Tetrahedron Letters No.52, pp. 4593-4596, 1970. Pergamon Press. Printed in Great Britain.

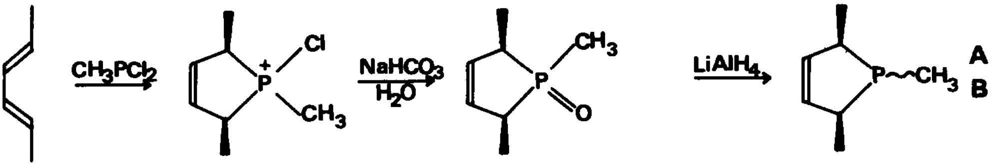
USE OF THE NMR COUPLING CONSTANT J(P-C-H) FOR THE IDENTIFICATION OF CYCLIC PHOSPHINES

Jean-Pierre ALBRAND, Didier GAGNAIRE, Mireille PICARD and Jean-Bernard ROBERT
Laboratoire de Chimie Organique Physique, Centre d'Etudes Nucléaires de Grenoble,
CEDEX n° 85 F. 38 - Grenoble-Gare

(Received in UK 30 September 1970; accepted for publication 14 October 1970)

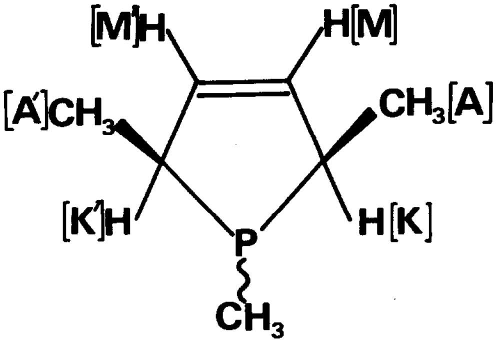
It is now well established that tertiary phosphines have a conformationally stable pyramidal structure [1]. It follows that suitably substituted cyclic phosphines should exist in geometrical isomeric forms as demonstrated by the studies of 3-phospholenes [2], 9-Phenyl-9-phosphabicyclo(6-1-0) nonatriene [3], phosphetanes [4], phosphorinanols [5] and phosphirans [6]. The separation of such geometrical isomers has been performed in several instances but their configuration has been reported [3] of proposed [5] in only a few cases. Such configurational attributions have important implications for stereochemical studies like nucleophilic displacements at phosphorus. We wish to illustrate here the ability of the $^2J(P-C-H)$ geometrical dependence [7] for such an attribution in the case of 3-phospholen derivatives and to point out a new influence of the phosphorus lone pair orientation on the $^4J(H-C-P-C-H)$ n. m. r. coupling constants. The stereochemistry of 3-phospholen derivatives has already been investigated [8] using the phenyl ring shielding effect but without any examination of the $^2J(P-C-H)$ n. m. r. coupling constants.

According to the procedure of M. GREEN [9], by reaction of methyl phosphonous dichloride with trans, trans-2, 4-hexadiene and hydrolysis of the resulting cycloadduct, one gets a mixture of two 1, 2, 5-trimethyl-3 phospholen-1 oxides (80 %, 20 %). The reduction of this mixture by lithium aluminium hydride affords a mixture of two 1, 2, 5-trimethyl-3-phospholens (A 40 % ; B 60 %). The symmetry of the n. m. r. spectrum of this mixture readily indicates that in both isomers the 2, 5-methyl groups have a cis relationship.



The proton n. m. r. spectrum analysis of the phospholens (A) and (B) was performed on the neat mixture of the two isomers which exhibits well separated lines. Lines belonging to the same isomer are easily identified from line intensity examination and double resonance experiments. Both spectra of (A) and (B) are $A_3A'_3KK'MM'X$ systems (AA' methyl protons, KK' methine protons, MM' vinylic protons, X phosphorus), which are reduced to $A_3A'_3KK'X$ by irradiation of the vinylic protons. Such a system is the superposition of two $A_3A'_3KK'$ subspectra [10]. Assuming a zero value for the coupling constant between the methyl protons A and A', the coupling constant between the methine protons can be read directly on the $A_3A'_3$ part of the spectrum [10]. The results of the n. m. r. spectra analysis are shown in the table. The relative signs of the coupling constants were obtained from homonuclear double resonance experiments. The absolute signs are given, assuming that $^3J(P\text{-}C\text{-}C\text{-}H_3)$ is positive, as found in each case for which this sign has been determined for phosphine-like compounds [11].

	A	B
$^2J(PH)$ KX	+ 22.7 Hz	- 2. Hz
$^3J(PH)$ AX	+ 10. "	+ 17.5 "
$^3J(PH)$ MX	+ 4.9 "	+ 6.0 "
$^4J(HH)$ KK'	3.2 "	1 "
$^3J(HH)$ AK	7.3 "	7.4 "
$^2J(P\text{-}CH_3)$	3.9 "	3.4 "
δ(H) K, K'	2.80 ppm	2.18 ppm
δ(H) M, M'	5.47 "	5.57 "
$\delta(CH_3)$ A, A'	1.01 "	1.09 "
$\delta(CH_3)$	0.64 "	0.84 "



δ : Downfield from internal T. M. S.

Before discussing the configuration of compounds (A) and (B) which will be performed using the difference between the ^{2}J(P-C-H) n. m. r. coupling constants values in (A) and (B), it must be pointed out that the pairs of ^{2}J(P-C-H) values are very close for the 1-phenyl -3, 4-dimethyl-3-phospholene (+ 25 Hz, - 6 Hz) and the 1-methyl-3-phospholene (+ 22 Hz, -4 Hz). This indicates that the plot of ^{2}J(P-C-H) against the dihedral angle α previously studied [7] is approximately the same when a methyl group is attached to the phosphorus instead of a phenyl group.

Thus, from the plot of ^{2}J(P-C-H) = f(α), the largest ^{2}J(P-C-H) n. m. r. coupling constant (22. 7 Hz) must be attributed to the isomer in which the CH bonds and the phosphorus lone pair have a cis arrangement (fig. 1). This result is in agreement with the attribution made by QUIN and BARKET [8].

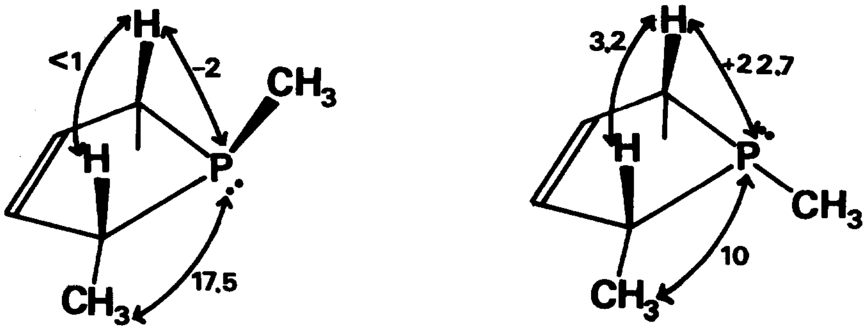


Fig. 1 : Stereospecificity of coupling constants in phospholenes.

Using this attribution, two more remarks concerning the n. m. r. coupling constant stereospecificity can be made :

- First, the ^{3}J(P-C-CH$_3$) coupling constant is larger when the methyl groups are cis with respect to the phosphorus lone pair. This result can be useful in making isomer assignments in other examples.

- Secondly, the long range ^{4}J(H-C-P-C-H) coupling constant is larger when the CH bonds are cis with respect to the phosphorus lone pair orientation. This coupling between the methine protons can occurs through two different paths, one through the double bond (homoallylic coupling ^{5}J), one through the H-C-P-C-H fragment (^{4}J). It seems reasonable to consider that the difference occuring between this coupling constant in (A) and (B) is due not to the homoalylic contribution which is probably quite similar in both isomers, but to the difference in the pathway through the phosphorus atom (CH bonds cis in (A) and trans in (B) with respect to the phosphorus lone pair orientation).

REFERENCES

1. M. J. Gallagher and I. D. Jenkins, "Topics in Stereochemistry", vol. 3, chap. I, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New-York, N. Y., 1968.
2. L. D. Quin, J. P. Gratz and R. E. Montgomery, Tetrahedron Letters, 2187 (1965).
3. T. J. Katz, C. R. Nicholson and C. A. Reilly, J. Amer. Chem. Soc., **88**, 3832 (1966).
4. S. E. Cremer and R. J. Chorvat, J. Org. Chem., **32**, 4066 (1967).
5. H. E. Shook Jr., and L. D. Quin, J. Amer. Chem. Soc., **89**, 1841 (1967).
6. S. Chan, H. Goldwhite, H. Keyzer, D. G. Rowsell and R. Tang, Tetrahedron, **25**, 1097, (1969) ; M. T. Bowers, R. A. Beaudet, H. Goldwhite and R. Tang, J. Amer. Chem. Soc., **91**, 17 (1969).
7. J. P. Albrand, D. Gagnaire and J. B. Robert, Chem. Comm., 1469 (1968) ; J. P. Albrand, D. Gagnaire, J. Martin and J. B. Robert, Bull. Soc. Chim. France, 40 (1969).
8. L. D. Quin and T. P. Barket, J. Amer. Chem. Soc., **92**, 4303 (1970).
9. A. Bond, M. Green and S. C. Pearson, J. Chem. Soc. (B), 929 (1968).
10. R. K. Harris, Can. J. Chem., **42**, 2275 (1964).
11. S. L. Manatt, G. L. Juvinall, R. I. Wagner and D. D. Elleman, J. Amer. Chem. Soc., **88**, 2689 (1966) ; W. A. Anderson, R. Freeman and C. A. Reilly, J. Chem. Phys., **39**, 1518, (1962) ; J. P. Albrand, D. Gagnaire and J. B. Robert, J. Mol. Spect., **27**, 428 (1968) ; C. Schumann, H. Dreeskamp and O. Stelzer, Chem. Comm., 619 (1970).