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### FIRST EVIDENCE FOR AN YLID $\rightleftharpoons$ PHOSPHORANE EQUILIBRIUM

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# FIRST EVIDENCE FOR AN YLID = PHOSPHORANE EQUILIBRIUM

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The synthesis of a salt-free ylid and of a phosphorane obtained by addition of a trivalent phosphorus compound with dimethylacetylene dicarboxylate in the presence of a trapping reagent, benzoic acid is described. This paper is concerned with the first evidence for an ylid-phosphorane equilibrium.

In a previous note,<sup>1</sup> we have demonstrated the formation of carbanions obtained when trivalent phosphorus compounds react with an acetylenic compound. Trapping of these carbanionic species with protic reagents (e.g. alcohol) leads to an ylid A. An alternative pathway involves reaction on the phosphorus atom leading to a phosphorane

$$X_3P + MeOOC - C \equiv C - COOMe + ROH$$

$$X_3P = C$$
 $CO_2Me$ 
 $CO_2Me$ 

$$X_3P = (Me_2N)_3P, (MeO)_3P,$$

$$O$$

$$P-OMe, etc ...$$

Upon treatment with

and PhOH as trapping reagent we were able to clearly observe the evolution pathway from A to B. This paper is concerned with the first evidence for an equilibrium ylid⇒phosphorane when the trapping reagent is benzoic acid.

The reaction is easily performed between  $-20^{\circ}$ C and  $0^{\circ}$ C in carbon tetrachloride solution. Only two species 1 (18%) and 2 (82%) may be seen in the 31P NMR spectrum of the crude solution.

Relative percentages of these species are strongly solvent dependent. Addition of dichloromethane

1  $\delta^{-31}$ P 69 ppm, J<sub>POCH</sub> 13.2 Hz (doublet of quadruplet) J<sub>P=C-CH</sub> 22,87 Hz.  $\delta^{-1}$ H, CH<sub>3</sub>—C 1.41 ppm HC—C=P 6.15 ppm J 22.87 Hz, Ph 7.39 & 7.93 ppm (CCl<sub>4</sub>).

**2**  $\delta$  <sup>31</sup>P-49 ppm, J<sub>POCH</sub> 14.7 Hz (doublet of quadruplet) J<sub>P-C=C-H</sub> 25.12 Hz (E isomer alone).  $\delta$  <sup>1</sup>H, CH<sub>3</sub>-C 1.29 ppm HC=C-P 6.57 ppm J 25.12 Hz Ph 7.39 & 7.93 ppm (CCl<sub>4</sub>).

3 (E)  $\delta$  <sup>31</sup>P 19.8 ppm J<sub>P-C=CH</sub> 23.5 Hz  $\delta$  <sup>1</sup>H CH<sub>3</sub>—C 1.42 et 1.57 ppm; COOMe 3.79 & 3.87 ppm.  $\delta$  <sup>1</sup>HHC=CP 6.78 ppm J 22.5 Hz (CDCl<sub>3</sub>), vc = o 1740 cm<sup>-1</sup>, vc = c 1630 cm<sup>-1</sup> F = 120°.

3 (Z)  $\delta$  <sup>31</sup>P 19.1 ppm J<sub>P-C=CH</sub> 39.7 Hz  $\delta$  <sup>1</sup>H CH<sub>3</sub>—C 1.29 & 1.49 ppm COOMe 3.82 & 3.87 ppm.  $\delta$  <sup>1</sup>H H—C=C—P 7.2 ppm J 39.7 Hz.

in the previous  $^{31}P$  NMR tube immediately gives rise to a new equilibrium composition: 1 37% and 2 63% (if solvents are evaporated and a new solution made with carbon tetrachloride, then first percentages 1 (18%) and 2 (82%) may be observed again). In carbon tetrachloride solution, these two species 1 and 2 remained unchanged for a few days. With dichloromethane solution, the evolution takes a few hours only: NMR signals appear for 3 (Z + E) whereas the intensity of 1 and 2 signals decrease. When the percentage of 3 is 60% the relative ratio of ylid versus phosphorane remains unchanged 36%–64%. Finally, only the two isomers (Z + E) of the phosphonate 3 may be detected ( $^{31}P$  NMR).

It is also possible to follow the chemical changes in the system using <sup>1</sup>H NMR techniques especially the appearance and the disappearance of doublets for:

$$H-C-C=P$$
,  $H-C=C-P_v$  and  $H-C=C-P_{iv}$ 

Heating the mixture (50% E, 50% Z) of 3 shifts the equilibrium towards isomer E.

The latter readily crystallizes from an ethereal solution.

Recovery of crystals shifts the equilibrium in solution and favors isomer E; the Z isomer cannot be isolated.

Another equilibrium ylid ⇒ phosphorane has been reported a few years ago. Nevertheless it was obtained with addition or loss of a reagent.¹

$$(CH_3)_3P = CH_2 \xrightarrow{+MeOH} (CH_3)_4POCH_3$$

In our own research area, we observe also an addition reaction. Ylids add methanol for instance giving a saturated phosphorane.

OMe
$$CO_{2}Me$$

$$P=C$$

$$CO_{2}Me + MeOH$$

$$OPh$$

$$CCI_{4}$$

$$-10^{\circ}$$

$$O-P$$

$$CH-CH$$

$$CO_{2}Me$$

$$O-P$$

To our knowledge, the present work firmly establishes the first description of the equilibrium ylid  $\rightleftharpoons$  phosphorane following a rearrangement process which may be either intra or intermolecular. Only the E configuration is observed for phosphorane 2 and is consequently the more stable isomer.

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