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On the Extension of the Atherton-Todd Reaction to the 1-Organyloxy 1-hydridobicyclophosphoranes

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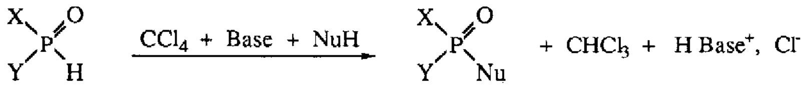
Abstract : The 1-methoxy 1-hydridobicyclophosphorane **1** undergoes oxidation reactions with CCl_4 in basic solutions which allow the replacement of the hydrogen linked to phosphorus by several nucleophile groups . The same reaction carried out with the bicyclophosphorane **8** leads to a new compound **10** in which two P^V atoms are included in a ten membered ring.

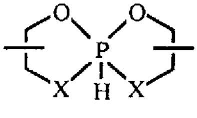
The so-called Atherton-Todd reaction[1] (A) known since 1945 and widely used with tetra - coordinated phosphorus compounds[2], has been recently extended to hydrido spirophosphoranes[3] (II).

(A)



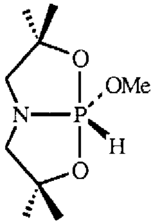
$$\mathrm{XY P(O)H} \xrightarrow{CCl_4 + \text{Base} + \text{NuH}} \mathrm{XY P(O)Nu} + CHCl_3 + \text{H Base}^+,\ Cl^-$$

As a part of our investigations on the reactivity of 1-hydrido bicyclophosphoranes[4,5] (III) we wish to report the results we have obtained in using this reaction with compounds **1** and **8**.

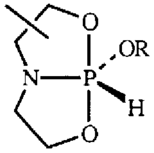


X = O, N - H

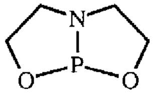
II



1



III



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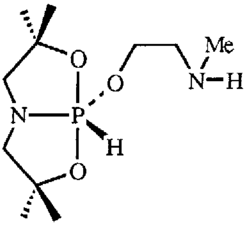

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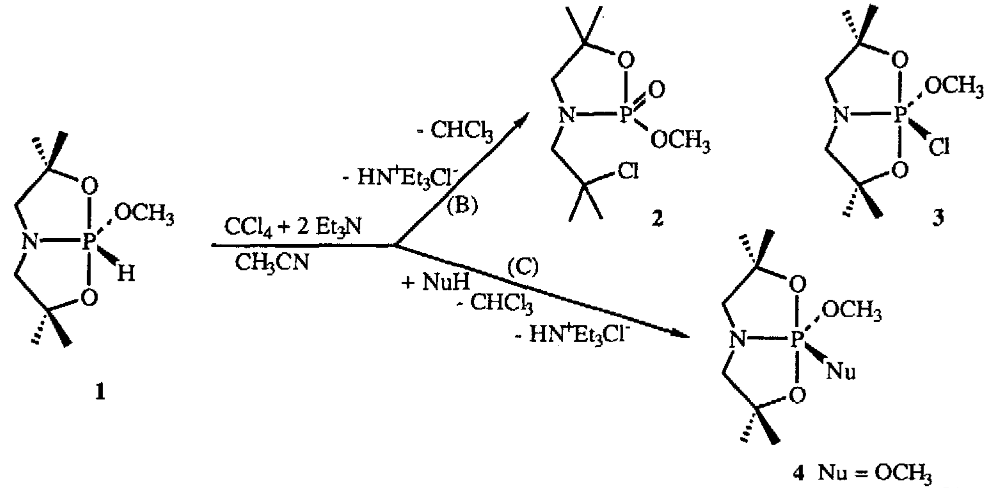
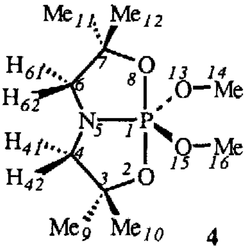
In the case of **1** the Atherton-Todd reaction has been carried out, in acetonitrile as solvent, at room temperature, without (reaction B) and with a nucleophile (reaction C). The molar ratio of the reactants was always approximately **1** : CCl_4 : Et_3N: NuH = 1 : 1 : 2 : 1



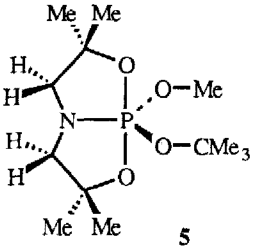
4 Nu = OCH_3
5 Nu = $OC(CH_3)_3$
6 Nu = $N(C_2H_5)_2$

Reaction B gives two compounds with the chemical shifts 25.4 ppm (30%) and -42.9 ppm (40%) as main products. The obvious assignements are respectively **2**[6] and **3**. Heating the sample to 80°C does not lead to an increase of **2**. Therefore, it is excluded that **2** is formed from **3**.

Reaction C leads to the exclusive replacement of the hydrogen linked to phosphorus by the nucleophile OMe, Ot.Bu, NEt_2. The bicyclophosphoranes **4**, **5** and **6** were distilled under reduced pressure : **4** bp $_{0.05}$ = 35°C (95%), **5** bp $_{0.05}$ = 44°C (95%), **6** bp $_{0.05}$ = 43°C (85%).



4



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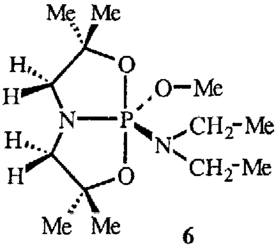

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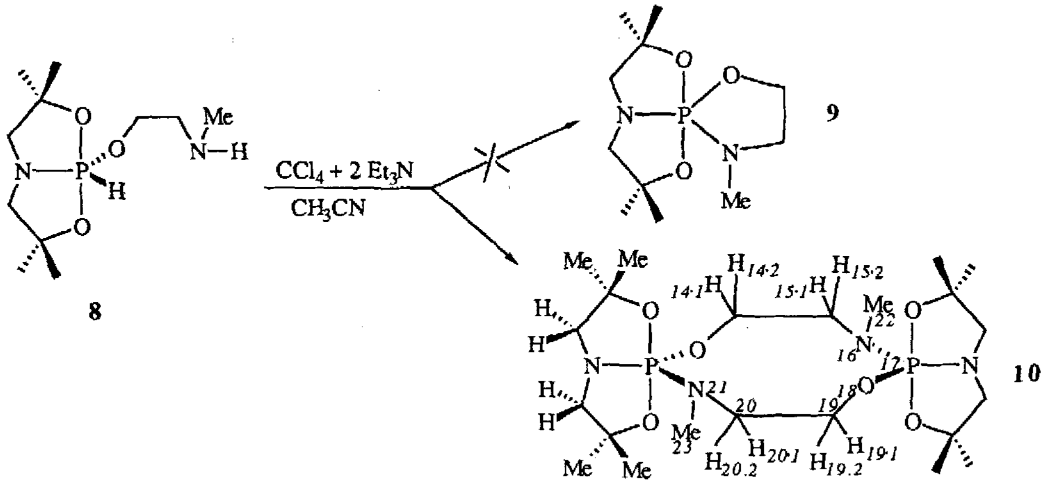
They have been fully characterized by NMR (^{31}P, ^1H, ^{13}C) and elemental analysis[7].

It must be mentioned that a compound similar to **4** has been prepared for the first time by Denney *et al.*[8] by the addition reaction of two moles of benzenesulfenate $C_6H_5SOCH_3$ on the bicyclophosphane **7**. However this reaction does not allow the preparation of mixed dialkoxyphosphoranes like **5** or **6** which can be easily obtained by our procedure.

We have also carried out the reaction B with the bicyclophosphorane **8**[9]. An intramolecular reaction could lead to the bicyclophosphorane **9**, while an intermolecular reaction could give the bis (bicyclophosphorane) **10** bearing a ten membered ring.

After 40h stirring at room temperature followed by 2h heating at 40°C, the starting material is consumed and the ^{31}P NMR spectrum exhibits only one peak at -23,1 ppm. The mass spectrum (chemical ionisation by NH_3) establishes that the compound obtained is the ten-membered ring **10** (m/z$^+$: 525 $(M+1)^+$ 0,65%, 263 $(M/2 + 1)^+$ 100%).



The ^{1}H and ^{13}C NMR[7] spectra provide further information about this compound. ^{1}H NMR : 1.17 (s, 12H, $Me_{9,10,11,12}$), 2.55 and 2.63 (2 quadruplets ABX (X=P), 4H, $H_{41,61}$ and $H_{42,62}$ $^2J_{HH}$ = -10.2 , $^3J_{H(41)P} = {}^3J_{H(61)P}$ = 11.1, $^3J_{H(42)P} = {}^3J_{H(62)P}$ = 15.1), 2.68 (dt, 2H, $H_{15.1,15.2}$ $^3J_{HH}$ = 6.3 , $^3J_{HP}$ = 9.3), 2.74 (d, 3H, Me_{22} $^3J_{HP}$ = 9.4), 3.76 (dt, 2H, $H_{14.1,14.2}$ $^3J_{HP}$ = 14.1). ^{13}C NMR : 29.1 (d, $C_{9,11}$ or $C_{10,12}$, $^3J_{CP}$ = 1.9), 29.6 (d, $C_{10,12}$ or $C_{9,11}$, $^3J_{CP}$ = 6.3), 34.5 (d, C_{22}, $^2J_{CP}$ = 5), 50.3 (d, C_{15} $^2J_{CP}$ = 18.8), 58.5 (d, C_{14}, $^2J_{CP}$ = 1.9), 59.1 (d, $C_{4,6}$, $J_{CP} = 1/2\ (^2J_{CNP} + {}^3J_{CCOP})$ = 11.9), 72.7 (d, $C_{3,7}$ $J_{CP} = 1/2\ (^2J_{COP} + {}^3J_{CCNP})$ = 3.8).

As one can observe, the OCH_2 ($H_{14.1}$, $H_{14.2}$, $H_{19.1}$, $H_{19.2}$) as well as the NCH_2 ($H_{15.1}$, $H_{15.2}$, $H_{20.1}$, $H_{20.2}$) protons give rise to one first order signal , a doublet of triplets. Furthermore there is only one ABX system (X = P) corresponding to the five-membered ring N-CH_2 protons (H_{41} $H_{42} \equiv H_{61}$ H_{62} ; $H_{41} \neq H_{42}$). These observations are consistent with the following characteristics (i) the center of the ten-membered ring, whose mean conformation is nearly plane, is a symmetry center of the molecule (ii) the equatorial plane of the trigonal bipyramidal bicyclophosphorane group, which contains the ten-membered ring plane, is also a mean symmetry element of the molecule. The analysis of the ^{13}C NMR spectrum confirms these conclusions.

Finally these results confirm the previous observation[3] concerning the extension of the Atherton-Todd reaction to the spirophosphoranes bearing a P-H bond. Moreover the obtention of the ten-membered ring **10** represents a new and interesting coupling reaction.

References and notes

1. Atherton, F.R., Openshaw, H.T. and Todd, A.R., J. Chem. Soc., 660 (1945).
2. Kosolapoff, G.M. and Maier L., "Organic Phosphorus Compounds". Wiley-Interscience, New-York, 1972, Volume 4, p. 294.
3. Riesel, L., Lindemann, D. and Ohms, G., Z. Chem., **27**, 181 (1987).
4. Correct nomenclature : 1-organyloxy 2,8-dioxa 5-aza 1-phospha^{V} bicyclo (3,3,0) octane.
5. Bounja, Z., Houalla, D., Revel, M. and Taieb, M. accepted by Phosphorus, Sulfur and Silicon and the Related Elements , (1992) and references cited therein.
6. Devillers, J. and Navech, J. Bull. Soc. Chim. Fr., 4341 (1970).
7. The ^{31}P (32,44 MHz), ^{1}H (250.13 MHz) and ^{13}C (62.89 MHz) NMR spectra of **4, 5, 6** and **10** have been recorded in C_6D_6 as solvent (δ in ppm, J in Hz).

   4 ^{31}P NMR : -43.2 . ^{1}H NMR : 1.19 (d, 12H, $Me_{9,10,11,12}$ $^{4}J_{HP} = 0.5$), 2.48 (d, 4H, $H_{41,42,61,62}$ $^{3}J_{HP} = 12.8$), 3.53 (d, 6H, $Me_{14,16}$ $^{3}J_{HP} = 13.1$). ^{13}C NMR : 28.9 (d, $C_{9,10,11,12}$ $^{3}J_{CP} = 3.9$), 54.8 (d, $C_{14,16}$ $^{2}J_{CP} = 9,4$), 55,2 (d, $C_{4,6}$ $J_{CP} = 1/2\ (^{2}J_{CNP} + {}^{3}J_{CCOP}) = 20,4$), 69,3 (s, $C_{3,7}$). Elemental analysis $C_{10}H_{22}NO_4P$ Calc. % C 47.79, H 8.82, N 5.57. Found C 47.8, H 9.0, N 5.9.

   5 ^{31}P NMR : -45.3 . ^{1}H NMR : 1.22 (s, 6H, $Me_{9,11}$ or $Me_{10,12}$), 1.23 (s, 6H, $Me_{10,12}$ or $Me_{9,11}$), 1.42 (d, 9H, Me_{17} $^{4}J_{HP} = 1$), 2.47 and 2.56 (2 quadruplets ABX (X = P), 4H, $H_{41,61}$ and $H_{42,62}$ $^{2}J_{HH} = -7.8$ $^{3}J_{H(41)P} = {}^{3}J_{H(61)P} = 16.3$, $^{3}J_{H(42)P} = {}^{3}J_{H(62)P} = 7.9$), 3.59 (d, 3H, Me_{14} $^{3}J_{HP} = 12.8$). ^{13}C NMR : 28.8 (s, $C_{9,11}$ or $C_{10,12}$), 28.9 (d, $C_{10,12}$ or $C_{9,11}$ $^{3}J_{CP} = 3.2$), 30.8 (d, C_{17} $^{3}J_{CP} = 5$), 54.5 (d, C_{14}, $^{2}J_{CP} = 10.2$), 55.2 (d, $C_{4,6}$ $J_{CP} = 1/2\ (^{2}J_{CNP} + {}^{3}J_{CCOP}) = 20.7$), 69.3 (s ,$C_{3,7}$), 77.2 (d, C_{16} $^{2}J_{CP} = 12$). Elemental analysis $C_{13}H_{28}NO_4P$ Calc. % C 53.22, H 9.62, N 4.77. Found C 52.4, H 9.6, N 5.0

   6 ^{31}P NMR : - 42.8. ^{1}H NMR : 1.07 (d, 6H, Me_{17} $^{3}J_{HH} = 6.8$), 1.19 (s, 6H, $Me_{9,11}$ or $Me_{10,12}$), 1.23 (s, 6H, $Me_{10,12}$ or $Me_{9,11}$), 2.5 and 2.59 (2 quadruplets ABX (X=P), 4H, $H_{41,61}$ and $H_{42,62}$ $^{2}J_{HH} = -7.5$ $^{3}J_{H(41)P} = {}^{3}J_{H(61)P} = 21.8$, $^{3}J_{H(42)P} = {}^{3}J_{H(62)P} = 7.7$), 3.08 (dt, 4H, CH_2 $^{3}J_{HP} = 6.8$), 3.42 (d, 3H, Me_{14} $^{3}J_{HP} = 14.2$). ^{13}C NMR : 15.8 (s, C_{17}), 28.6 (d, $C_{9,11}$ or $C_{10,12}$ $^{3}J_{CP} = 6$), 28.7 (d, $C_{10,12}$ or $C_{9,11}$ $^{3}J_{CP} = 0.6$), 44.3 (d, C_{16} $^{2}J_{CP} = 5$), 53.6 (d, C_{14} $^{2}J_{CP} = 9$), 55.8 (d, $C_{4,6}$, $J_{CP} = 1/2\ (^{2}J_{CNP} + {}^{3}J_{CCOP}) = 19.4$), 69.3 (s, $C_{3,7}$). Elemental analysis $C_{13}H_{28}N_2O_3P$ Calc. % C 52.37, H 9.99, N 9.5. Found C 53.0, H 10.0, N 9.7.
8. Denney, D.B., Denney, D.Z., Hammond, P.J., Huang C. and Tseng, K.S., J. Amer. Chem. Soc. **102**, 5073 (1980).
9. **8** has been obtained by the oxidative addition of N-methylethanolamine to the corres-ponding bicyclophosphane as described in ref. 5. It was fully characterized by ^{31}P ($\delta^{31}P = -35,4$ ppm, $^{1}J_{PH} = 796,6$ Hz) ^{1}H and ^{13}C NMR. The ^{1}H and ^{13}C NMR spectra will be reported and discussed elsewhere.

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