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PHOSPHORUS HETEROCYCLES SYNTHESIS USING $RPX_2 \cdot AlX_3$ ADDITION TO [1,n]-DIENES. II

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The reaction of $RPX_2 \cdot AlX_3$ complexes (1) with olefines is well known and has been developed as one of the more used methods for the preparation of phosphetanes.[1] The reaction of these complexes with dienes was first illustrated by us in the reaction with 1-allyl cyclohex-1-ene.[2] It turns out that the reaction is not only limited to [1,4]dienes, but that other [1,n]dienes also react with 1.[3] The new compounds illustrated below exhibit the potential synthetic applications, in the phosphaheterocycle field, embodied in this reaction. Addition of 2,4-dimethyl-1,4-pentadiene(2)to a preformed complex of $PhPCl_2 \cdot AlCl_3$ in CH_2Cl_2 at 0°, gave, following quenching in aq.$NaHCO_3$ solution, two main compounds 3 and 4 which could be separated by chromatography:compound 3, m.p.113°,$C_{13}H_{17}PO$[4] and compound 4, m.p.78°,$C_{13}H_{17}PO$[5]. The NMR spectra[4,5] of both compounds indicated the existence of a cyclopropane moiety, which is included in the suggested 3-phosphabicyclo[3.1.0]-hexane structure.[2]

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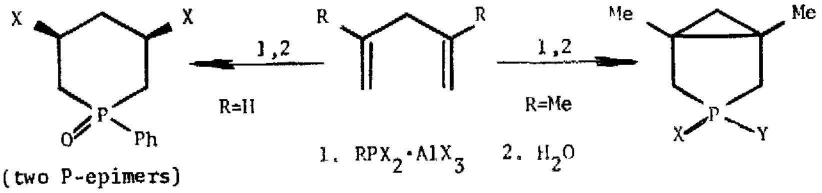


3	X=Ph	Y=O
4	X=O	Y=Ph
5	X=Me	Y=O
6	X=O	Y=Me

The other peaks in the NMR spectra are also in accord with the bicyclic structures. Compounds 3 and 4 are believed to differentiate by their P-configuration only. Further support for the structures was obtained from the CMR spectra (Table 1). $MePCl_2 \cdot AlCl_3$ gave with 2 two compounds similar to 3 and 4: compound 5 and compound 6 respectively.

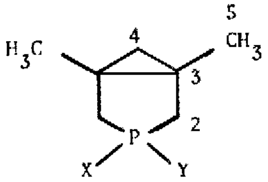
Attempts to determine the P-configuration in both isomer pairs using a shift-reagent[6], were ambiguous because of the small differences in the line slopes of the C_4-cyclopropane protons (the ones directed towards the P=O site in both P-epimers) measured from the δ to $Eu(dpm)_3$/substrate plot.[7] The conformation of the phospholane moiety in 3-6 (vide infra) must still be established to obtain more reliable conclusions.[8]

The reaction between 1 and the unsubstituted 1,4-pentadiene leads mainly to 3,5-dihalophosphorinanes (7)[9], accompanied by only minute quantities of the bicyclo[3.1.0]hexane system.

In the latter reaction the $AlX_4^{\ominus}$ -quenching of the secondary carbonium ion seems to prevail over the intramolecular double bond attack, which would, in its turn, lead to a bicyclic compound as in the case of 3. The intermediate obtained after the initial attack of one of the 1,4-pentadiene's double bonds, may then undergo ring closure by a consecutive internal attack of the newly formed $R_1R_2\overset{\oplus}{P}AlX_4^{\ominus}$ complex (R_1-being the pentene unit) on the second double bond.

Table - 1

^{13}C chemical shifts and ^{13}C-^{31}P nuclear spin coupling constants for 3-6.[a]

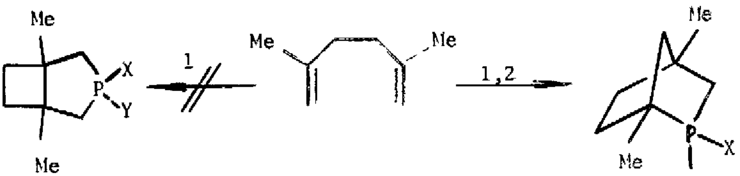


Compound	X	Y	C-2	C-3	C-4	C-5	P-CH_3
3	Ph	O	39.9 (66)	26.0 (3)	25.0 (0)	19.3 (13)	
4	O	Ph	38.6 (66)	24.8 (7)	26.3 (0)	19.6 (12)	
5	Me	O	38.5 (64)	24.9 (3)	26.4 (0)	19.5 (14)	16.9 (63)
6	O	Me	38.9 (66)	24.8 (6)	27.0 (3)	19.7 (11)	16.9 (62)

[a] Chemical shifts ($CDCl_3$) in parts per million, relative to carbons of TMS, were determined on a Bruker WH-90 instrument under conditions of proton noise decoupling. ^{13}C signals were assigned using known chemical-shift rules and $J_{^{31}P-^{13}C}$-values, off-resonance experiments, and intensity comparisons of the proton decoupled spectra with the gated decoupled one. Numbers in parentheses stand for the coupling constants in Hz.

Compounds 3-6 as well as 8-11 (vide infra) are good models for studying changes in ^{31}P-^{13}C coupling constants with geometry. The measured $^3J_{P-C}$ values, for C_4 and C_5 (Table 1), are in accordance with the suggested Karplus relationship of these coupling constants[10], and lie within the ^3J-range measured in the phosphetane series.[11] Only slight changes with P-epimerization could be observed in 3-6 for the $^3J_{P-C}$ constants. However, the variations in $^2J_{^{31}P-^{13}C}$ values, measured for C_3 with P-substitution and configuration are more significant (Table 1) and may enable conformational analysis of the phospholane moiety in these molecules; further compounds for a more comprehensive study are under preparation.

The first [1,5] diene to be investigated was 2,5-dimethyl-hexa-1,5-diene. A priori this diene may react with 1 in two different ways to give bicyclic compounds: either a bicyclo [3.2.0] heptane (m) or a bicyclo[2.2.1] heptane system (n).



m

1. $RPX_2 \cdot AlCl_3$ 2. H_2O

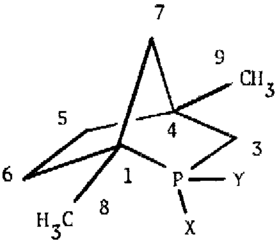
n

8 X=Ph Y=O
9 X=O Y=Ph
10 X=Me Y=O
11 X=O Y=Me

In the event, under similar conditions to the ones described for the preparation of **3** and **4**, two compounds were obtained: compound **8**, m.p.147°,$C_{14}H_{19}PO$,[12] and compound **9**, m.p.93°,$C_{14}H_{19}PO$.[13] The NMR spectra of the two,[12,13] exhibiting two different Me group signals, together with the CMR spectra, showing separate signals for each one of the skeleton carbon atoms (Table 2), establish structure **n**, thus excluding the symmetrical bicyclic[3.2.0]heptane (**m**). Obtaining structure **n** rather than **m** may result from a less strained bicyclic product and/or a better geometrically oreinted transition state leading to this compound. The spectroscopic data, and mainly the CMR, lead us to believe that **8** and **9** are again P-epimers. A second pair of such epimers **10** and **11** were obtained when starting with $MePCl_2AlCl_3$: compound **10** and compound **11** b.p. 80°/0.1 mm respectively.

Table - 2

^{13}C Chemical shifts and ^{13}C-^{31}P nuclear spin coupling constants for **8**-**11**.[a]



Compound	X	Y	C-1	C-3	C-4	C-5[b]	C-6[b]	C-7	C-8	C-9
8	Ph	O	43.4 (68)	40.0 (59)	43.8 (0)	37.5 (0)	31.5 (4.5)	50.1 (12)	14.9 (0)	24.1 (12)
9	O	Ph	45.2 (68)	41.5 (59)	43.2 (0)	36.9 (0)	31.1 (0)	50.4 (8)	13.9 (0)	23.5 (12)
10	Me	O	44.4 (68)	41.1 (60)	43.6 (0)	37.4 (0)	30.4 (6)	50.6 (6)	14.0 (0)	24.3 (11)
11	O	Me	44.4 (68)	44.7 (56)	43.5 (0)	36.8 (0)	32.3 (0)	49.4 (7)	14.2 (0)	23.8 (13)

a. See footnote of table 1. b. Tentative assignment.

The 2-phosphabicyclo[2.2.1]heptanes (**8**-**11**) are additional good model compounds for chemical shifts and ^{31}P-^{13}C coupling constants correlations. The different J-values found for the particular carbon atoms in the pairs of this rigid series, support the assumption that the P=O stereochemistry may affect the J_{P-C} values (although an explanation for this is difficult).[10] As in the former series the geminal coupling constants seem to be more influenced by the structure than the vicinal ones. The CMR of both series is being further studied.

Other [1,n] dienes are being presently investigated in order to elucidate the scope of the described reaction.

References and Footnotes

1.a. E. Jungerman, J.J. McBride, R. Clutter and A. Mais, J. Org. Chem. 27, 606 (1962).

b. J.J. McBride, E. Jungermann, J.V. Killheffer and R.J. Clutter, ibid, 27, 1833(1962).

c. S.E. Cremer and R.J. Chorvat, ibid, 32, 4066(1967).

2. Y. Kashman, Y. Menachem and E. Benary, Tetrahedron, 29, 4279(1973).

3. 1,3-Dienes like 2,3-dimethylbuta-1,3-diene were also found to react with complex 1 to give the corresponding phosphol-3-enes. However whether this reaction may have any advantage over the excellent cycloaddition of conjugated dienes with trivalent phosphorus halides have still to be established.

4. Compound 3: m/e(%) 220(100,M^+), 205(80,M-Me), 125(40,PhPOH); ν_{max}^{KBr} 3080,2970,1590, 1460,1440,1410,1310,1210,1175,1150,840,750,700 cm^{-1}; NMR(δ,P-decoupled): 0.52d (J=6 Hz,1H), 1.2d(J=6 Hz,1H), 1.3s(2CH_3), 2.3(4H), and 7.4-8.0(5H,Ph). NMR spectra were taken on a Jeol JNM-C-60HL spectrometer and mass spectra on a Du-Pont 21-491B instrument.

5. Compound 4: mass spectrum identical with that of 3. ν_{max}^{KBr} 2900,1440,1410,1230,1200, 1170,1140,1110 cm^{-1}; NMR(δ,P-decoupled): 0.35, AB quartet(2H), 1.3s(2 CH_3), 2.4 AB quartet(4H), 7.2-7.8(5H,Ph).

6. Y. Kashman and O. Awerbouch, Tetrahedron, 27, 5593(1971).

7. H.M. McConnell and R.E. Robertson, J. Chem. Phys. 29, 1361(1958).

8. Observations of Dreiding models show that the r and θ values[7] for the cyclopropane protons in both isomers are such that only small ΔΔδ values are expected; hence the conformations of the phospholane moiety are of utmost importance.

9. Starting with $PhPBr_2 \cdot AlBr_3$ compound 7(X=Br) was obtained: m.p.187°, $C_{11}H_{13}Br_2OP$, NMR δ(P-decoupled): 2.0-2.3m(6H), 4.5dt(J=12, and 3.5 Hz) and 7.2-7.9m(Ph).

10. R.B. Wetzel and G.L. Kenyon, J. Am. Chem. Soc., 96, 5189(1974).

11. G.A. Gray and S.E. Cremer, J. Org. Chem., 37, 3458, 3470(1972).

12. Compound 8: m/e(%)234(47,M^+),219(10,M-Me),206(20,M-28),140(100,PhP(OH)CH_3),125(50, PhPOH,m*140 → 125); ν_{max}^{KBr} 1440,1210,1180,1110,830,750 cm^{-1}; NMR(δ,P-decoupled): 1.0s(Me), 1.3s(Me), 1.4-2.2m(7H) 2.6bs(1H) and 7.2-8.0m(5H,Ph).

13. Compound 9: mass spectrum identical with that of 8; ν_{max}^{neat} 1450, 1440, 1210, 1170, 1110, 1050, 750 cm^{-1}; NMR(δ,P-decoupled): 1.3s(2 CH_3), 1.3-1.7m(4H), 1.9-2.5m(3H), 2.85bs (1H) and 7.3-8.0m(5H,Ph).