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PHOSPHORUS HETEROCYCLE SYNTHESIS BY $RPX_2 \cdot AlX_3$ ADDITION TO [1,n]DIENES V. A NEW SYNTHESIS OF SUBSTITUTED PHOSPHORINENES

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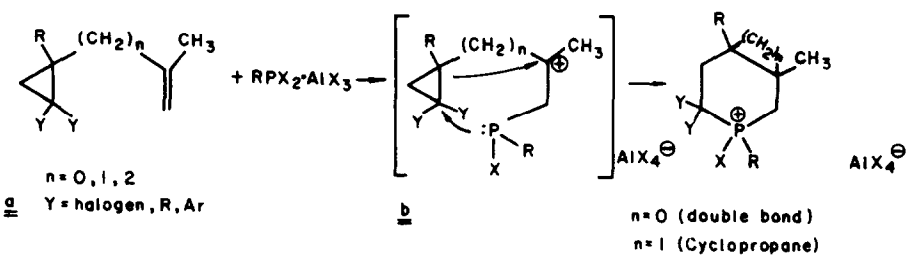
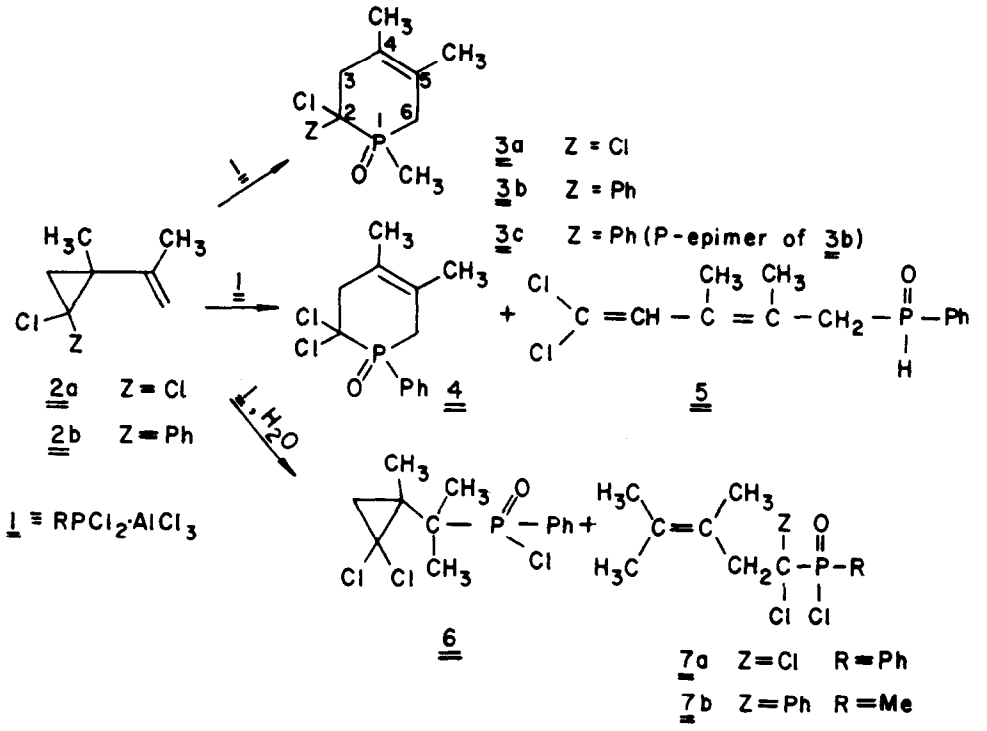
The $RPX_2 \cdot AlX_3$ complex (1) was found to be an efficient reagent for the synthesis of phospha-heterocycles starting from [1,n]dienes[1]. The reaction of these complexes with α-cyclopropyl-ω-olefines and in particular with vinyl cyclopropanes, is the subject of this report.

Monoenes are known to react rapidly with 1[2]. However, the products are well-defined only in special cases like branched monoenes[3] yielding phosphetanes, and 1,1-disubstituted ethylenes[1d] in a 2:1 addition, yielding phospholanes.

Gem-dihalocyclopropanes, easily prepared by the addition of dihalocarbene to double bonds[4a,b], and known to be opened by various electrophiles, were found by us[5] to be unreactive towards 1, (under the conditions usually employed in the reactions of this reagent with olefines; 0-30° for 1-2 hours in CH_2Cl_2 solution)[1]. Applying these results to the case of the cyclopropyl olefines (a), one would expect the double bond to be the first to be attacked by complex 1, giving an intermediate carbonium ion (b). This ion could then potentially interact intramolecularly to give a phospha heterocycle, as follows:



Addition of 1,1-dichloro-2-methyl-2-isopropenyl cyclopropane (2a) to a preformed solution of $MePCl_2 \cdot AlCl_3$ in CH_2Cl_2 at 0°, followed by quenching in aq.$NaHCO_3$ solution, gave in ca. 15% yield a crystalline compound 3a; $C_8H_{13}Cl_2OP$[6], m.p. 84° (acetone-hexane), m/e(%): 228/226 (M^+,6/10), 193/191 (M^+-Cl,30/100)[7]; $\nu_{max}^{CHCl_3}$ 3050,1650,1430,1210,1180,1160,1090 cm^{-1}; ^{1}H-NMR[8]: 1.77s (3H), 1,80s (3H), 2.75brs (2H,J_{PH}=14Hz) and 3.3m (2H,J_{PH}=15); ^{13}C-NMR[8]; 124.6d (C-4,J_{PC}=9), 120.6d (C-5,J_{PC}=6), 79.1d (C-2,J_{PC}=65H_z), 49.8t (C-3), 31.4dt (C-6,J_{PC}=66Hz), 21.4dq (C-9,J_{PC}=12), 20.2q (C-8) and 9.7dq (C-7,J_{PC}=74Hz). All these above data are in good agreement with a 2,2-dichloro-4,5-dimethyl-phosphorin-4-ene system (3a, Scheme 1). The ^{1}H-NMR spectrum indicates the presence of two vinyl methyl groups which, in the absence of vinylic-protons, must be part of a tetra substituted double bond. The same is concluded from the ^{13}C-NMR spectrum, which shows two doublets



Scheme - 1

due to P-C couplings at 120.6 and 124.6. The ^{13}C-NMR spectrum confirms also the phospha heterocycle, since two of the carbon atoms are adjacent to the P-atom; one appears as a double triplet at 31.4 (J_{PC}=66Hz) and the other which bears the two chlorines at 79.1d (J_{PC}=65H$_z$). The obtaining of 3a alone may result from the preferential opening of the cyclopropane ring to give the more stable R-$\overset{+}{C}Cl_2$ ion.

The reaction of 2a with $PhPCl_2 \cdot AlCl_3$ gave compound 4[9] (Scheme 1), the P-phenyl analog of 3a, and a second unstable oily substance 5; $C_{13}H_{15}Cl_2OP$, m/e(%) 290/288 (M^+,40/60), 255/253 (M^+-Cl, 30/100) and 204(60); $\nu_{max}^{CHCl_3}$ 3020,1630,1460,1200,980,860 cm^{-1}; ^{1}H-NMR: 1.70brs (6H), 2.85d(2H, J_{PH}=19), 6.20brs (1H,J_{PH}=3Hz), 6.5brs (1H,J_{PH}=460Hz, P-H) and 7.5-8.0m (Ph); ^{13}C-NMR: 132.7d (C-4), 126.2d (J_{PC}=10), 121.3d(J_{PC}=5)[10], 38.7dt (C-1,J_{PC}=63), 20.1q and 17.4q (C_2 and C_3-Me's). In the absence of two carbon atoms with large J_{PC} values (ca. 65Hz), the phosphorus moiety has to be linked to the rest of the molecule by a single P-C bond. The elemental composition together with the other spectral data suggest for this oil structure 5 a secondary phosphine oxide (resulting from P-Cl hydrolysis) The obtaining of 5 in ca. threefold ratio compared to 4 and the complete absence of a possible counterpart in the reaction with CH_3PCl_2 may be explained

by enhanced steric crowdedness in intermediate b, which leads to a process of elimination rather than to internal closure to the heterocycle[11].

Performing the above reaction without taking special precautions to avoid the presence of water (or when 1eq. of water is added intentionally) led to the production of two new compounds (6 and 7a)[12], without either of the former products (4 or 5). The spectral data of compounds 6 and 7a[13] suggest that they are the addition products of a hydrogen and a P(O)PhCl group to the double bond (with and without corporation of the cyclopropyl ring). This addition, previously described[1d,14], does not seem to be a simple protonation followed by quenching of the carbanium ion with RPX_2 [15].

Starting from the vinyl halophenyl cyclopropane (2b), complex 1 gave two isomeric P-epimer phosphorinenes, 3b and 3c - the C_2-phenyl analogs of 3a[17]. As before, in the presence of water the main compound isolated from the reaction mixture was 7b[18], the phenyl analog of 7a. Although the yields of the above-described phosphorinene synthesis are quite modest at present, the reaction seems to us to have value. It is an easy one-step synthesis starting with readily available compounds, and the special substitution pattern of the phosphorinane may enable further interesting transformations of the obtained compounds.

Efforts to perform the $RPX_2 \cdot AlX_3$ addition reaction with allyl or homoallyl cyclopropanes a,n=1 or 2 have failed thus far to give any phosphaheterocycle. If water (0.1-1 eq) is added, however, the higher homologes of 6 can be obtained in minute quantities.

References and Notes

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b. Y. Kashman and A. Rudi, Tetrahedron Letters, 2819 (1976).

c. M. Rotem and Y. Kashman, ibid, 63 (1978).

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4a. R. Maurin, M. Bertrand, Bull.Soc.Chim.Fr. 998 (1970) and Synthesis 81 (1978).

b. T. Shono and R. Oda, Chem.Abs. 55, 4381 (1961).

c. R.M. Moss, J.Org.Chem. 27, 2683 (1962); b.p. 80/0.5 mm Hg.

5. The cyclopropane derivatives examined were: 1,1-dichloro-2,2-dimethylcyclopropane and 1,1-dichloro-2-methyl-2-phenylcyclopropane.

6. Satisfactory microanalysis was obtained for 3a.

7. Performing the mass spectra at 15eV rather than 70eV gave a $2M^+$ ion. The MWt of the compound was established by its vapour pressure; E.P. Clark, J.Anal.Chem. 820, (1941).

8. Chemical shifts ($CDCl_3$) are given in ppm relative to TMS. ^{1}H-NMR spectra were recorded either on a Jeol-JNM C-60HL spectrophotometer (P-decoupled) or on a Bruker WH-90 instrument ^{13}C-NMR spectra were recorded on the Bruker WH-90 instrument under conditions of PND . Signals were assigned using known δ-values, J_{PC} values and off-resonance experiments.

9. $C_{13}H_{15}Cl_2OP$, m.p. 135° (acetone-hexane); $\nu_{max}^{CHCl_3}$ 3020,1450,1400,1300,1210,1180,1130,860, 830,700 cm^{-1}; m/e(%) 290/288 (M^+,8/25) and 255/253 (M^+-Cl, 30/100); ^{1}H-NMR: 1.75s (3H),

1.85s (3H), 2.8-3.5m (4H) and 7.6-8.4 (5H); ^{13}C-NMR: 125.5d (J_{PC}=7), 121.5d (J_{PC}=6), 82.6d (J_{PC}=66), 50.9t, 31.2dt (J_{PC}=68), 21.7dq (J_{PC}=12) and 20.3q.

10. An additional sp^2 carbon atom appeared together with the phenyl carbon atoms and could not be identified.

11. A similar example observed by us (unpublished) was the failure of phenyl(3-phenylpropyl)-halophosphane to undergo internal cyclisation by AlX_3, whereas the methyl analog did undergo ring closure.

12. Compounds 6 and 7a were obtained in ca. 5% and 10%, respectively.

13. Compound 6 is an oil; $C_{13}H_{16}Cl_3OP$; m/e(%) 326/324 (M^+,100/100), 291/289 (M^+-Cl,25/30) and 229/227 (30/100): $\nu_{max}^{CHCl_3}$ 3000,1600,1390,1370,1090,1080,1000,950,850 cm^{-1}. ^{1}H-NMR: 1.4 an AB system (2H), 1.45s(6H,J_{PH}=21), 1.85s(3H) and 7.8m (5H). Compound 7a is an oil; $C_{13}H_{16}Cl_3OP$, m/e(%) 326/324(M^+,1/1), 291/289 (M^+-Cl, 25/40) and 256/254 (M^+-2Cl, 40/100); ν_{max}^{neat} 3000,2960,2930,1590,1440,1380,1240,1110 cm^{-1}; ^{1}H-NMR: 1.6d (3H,J_{PH}=2), 1.7s (3H), 1.9s (3H), 3.4s (2H,J_{PH}=5), 7.7m (3H) and 8.4m (2H); ^{13}C-NMR: 123.3s, 120.0d (J_{PC}=10), 87.6d (J_{PC}=96), 43.9dt (J_{PC}=6) 21.3q, 20.7q and 20.4q.

14. P. Crews, J.Org.Chem., 40, 1170 (1975).

15. We came to the conclusion that the mechanism of this addition is not simply a protonation by HX, obtained from hydrolysis of AlX_3 followed by quenching with RPX_2, as the addition of $RPX_2 \cdot HX$ to the olefin failed to give the same products; rather, it appears to involve either a phosphiranium ion or the participation of a special complex produced under the reaction conditions[16]. A full description of the experiments carried out to elucidate this problem will be described elsewhere.

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b. H.C. Brown and H. Peasall, J.Am.Chem.Soc., 73, 4681 (1951).

17. Compound 3b is crystalline $C_{14}H_{18}ClOP$ m.p. 115° (acetone-hexane), $\nu_{max}^{CHCl_3}$ 3000,1500,1460, 1310,1190,1160,970,910 and 900 cm^{-1}; m/e(%): 270/268 (M^+,20/50), 233(M^+-Cl,50) and 231 (100); ^{1}H-NMR: 1.50s (3H,J_{PH}=12),1.85s(6H),2.5m(2H),3.2 AB quar.(2H), 7.5m (3H) and 7.9m (2H); ^{13}C-NMR: 125.4d (J_{PC}=8), 119.9d (J_{PC}=5), 66.1d (J_{PC}=64), 46.5t, 32.4dt (J_{PC}=69), 21.5dq (J_{PC}=12), 20.0q and 10.0dq (J_{PC}=72).
Compound 3c is also crystalline; m.p. 160°, mass spectrum identical with 3b, $\nu_{max}^{CHCl_3}$: 3100, 1510,1470,1410,1200,1180,1150,980,920,900 and 850 cm^{-1}; ^{1}H-NMR: 1.5s (3H,J_{PH}=15), 1.8s (6H), 2.5brs (1H,J_{PH}=12), 2.9brs (1H,J_{PH}=18), 3.2brs (2H,J_{PH}=18) 7.4-7.6m (3H) and 7.8-8.2m (2H).

18. Compound 7b, $C_{14}H_{19}Cl_2OP$ is an oil; ν_{max}^{neat} 3000,2950,1490,1450,1300,1220 and 1180 cm^{-1}; m/e(%) 306/304 (M^+,8/13), 269/267 (M^+-Cl,3/10), 223(63), 221(100), 205(25) and 170(40); ^{1}H-NMR: 1.22s (3H) 1.61s (3H), 1.7s (3H), 2.2s (3H,J_{PH}=15), 3.46brs (2H,J_{PH}=9), 7.7m (3H) and 8.1m (2H); ^{13}C-NMR: 131.5s, 121.3d (J_{PC}=12), 76.3d (J_{PC}=76), 40.9dt (J_{PC}=6), 21.2q, 20.8q, 19.6q and 17.7dq (J_{PC}=75).

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