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PHOSPHORUS HETEROCYCLE SYNTHESIS BY $RPX_2 \cdot AlX_3$ ADDITION TO [1,n] DIENES. III.

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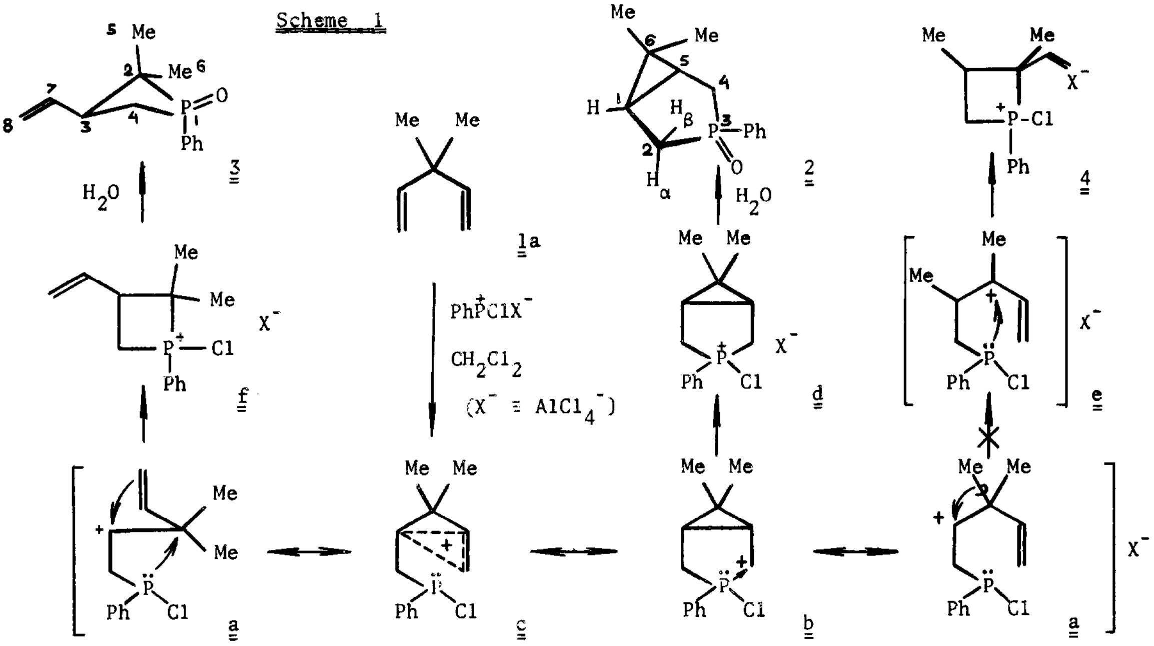
Our studies of the addition of $RPX_2 \cdot AlX_3$ complexes to [1,n]-dienes[1] brought us to consider a comparable reaction with 3,3-disubstituted-1,4-pentadienes (1). The particularity of compound 1 arises from its special structure: on one hand, 1 incorporates in itself a branched, α-substituted double bond which, on reacting with the dihalophosphane complex, is supposed to enable the closure to a phosphetane.[2] However, on the other hand, 1 also contains a 1,4-diene which under similar conditions has been shown previously to yield either a phosphorinane or a phosphabicyclo[3.1.0]hexane system.[1b] It was thus of special interest to find out what would be the actual products of 1 following the discussed reaction.

Addition of 3,3-dimethyl-1,4-pentadiene (1a)[3] to a preformed complex of $PhPCl_2 \cdot AlCl_3$ [4] in CH_2Cl_2 at r.t., followed by quenching in aq. $NaHCO_3$ solution, gave two main products (2 and 3) which could be separated by chromatography: compound 2, b.p.$_{0.05}$ 100°, $C_{13}H_{17}OP$, ν_{max}^{neat} 2960, 1440, 1400, 1175, 1115, 750, 690 cm^{-1} (η≈25%); and compound 3, b.p.$_{0.05}$ 105°, $C_{13}H_{17}OP$, ν_{max}^{neat} 2960, 2930, 2860, 1460, 1440, 1200, 1165, 1115, 1000, 915 cm^{-1} (η≈20%). On the basis of their spectral data, the structures suggested for compounds 2 and 3 are 6,6-dimethyl-3-oxo-3-phenyl-3-phosphabicyclo[3.1.0]hexane and 2,2-dimethyl-1-oxo-1-phenyl-3-vinylphosphetane, respectively.
Compound 2: mass spectrum m/e (%): 220 (100, M^+), 205 (49, $[M-CH_3]^+$), 125 (22, $Ph\overset{+}{P}OH$), 95 (12, $[M-PhPOH]^+$) and 77 (22, Ph^+); ^1H-NMR (δ, $CDCl_3$, 90 MHz): 0.94s (CH_3), 1.12s (CH_3) and 1.15-3.0 m (6H); ^{13}C-NMR (δ, $CDCl_3$, 22.63 MHz, PND)[5]: 14.7s (Me), 22.1d (J_{P-C}=2.9 Hz, C-1(5)), 26.3s (C-6), 27.6s (Me) and 27.7d (J_{P-C}=69 Hz, C-2(4)).
Compound 3: mass spectrum m/e (%): 220 (17, M^+), 165 (40, $[M-C_4H_7]^+$), 125 (17, $Ph\overset{+}{P}OH$), 77 (20, Ph^+) and 69 (100, $CH_2=CHC(CH_3)_2{}^+$); ^1H-NMR (δ, $CDCl_3$, 270 MHz)[6]: 0.94d ($^3J_{P-H}$=20 Hz, CH_3), 1.37d ($^3J_{P-H}$=16 Hz, CH_3), 2.40m (H-3), 2.73 ddd ($^2J_{P-H}$= 17.9, $J_{H(4)-H(4')}$=15 and $J_{H(4)-H(3)}$=11.5 Hz, H-4), 2.97 ddd$_7$ ($^2J_{P-H}$=9.7, $J_{H(4)-H(4')}$=15 and $J_{H(4')-H(3)}$=8.3, H-4'), 5.72 dddd ($^4J_{P-H}$=1.1, $J_{H(3)-H(7)}$=7.2[7], $J_{H(7)-H(8')}$=10.5 and $J_{H(7)-H(8)}$=18, H-7), 5.12 d ($J_{H(7)-H(8)}$=18, H-8), 5.20 d ($J_{H(7)-H(8')}$=10.5, H-8'), and 7.4-8.1 m (Ph); ^{13}C-NMR (δ, $CDCl_3$, 22.63 MHz, PND)[5]: 52.0 d (J_{P-C}=63 Hz, C-2), 39.5 d (J_{P-C}=10 Hz, C-3), 34.2 d (J_{P-C}=54 Hz, C-4), 17.3 s (C-5), 23.4 s (C-6), 135.2 d (J_{P-C}=29 Hz, C-7) and 117.2 s (C-8).
A possible mechanism which accounts for the formation of products 2 and 3 is summarized in Scheme 1.

The unique feature of the adduct (a) initially obtained from the attack of the dihalophosphane complex on one of the double bonds of 1a is its homoallylcation structure (c).[8] Ion c can undergo a variety of transformations, starting from different isomeric ions, as is illustrated in Scheme 1 (i.e., a→e→4, a→f[8c] or b→d). Compounds 2 and 3, obtained in ca. 20-25% each, are accompanied by a polymeric substance which accounts for an additional 50% of the material.

Scheme 1



There is no indication whatsoever that compound 4 is obtained in this reaction, the rationale for which may be sought in the easier rearrangement of the electron-rich vinyl group compared to the methyl group. However, when one of the two methyls is replaced by a phenyl group (as in 3-methyl-3-phenyl-1,4-pentadiene (1b)) the a→4 route (Scheme 1) takes place primarily (vide infra).

The stereochemistry of compound 2 was elucidated with the help of an LIS experiment (Table 1).

Table 1

Observed Proton	δ(ppm)[a]	J_{H-H}(Hz)	J_{P-H}(Hz)	LIS[b]
H-1	2.4 d	6	^3J=13	1.3
H-2β	3.4 d	16.5	^2J= 7.5	3.5
H-2α	6.1 dd	6; 16.5	^2J=16.5	8.0

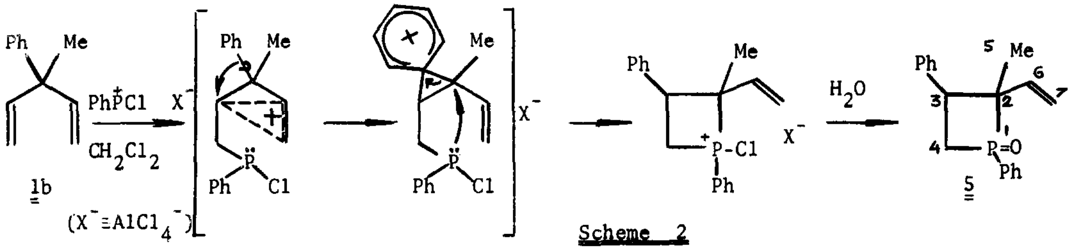
a. Observed chemical shift for Eu(fod)$_3$/Sub.=0.48, P-atom decoupled.[6] b. Δδ for Eu(fod)$_3$/Sub.=1.

Measurement of $\phi_{H_1H_{2\beta}}$ and $\phi_{H_1H_{2\alpha}}$ (the proper dihedral angles between the vicinal protons) from a Drieding model of 2 gave values of ≈90° and ≈30°, respectively, for which coupling constants of 0 and 5-7 Hz, respectively, should be observable. Indeed, such values could be measured after addition of the shift reagent (Table 1). Since $\Delta\delta(H_{2\alpha}) > \Delta\delta(H_{2\beta})$, the P=O bond must be oriented to the same side as $H_{2\alpha}$; i.e., *trans* to the cyclopropane ring.[9]

A *trans* relationship between the vinyl and the phenyl groups of compound 3 is suggested according to the $^3J_{P-C7}$ value (29 Hz); the corresponding values measured from the spectra of the two isomers of 1-phenyl-2,2,3-trimethyl-phosphetane-1-oxide are 16 and 28 Hz for the *cis* and *trans* isomers, resepctively.[10]

Employing the same procedure as described above, we were able to isolate a phosphetane (5) by mixing equal molar amounts of $PhPCl_2 \cdot AlCl_3$ with 3-methyl-3-phenyl-1,4-pentadiene (**1b**). Compound **5** was obtained in ca. 5% yield by repeated chromatographies of a three-component mixture, which was obtained in ca. 40% yield from the reaction.[11]

Compound **5**, $C_{18}H_{19}OP$ is obtained, with a purity of at least 95%, as a very hygroscopic crystalline material; mass spectrum m/e (%): 282(0.1,M^+), 170(48),143(30,[CH_2=CH-C(CH_3)=CPh^+]), 125 (23, $Ph\overset{+}{P}OH$) and 77 (100, Ph^+); ^{1}H-NMR (δ, $CDCl_3$, 270 MHz): 1.24 d (J_{P-H}=16.7 Hz, CH_3), 3.13-3.25 m (3H), 4.95 dd (=CH_2), 5.62 ddd ($J_{H(6)-H(7)}$=17.3, $J_{H(6)-H(7')}$=10.9, $J_{P-H(6)}$=7 Hz, H-6)[7] and 7.1-8.0 m (2 Ph). The double irradiation experiment of **5** confirmed unequivocally the proposed structure and excluded the 2-methyl-2-phenyl-3-vinylphosphetane - the analog of compound **3**. A possible mechanism leading to compound **5**, which involves a phenonium ion, is illustrated in Scheme 2. To the best of our knowledge, this is the first example of a phenyl migration leading to a phosphetane ring.



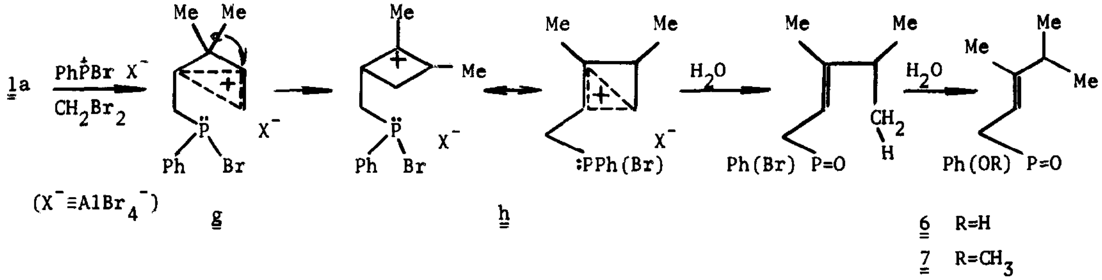
Scheme 2

Applying the dihalophosphane complex on 3-methyl-1,4-pentadiene gave only unidentified material.

Mixing of compound **1** with the $PhPBr_2 \cdot AlBr_3$ complex in CH_2Cl_2 resulted in compounds **2** and **3** as with the chloro complex.[12] However, if the reaction was performed in CH_2Br_2 instead of CH_2Cl_2, a new compound (**6**) was the almost exclusive product (ca. 60% yield).[13] No trace whatsoever of compounds **2**, **3** or **4** could be detected. Compound **6** was purified, after esterification with CH_2N_2, as its Me-ester **7**: $bp_{0.2}$ 90°, $C_{14}H_{21}O_2P$, ν_{max}^{neat} 2960, 1690, 1480, 1465, 1440, 1230, 1120, 1030, 790, 750, 700 cm^{-1}; mass spectrum, m/e (%): 252 (47, M^+), 237 (9, $[M-CH_3]^+$), 169 (45, $[PhP(O)OMeCH_2]^+$), 156 (100, $Ph\overset{+}{P}(OH)OMe$), 155 (57, $Ph\overset{+}{P}OMe$), 125 (7, $Ph\overset{+}{P}OH$), 97 (12, $[M-PhP(O)OMe]^+$), 77 (71, Ph^+); ^{1}H-NMR (δ, $CDCl_3$, 90 MHz): 0.90 d (J=6.8 Hz, two Me's of iPr), 1.28 d (J_{P-H}=3.8, Me-C=), 2.2 hep. (J=6.8 Hz, H of iPr), 2.71 dd (J_{P-H}=19, J_{H-H}=7.9, $\underline{CH_2}$-P), 3.67 d (J_{P-H}=11, OCH_3), 5.2 dt (J_{P-H}=7.6, J=7.9 Hz, =CH) and 7.65m (Ph); ^{13}C-NMR (δ, $CDCl_3$, 22.63 MHz, PND)[5]: 21.3 s (Me's of iPr), 30.4 d (J_{P-C}=98 Hz, CH_2P), 37.1 s (<u>Me</u>-C=), 51.3 d (J_{P-C}=6, CH_3O-P), 110.4 d (J_{P-C}=8.8, HC=).[14]

The structure of compound **6**, concluded from the spectral data of **7**, as well as the proposed mechanism leading to this compound are illustrated in Scheme 3:

Scheme 3



Quenching of the cyclobutyl carbonium ion (h) may involve an oxidation-reduction step in which, on one hand, the trivalent phosphorus is oxidized to the corresponding oxide (P^{IV}), while on the other hand, the cyclobutyl cation (which is better illustrated by its homoallylic resonance hybrid) is reduced to the proper olefin.[15,16,17]

The relatively crowded phosphorus atom in intermediate g (Scheme 3) in comparison to c (Scheme 1) may reduce the possibility of intermediate g's closure to compounds such as d and f (Scheme 1) and thus encourage the rearrangement of g to h. Cyclization of the latter ion to a phosphetane is unlikely as it would result in a very tense bicyclo[2.2.0]hexane system. Additional observations concerning the quenching of similar intermediates are now under further investigation.

References and Footnotes

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

2a. J.J. McBride, E. Jungermann, J.V. Killheffer and R.J. Clutter, J.Org.Chem., 27, 1833 (1962).
 b. S.E. Cremer and R.J. Chorvat, ibid, 32, 4066 (1967).
 c. J. Emsley, T.B. Middleton and J.K. Williams, J.Chem.Soc. Dalton, 979 (1976).

3. R. Ciola and R.L. Burwell, J.Org.Chem., 23, 1063 (1958).

4. J.P. Clay, ibid, 16, 892 (1951).

5. δ-values are in parts per million from internal TMS; multiplicity was assigned by off-resonance experiments.

6. The 270 MHz ^{1}H-NMR were recorded on a Bruker WH-270 instrument; $^nJ_{P-H}$ values were measured on a Jeol-HNM-C-60HL spectrometer equipped with a heterodecoupler.

7. Coupling constant confirmed by a double irradiation experiment.

8a. K.B. Wiberg, B.A. Hess, Jr. and A.J. Aske, in "Carbonium Ions", Vol. III, p. 1295 (Eds. G.A. Olah and P.R. Schleyer, Interscience Wiley, 1972).
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 c. For a 1,2-shift of the vinyl group see: A.F. Thomas, Chem.Commun., 1054 (1970).

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

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

11. The rest of the material was again a polymeric substance. Whether the three compounds are different stereoisomers of 5, which contains three chiral centers, or if it contains also a phosphetane with a substitution pattern similar to that of compound 3, is yet unknown.

12. A $PX_3+RX+AlY_3 \rightleftharpoons [RPX_3]^+[AlY_3X]^-$ equilibrium is known in the literature; J. Emsley, T.B. Middleton and J.K. Williams, J.Chem.Soc. Dalton, 2071 (1973). The complex with the stronger P-X bond (P-Cl) will be the one which enters the reaction.

13. Again, the remaining material was a polymeric substance.

14. The second olefinic carbon atom appears together with the phenyl group. The remaining C-atom could not be determined unequivocally. The J_{P-C} value (98 Hz) of the CH_2P carbon atom is in good agreement with a two oxygen bearing P-atom; L. Ernst, Org.Mag.Res. 9, 35 (1977).

15. The olefin stereochemistry is tentative, based mainly on the relatively high field chemical shift of the vinyl methyl group (δ 1.28). The latter may be explained by a Ph-diamagnetic influence in one of the possible trans conformers.

16. The tentative quenching mechanism suggested by Crews for his phosphiranium ion starts with a hydride transfer leaving the phosphorus atom in the P^{III} stage. P. Crews, J.Org.Chem., 40, 1170 (1975).

17. A phosphiranium ion followed by an oxidation-reduction quenching may explain also one of our earlier observations in this series, namely, the synthesis of 1-PPh(O)Cl-1-allylcyclohexane as the main product of the reaction between 1-allylcyclohex-1-ene and $PhPCl_2 \cdot AlCl_3$.[1a]