	⑫ 57.6	14.7	16.5	11.8
④ O, Ph	59.6		23.1		⑬ 72.3		28.3	
⑤ OCH_3, O	--	--	18.5	5.3	⑭ --	--	12.1	15.7
⑥ O, OCH_3	--		23.8		⑮ --		27.8	
⑦ CH_3, CH_3	29.1, 34.7[d]	5.6	18.1,18.1	0.0				
⑧ CH_3, Ph	31.1,[e]48.9[f]	4.8,6.0	17.6	4.6	⑯ 31.5,[e]58.4[f]	5.8,6.3	21.2	2.5
⑨ Ph, CH_3	35.9, 54.9		22.2		⑰ 37.3, 64.7		23.7	
⑩ CH_3, Bz	28.2,[e]18.6[g]	6.1,3.3	16.8	2.3				
⑪ Bz, CH_3	34.3, 21.9		19.1					

(a) The couplings were obtained from noise-decoupled 25.1 MHz ^{13}C nmr spectra of neat or saturated solutions in $CHCl_3$ using a Varian HA-100. Details of samples, instrumentation, ^{13}C shifts and ^{13}C-^{31}P couplings of a large number of phosphetane oxides and phosphetanium salts will be the subject of a forthcoming full publication. (b) Coupling to exocyclic carbon bound to phosphorus. (c) Coupling to methyl carbon directly across ring. (d) Methyls assigned using 1-deuteriomethyl-1,2,2,3,4,4-hexamethylphosphetanium bromide (1-CD_3, 3-CH_3 trans). (e) Methyl carbon. (f) Phenyl carbon. (g) Benzyl carbon.

and 3-phenyl-1-azabicyclo[1,1,0]butane (2), and as well as $^{13}C-^{19}F$ couplings in some methyl substituted 2,2-difluoronorbornanes (3). Although dipole contributions may be important in $^{13}C-^{19}F$ couplings (4), approximate M.O. methods based solely on the Fermi contact contribution have proved successful in calculation of $^{13}C-^{13}C$ and $^{13}C-^{1}H$ couplings (5a-f) and have been able to account for the stereospecificity of the $^{13}C-^{1}H$ coupling in bicyclobutane (5f). Similar calculations of $^{13}C-^{31}P$ couplings (6) in the series $(EtO)_2P(O)CH_2X$ showed that the experimental couplings were about twice as sensitive to substituents as was the s-orbital bond order between the coupled atoms. However, $^{13}C-^{13}C$ and $^{13}C-^{1}H$ couplings closely parallel the calculated s-orbital bond order for *structural* rather than *substituent* changes. If this pattern holds for $^{13}C-^{31}P$ couplings involving P(IV), the greater exocyclic coupling for the pseudoaxial bond predicts a corresponding greater s-orbital bond order for this bond. This conclusion is on safest grounds in ⑦ where the exocyclic groups are identical.

No large one-bond coupling stereospecificity is present in the larger ring compounds *cis*- and *trans*-1,2,5-trimethyl-3-phospholene-1-oxide (*cis*- 58.8 Hz, *trans*- 59.7 Hz). However, very recently a *cis-trans* stereospecific $^{13}C-^{31}P$ coupling has been reported for the methyl carbon on phosphorus in a six-membered ring *tert*-butyl-substituted methyl phosphonite (7). Here phosphorus is P(III) and one of the exocyclic substituents is a lone pair.

Stereospecific long-range $^{13}P-^{1}H$ couplings have been used in the past to give relative spatial orientation (18a-g). In these cases, however, one of the coupled atoms assumes various possible orientations leading to a variation in coupling with, *e.g.* dihedral angle. Very little data, if any, has been presented for an effect like that illustrated in Table I for the three bond $^{13}C-^{31}P$ coupling in *cis-trans* pairs. Here the relative orientation of the coupled atoms remains *fixed* while the exocyclic substituents are switched, resulting in a sometimes drastic change in coupling. The disparity in coupling within isomer pairs seems directly related to the degree of difference of the exocyclic substituents. Though-space steric or electronic effects seem unlikely as direct causes of the stereospecificity since the 3-methyl carbon and exocyclic group *cis* to it are well separated.

The stereospecific exocyclic $^{13}C-^{31}P$ couplings in phosphetane oxides or phosphetanium salts allows facile determination of *cis-trans* isomer ratios in mixtures when both isomers are present in significant amounts or isolable separately. There is no difficulty in assignment of resonances as there often is in ^{1}H spectra (at 60 MHz) because of the large range of ^{13}C shifts and lack of overlapping peaks. This method neatly complements the use of two-bond ^{31}P-^{1}H couplings (8d) to determine *cis-trans* ratios in the related P(III) phosphetane compounds which has not been generally applicable in their oxides or salts. The technique will be especially useful in making isomer assignments in salts and oxides which do not follow from synthetic analogy or cannot be related to the few compounds whose assignment was made by x-ray study.

References

(1) K. B. Wiberg, G. M. Lampman, R. P. Giula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(2) A. G. Horfmann and D. A. Robertson, *J. Amer. Chem. Soc.*, **89**, 5974 (1967).

(3) J. B. Grutzner, M. Jantelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

(4) A. C. Blizzard and D. P. Santry, *Chem. Comm.*, 87 (1970).

(5) (a)-(e) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1, 11, 4151, 4497, 4506 (1970); (f) P. D. Ellis and G. E. Maciel, *ibid.*, **92**, 5829 (1970).

(6) G. A. Gray, *ibid.*, **93**, 2132 (1971).

(7) W. G. Bentrude, K. C. Yee, R. D. Bertrand and D. M. Grant, *J. Amer. Chem. Soc.*, **93**, 797 (1971).

(8) (a) J. P. Albrand, D. Gagnaire, and J. B. Robert, *Chem. Comm.*, 1469 (1968); (b) L. D. Hall and R. B. Malcomb, *Chem. and Ind.*, 92 (1968); (c) G. Mavel, *J. Chim. Phys.*, **65**, 1692 (1968); (d) J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.*, 40 (1969); (e) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970); (f) W. G. Bentrude and J. H. Hargis, *ibid.*, **92**, 7136 (1970); (g) J. P. Albrand, D. Gagnaire, M. Picard and J. B. Robert, *Tetrahedron Lett.*, 4593 (1970).