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

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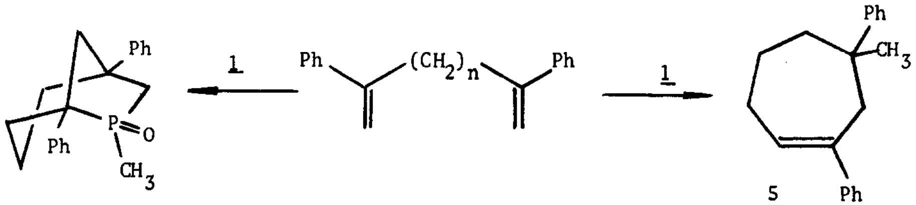
In previous reports in this series we described the reaction of $RPX_2 \cdot AlX_3$ complex (1) with [1,4] and [1,5] dienes to give phospha mono and bicyclic compounds[1]. For the purpose of finding out the scope of this reaction, additional other dienes were submitted to similar reaction conditions (mixing equal amounts of the diene with 1 (R=Ph or CH_3) in CH_2Cl_2 at 0° followed by quenching of the reaction mixture in aq. $NaHCO_3$). As a result it was found that while 2,6-diphenyl-1,6-heptadiene (2) still reacts in a similar manner to that of the [1,5] diene, producing an analogous phospha bicyclic compound (3) (two P-epimers), 2,7-diphenyl-1,7-octadiene (4) does undergo an internal cyclisation without incorporation of the phosphorus moiety to give 2,4-diphenyl-4-methylcyclohept-1-ene (5)[2,3].



3 (two P-epimers)

2 n=3
4 n=4

5

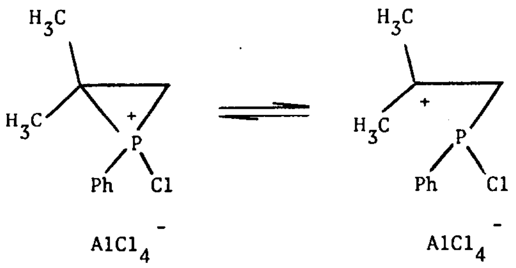
1 = $MePCl_2 \cdot AlCl_3$

Whether other [α,ω]-dienes, in which the two double bonds are separated by still a longer chain compared to compound 4 and thus being of lower tendency to undergo intracyclisation, will again produce phosphabicyclic compounds have not yet been examined. However, we thought it would be of special interest to check the possibility of a reaction between 1 and two separate double bonds (which are not anymore linked one to the other by a $-(CH_2)_n-$ chain, in the same molecule, as in the previous cases). Indeed, the reaction of 1 with monoenes has already been examined[4], however, only in the case of branched monoenes yielding phosphetanes (via alkyl migration)[1c,4c] could the end product be unequivocally defined[5]. In other cases, reported by McBride et al.[4b,6] a 1:1 adduct (between the olefin and 1) is believed to be obtained but no explicit structure has been suggested. Furthermore, it was found by P. Crews[7] and by us[1a,c] that specific olefins do undergo a unique reaction with 1, essentially containing small amounts of water[8], to give an addition product containing, on one of the originally double bond carbon atoms, the phosphorus moiety and an hydrogen in place of the quenched carbonium ion.

For testing the above idea two olefins (6 and 7), which were expected to be able to generate following the attack of 1 a tert. carbonium ion[6], have been chosen.

Addition of isobutylene (6) to a preformed solution of the $PhPCl_2 \cdot AlCl_3$ complex in CH_2Cl_2 at 0°, followed by quenching in aq. $NaHCO_3$ solution gave mainly one crystalline compound (8a), in ca 45% yield: m.p. 115° (acetone-petrol ether), γ_{max}^{KBr} 2880, 1440, 1180, 720, 700 cm^{-1}; ^{1}H-NMR (δ, $CDCl_3$, P-decoupled): 0.90s(3H, J_{PH}=16 Hz), 1.38s(3H), 1.40s(3H, J_{PH}=12 Hz) 1.40s(3H), 1.45 and 2.25 AB quartet (2H, J=16 Hz and J_{PH}=12 Hz), 1.98 and 2.40 AB quartet (2H, J=16 Hz and J_{PH}=9 Hz), and 7.4 - 7.7 m (5H); ^{13}C-NMR (22.63 MHz δ, $CDCl_3$) 23.9q, 27.1q, 32.2q, 33.3dq (J_{PC}=9 Hz), 35.4d (J_{PC}=8 Hz), 38.9d (J_{PC}=67 Hz), 40.1dt (J_{PC}=64 Hz) and 55.5dt (J_{PC}=15 Hz); m/e (%): 236 (M^+, 80), 221 (M^+-CH_3, 25), 194 (15), 180 (15), 168 (30) and 125 ($Ph\overset{+}{P}OH$, 100). The above data are in good agreement with the proposed 1-oxo-1-phenyl-2,2,4,4-tetramethylphospholane (8a)[9]. The ^{1}H-NMR clearly indicates on two pairs of methyl groups, among which one pair is vicinal to the phosphorus with $^3J_{PH}$ values of 12 and 16 Hz and the other pair is further away - uncoupled with the P-atom. Complementary evidence is obtained from the ^{13}C-NMR pointing on one C atom and one CH_2 group near the phosphorus ($^1J_{PC}$= 67 and 64 Hz respectively) and on two additional C and CH_2 ring carbons with smaller $^2J_{PC}$ values (8 and 15 Hz respectively) as expected.

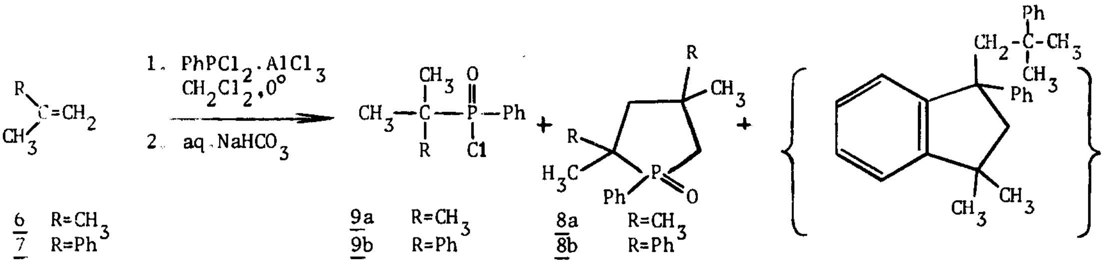
If however the reaction is carried out with 1 doped with H_2O, the yield of 8a falls to ca 3% only and the main product to be isolated in ca. 50% yield under these conditions, is a 1:1 adduct. According to the spectral data of 9a[10] it turned out to be t-butylphenylphosphinic chloride[11]. Obtaining this compound is an additional example to the above described insertion of an hydrogen and a PhP(O)Cl group by the doped $PhPCl_2 \cdot AlCl_3$ complex[12] which may involve an oxidation-reduction step[1c]. Moreover the fact that the t-butyl rather than the isobutyl compound is produced, supports in our opinion, a phosphiranium ion (a) as an intermediate, as otherwise the hydride should have been expected to quench the tert. carbonium ion (b)



a b

2-Methylstyrene (7) was next tested, under similar conditions as described for 8a and 9a, to give compounds 8b and 9b in ca. 5 and 15% respectively. Compound 8b the phenyl analog of 8a is again crystalline: m.p. 175° (acetone-petrol ether), γ_{max}^{neat} 2900, 1600, 1450, 1160, 1110, 900 cm^{-1}, ^{1}H-NMR (δ, CDCl$_3$ P-decoupled): 1.11s(3H, J_{PH}=15 Hz), 1.7s(3H), 2.4-3.6m(4H); ^{13}C-NMR (22.63 MHz, CDCl$_3$, δ): 27.2q, 36.9dq (J_{PC}=5 Hz), 41.4dt (J_{PC}= 66 Hz) 42.6s, 48.2d (J_{PC}=62 Hz) and 50.4dt (J_{PC}=10 Hz); m/e (%) 360 (M$^+$, 8), 278(4), 242(20), 241(20), 170(4) and 119(100). The structure assignment of 8b was deduced under the same rationale as for 8a. Compound 9b is an oil: γ_{max}^{neat} 3000, 1600, 1500, 1440, 1220, 1110 and 1030 cm^{-1}; ^{1}H-NMR (δ, CDCl$_3$, P-decoupled): 1.68s (3H, J_{PH}=18 Hz), 1.7s (3H, J_{PH}=18 Hz), 7.6-8.0 m (10H); ^{13}C-NMR (22.63 MHz, CDCl$_3$, δ): 23.3q, 23.8q and 47.0d (J_{PC}=72); m/e(%) 280/278 (M$^+$, 3 and 7), 221(2) 120(8), 119 (Ph$\overset{+}{C}$(Me)$_2$, 100).

Taking in the reaction excess of the 2-methyl styrene (7), up to two equivalents, improved the relative yield of 8b towards 9b; however, an additional compound (10) was obtained[13]. Compound 10 turned out to be a trimer of 7[14] in which the termination of the reaction has been occurred by internal attack of the carbonium ion on a phenyl group.



6 R=CH$_3$
7 R=Ph

9a R=CH$_3$
9b R=Ph

8a R=CH$_3$
8b R=Ph

10 (from 7 only)

The hitherto preliminary results suggest that the above reaction will enable the synthesis of substituted phospholanes starting from 1,1-disubstituted olefins. The scope of the reaction is presently further investigated.

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)
2. Compound 3a: an oil; m/e(%) 310(M$^+$, 1), 256(3), 228(3), 149(7), 129(6), 120(12), 119(20), 85(20), 84(85) and 83(100); $\gamma_{max}^{CHCl_3}$ 2900, 1600, 1480, 1450, 1300, 1150, 950 cm^{-1}; NMR (δ, CDCl$_3$) 7.4 m (10H), 3.25m (4H), 2.5m (4H), 1.9m (4H), 1.9d (3H, J_{PC}=12 Hz); ^{13}C-NMR (δ, CDCl$_3$) 48.0d (J_{PC}=63 Hz) 45.1d (J_{PC}=10 Hz), 42.0dt (J_{PC}=60 Hz), 44.2t, 39.9t, 34.3t, 19.8t and 11.5dq(J_{PC}=57 Hz). Compound 3b the P-epimer of 3a was also an oil: same IR and Mass spectra; NMR: 1.0d (3H, J_{PH}=12 Hz); ^{13}C-NMR: 44.2d (J_{PC}=4 Hz),

47.6d (J_{PC}=63 Hz), 39.5dt (J_{PC}=61Hz). Compound 5, m/e(%) 262(M^+, 80), 247(M^+-Me, 20), 219(20), 180(20), 171(M^+-PhCH$_2$, 100); NMR (δ, CDCl$_3$): 1.3s(3H), 1.4-2.6m (6H), 5.9m (1H) and 7.1m (10H); ^{13}C-NMR 22.5t, 26.3q, 29.1t, 39.0s, 44.3t, 45.9t, 151.2s, 145.6s and 141.6s.

3. AlCl$_3$ by itself seems to be a too strong Lewis acid for the cyclisation of 4 to 5.

4a. E. Jungermann, 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).

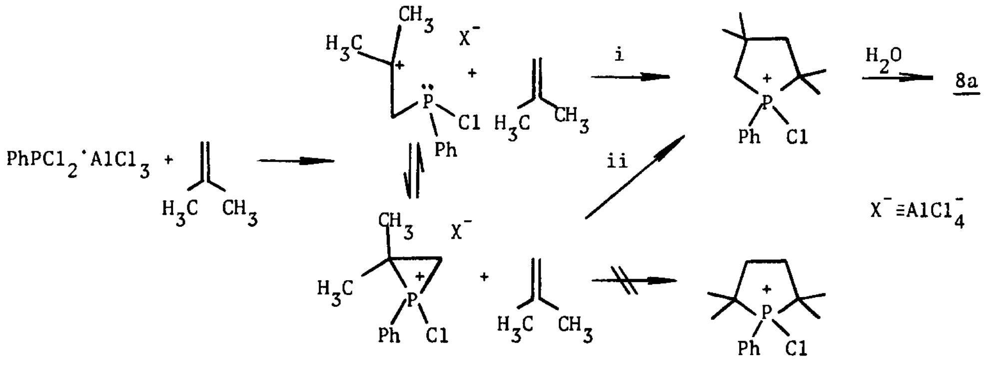
5. J.J. Weber, C.A. 62, 9174a (1965). After performing the reaction we have found in the literature a Patent which claims that bis (2-methyl-propenyl) phosphinic chloride is prepared by treating isobutylene with PCl$_3$ in the presence of AlCl$_3$ in an inert solvent e.g. CH$_2$Cl$_2$.

6. Being interested in the reaction of 1 with olefins we repeated part of McBride's work[4]. It seems to us that in many cases where no tert. carbonium ion can be formed, the reaction undertakes a rather complicated pathway leading to more than one product.

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

8. More than 0.2-0.3 equivalents of water reduces the general yield of the products; AlBr$_3$, unless used in a glove box will always contain some water.

9. As for the reaction mechanism two pathways may be suggested:



the differentiation between the two, if at all possible, needs additional study. Anyhow even if route i will turn out to be the correct one, it does not essentially exclude the existence of the phosphiranium ion.

10. Compound 9a: an oil, m/e(%) 216(M^+, 20), 160 (Ph$\overset{+}{\text{P}}$OCl, 100) and 162(30); NMR (δ, CDCl$_3$): 1.2d (J_{PH}=18 Hz, 9H), 7.6m (3H) and 7.8-8.0m (2H).

11. Using D$_2$O instead of H$_2$O for doping 1 gave d$_1$-9a as could be seen from the mass spectrum of the compound, see also ref. 7.

12. The nature of the doped complexes has still to be further investigated.

13. If the 7 to 1 ratio was 2 to 1 all three products (8b, 9b and 10) were obtained in almost equal amounts, ca. 10% each.

14. C.P. Brown and A.R. Mathieson, J. Chem. Soc. 3445, (1958).