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INSERTION OF ELECTROPHILIC PHOSPHORUS INTO CYCLOPROPANES; A NEW SYNTHESIS OF PHOSPHETANES

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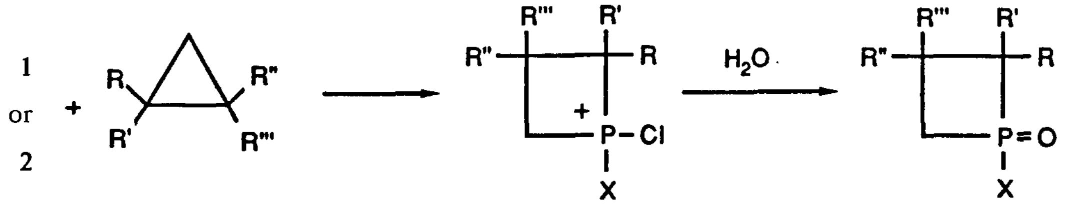
Abstract: Electrophilic phosphorus reagents such as $[(Cl)(i\text{-}Pr_2N)P]^+ [AlCl_4]^-$ and $PhPCl_2/AlCl_3$ are found to insert into monocyclic cyclopropanes to yield phosphetanes. The utility of this new method is demonstrated by synthesizing the first phosphetanes bearing phenyl substituents at carbon.

Phosphetanes have played an important role in the study of the stereochemical aspects of the substitution chemistry of phosphorus.[1] To date, there is only one general synthesis of phosphetanes which involves the addition of $RPCl_2/AlCl_3$ complexes to highly-branched alkenes. This approach, however, is largely limited to the synthesis of multimethyl derivatives.[1b,2,3] In the past, we and others have noted the usefulness of the cycloaddition of phosphenium ions (R_2P^+)[4] to unsaturated organic compounds for the synthesis of phosphorus-containing heterocycles.[5] Our recent observation of the insertion of R_2P^+ into the three-membered ring of quadricyclane[6] has prompted us to investigate the reaction of chloro-(diisopropylamino)phosphenium tetrachloroaluminate ($[(Cl)(i\text{-}Pr_2N)P]^+ [AlCl_4]^-$, **1**) with less strained cyclopropanes in the hope of finding a new general route to phosphetanes. We now report that said insertions occur readily and demonstrate the utility of our approach by synthesizing the first phosphetanes bearing phenyl substituents at carbon. We also report the insertion of $PhPCl_2/AlCl_3$ (**2**) into alkyl cyclopropanes.

Dropwise addition of one equivalent of **3** (in an equal volume of CH_2Cl_2) to a solution of either **1** or **2** (~0.5 M in CH_2Cl_2) gives the corresponding phosphetanium ions (**4**). The time required for complete reaction varies from 2 hr. for reactions **c** and **f** to about 13 hr. for reaction **a**. The yields of **4**, as determined by ^{31}P NMR spectroscopy of the crude reaction mixtures, are in general good. In fact, reactions **b**, **c**, **d**, and **f** are essentially clean and quantitative. The yields of **4a** and **4c** are about 80% and 50%, respectively. Reaction **c** gives two signals in the ^{31}P NMR spectrum of the reaction mixture, which we assign as the *cis* and *trans* isomers. In all cases, the compounds can be isolated after hydrolysis as the phosphinamides and phosphine oxides (**5**). Some relevant NMR data for **5a-d** are given in Table 1.[7] Since **5e** and **5f** have been previously reported in the literature,[2e] they are not included. Again, reaction **c** gives two isomers. Column chromatography on silica gel yields pure **5c'** which allows the determination of the spectral data for **5c** by subtraction of those for **5c'** from those of the mixture. On the basis of the upfield ^1H NMR shifts of the $i\text{-}Pr_2N$ groups of **5c** as compared to **5c'** (δ3.08 and δ1.05 versus δ3.50 and δ1.28) and the downfield shift of H_2 for 5c relative to 5c′ (δ4.39 versus δ3.99) we tentatively assign the *cis* structure to 5c and the *trans* structure to 5c′.

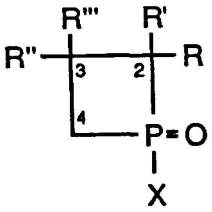


3 **4** **5**

	R	R′	R″	R‴	X
a	Me	Me	H	H	*i*-Pr_2N
b	Me	Me	Me	Me	*i*-Pr_2N
c	Ph	H	H	H	*i*-Pr_2N
d	Ph	Ph	H	H	*i*-Pr_2N
e	Me	Me	H	H	Ph
f	Me	Me	Me	Me	Ph

The insertions of **1** and 2 into 3 are unusual in that most electrophiles react with cyclopropanes to give ring-opened products. For example, HX and X_2 yield substituted propanes on reaction with cyclopropanes.[8] The only other reports of insertions into monocylic nonconjugated cyclopropanes are the additions of TCNE to dialkoxy-[9] and diphenylcyclopropanes.[10] Kashman and Rudi have reported that $RPCl_2/AlCl_3$ complexes are inert to simple *gem*-dihalocyclopropanes.[11] On the basis of the similar reactivities of phosphenium ions and $RPCl_2/AlCl_3$ toward unsaturated organic molecules[5,6,12] and the present work, it is tempting to invoke phosphenium ions as intermediates in the $RPCl_2/AlCl_3$ additions. However, Quin has show that the chemistry of $RPCl_2/AlCl_3$ probably does not involve phosphenium ions.[13]

Table 1. ^{13}C and ^{31}P NMR spectroscopic data for 5a-d.[a]



Nucleus	5a	5b	5c	5c'	5d
$^{31}P\{^1H\}$	49.8	46.4	48.6	46.7	48.4
$^{13}C\{^1H\}$					
C_2	51.4(78)	52.7(79)	58.7(67)	56.3(63)	71.9(68)
C_3	27.9(18)	34.8(14)	14.3(21)	19.3(22)	26.6(22)
C_4	31.3(59)	46.4(69)	34.5(61)	34.0(67)	33.7(63)
X	22.9(3)	22.8(4)	22.6(<2)	23.2(<2)	22.6(<2)
	23.9(2)	24.1(3)	22.7(<2)	23.4(2)	23.5(<2)
	46.4(2)	46.7(<2)	46.2(2)	46.1(4)	47.0(2)
R-R'''	23.8(4)	19.3(5)	126.4(4)	126.6(3)	[c]
	24.7(4)	21.9(4)	126.7(7)	128.0(7)	
		25.4(24)	136.8(12)	128.6(3)	
		26.8(5)	[b]	137.2(11)	

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[a] Spectra were ^1H noise-decoupled and obtained on a Bruker AM-300 spectrometer in $CDCl_3$ solution. The numbers in parentheses are J_{PC} values in hertz.

[b] Obscured.

[c] Many resonances between 126.2-145.6 ppm.

References and Notes:

1. Reviews: (a) R. R. Holmes, *Pentacoordinated Phosphorus*, Volume II, American Chemical Society, Washington, D.C., 1980, Chapter 2; (b) L. D. Quin, *The Heterocyclic Chemistry of Phosphorus*, Wiley-Interscience, New York, 1981, pp 156-176.

2. (a) E. Jungerman, J. J. McBride, Jr., R. Clutter, A. Mais, *J. Org. Chem.*, 27, 606 (1962); (b) J. J. McBride, Jr., E. Jungerman, J. V. Kilheffer, R. J. Clutter, *ibid.*, 27, 1833 (1962); (c) S. E. Cremer, R. J. Chorvat, *ibid.*, 32, 4066 (1967); (d) G. A. Gray, S. E. Cremer, *ibid.*, 37, 3458 (1972); (e) G. A. Gray, S. E. Cremer, K. L. Marsi, *J. Am. Chem. Soc.*, 98, 2109 (1976).

3. This method has also been used to synthesize some 4-bromo derivatives; see: Mazhar-ul-Haque, W. Horne, S. E. Cremer, P. W. Kremer, P. K. Kafarski, *J. Chem. Soc., Perkin II*, 1138 (1981).

4. (a) S. Fleming, M. K. Lupton, K. Jekot, *Inorg. Chem.*, 11, 2534 (1972); (b) B. E. Maryanoff, R. O. Hutchins, *J. Org. Chem.*, 37, 3475 (1972); (c) R. W. Kopp, A. C. Bond, R. W. Parry, *Inorg. Chem.*, 15, 3042 (1976); (d) C. W. Schultz, R. W. Parry, *ibid.*, 15, 3046 (1976); (e) M. G. Thomas, C. W. Schultz, R. W. Parry, *ibid.*, 16, 994 (1977); (f) Review: A. H. Cowley, R. A. Kemp, *Chem. Rev.*, 85, 367 (1985).

5. (a) C. K. SooHoo, S. G. Baxter, *J. Am. Chem. Soc.*, 105, 7443 (1983); (b) A. H. Cowley, R. A. Kemp, J. G. Lasch, N. C. Norman, C. A. Stewart, *ibid.*, 105, 7444 (1983); (c) A. H. Cowley, C. A. Stewart, B.R. Whittlesey, T. C. Wright, *Tetrahedron Lett.*, 25, 815 (1984); (d) A. H. Cowley, R. A. Kemp, J. G. Lasch, N. C. Norman, C. A. Stewart B. R. Whittlesey, T. C. Wright, *Inorg. Chem.*, 25, 740 (1986); (e) S. A. Weissman, S. G. Baxter, *Phosphorus Sulfur*, in press.

6. S. A. Weissman, S. G. Baxter, *Tetrahedron Lett.*, 28, 603 (1987).

7. Compounds **5a-d** were further characterized by ^{1}H NMR spectroscopy and either elemental analysis or high-resolution mass spectroscopy. Compounds **5b** and **5c'** are solids melting at 44-47^{0}C and 85-87^{0}C, respectively, while **5a** and **5d** were obtained as liquids.

8. Review: C. H. Depuy, *Top. Curr. Chem.*, 40, 73 (1973).

9. (a) A. A. P. Noordstrand, H. Steinberg, Th. J. de Boer, *Tetrahedron Lett.*, 2611 (1975); (b) P. G. Wiering, H. Steinberg, *J. Org. Chem.*, 46, 1663 (1981).

10. Th. Martini, J. A. Kampmeier, *Angew. Chem. Int. Ed. Eng.*, 9, 236 (1970).

11. Y. Kashman, A. Rudi, *Tetrahedron Lett.*, 1077, (1979).

12. For a leading reference, see: A. Rudi, Y. Kashman, *Tetrahedron*, 37, 4269 (1981).

13. C. Symmes, Jr., L. D. Quin, *J. Org. Chem.*, 43, 1250 (1978).

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