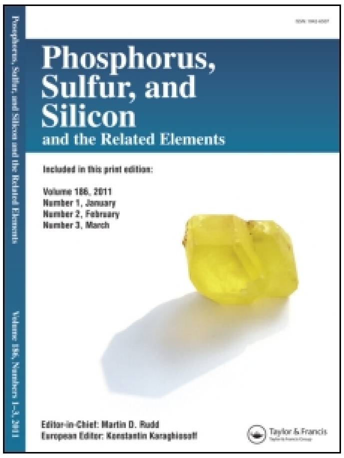


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

FIRST EVIDENCE FOR AN YLID ⇌ PHOSPHORANE EQUILIBRIUM

Ramon Burgada[a]; Yves Leroux[a]; Y. O. El Khoshnieh[a]
[a] Laboratoire des Organo-Elements, E.R.A. 825, Université P. et M. Curie Tour 44-45, Paris Cédex 05, France

To cite this Article Burgada, Ramon , Leroux, Yves and Khoshnieh, Y. O. El(1981) 'FIRST EVIDENCE FOR AN YLID ⇌ PHOSPHORANE EQUILIBRIUM', Phosphorus, Sulfur, and Silicon and the Related Elements, 10: 2, 181 — 182
To link to this Article: DOI: 10.1080/03086648108077502
URL: http://dx.doi.org/10.1080/03086648108077502

Phosphorus and Sulfur, 1981, Vol. 10, pp. 181–182
0308-664X/81/1002-0181$06.50/0

FIRST EVIDENCE FOR AN YLID$\rightleftharpoons$PHOSPHORANE EQUILIBRIUM

RAMON BURGADA, YVES LEROUX, and Y. O. EL KHOSHNIEH

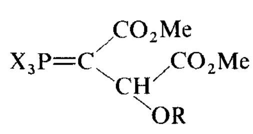
Laboratoire des Organo-Elements, E.R.A. 825, Université P. et M. Curie Tour 44–45,
4 Place Jussieu, 75230 Paris Cédex 05 France.

(*Received September 22, 1980*)

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.

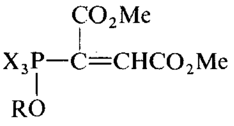
In a previous note,[1] we have demonstrated the formation of carbanions obtained when trivalent phosphorus compounds react with an acetylenic compound. Trapping of these carbanionic species with protic reagents (e.g. alcohol) leads to an ylid **A**. An alternative pathway involves reaction on the phosphorus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

$$X_3P + MeOOC{-}C{\equiv}C{-}COOMe + ROH \longrightarrow$$

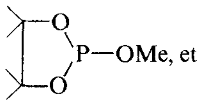


A

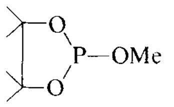
or



B

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

Upon treatment with

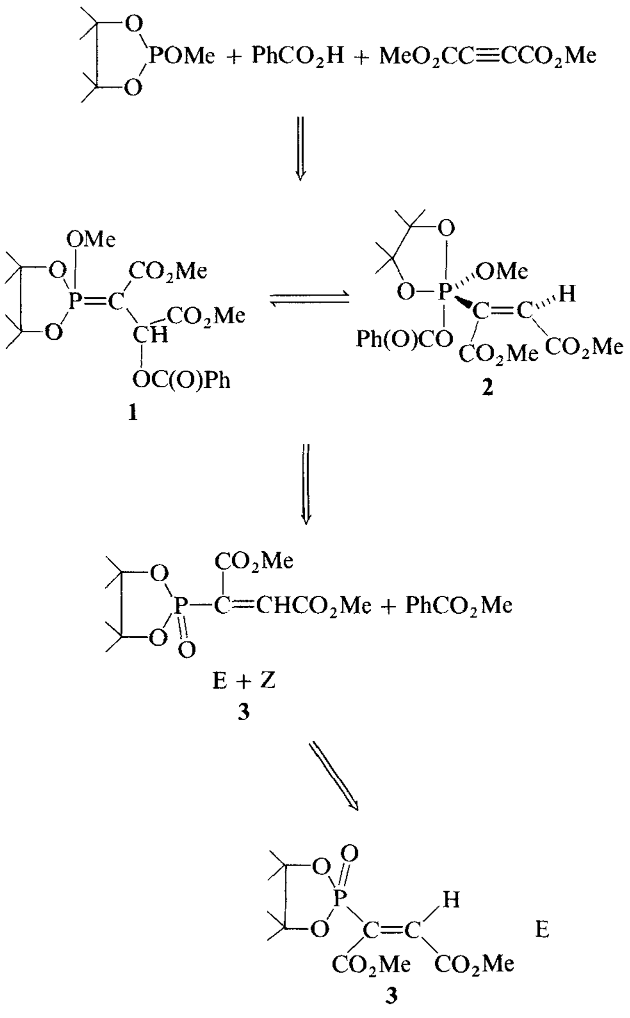


and PhOH as trapping reagent we were able to clearly observe the evolution pathway from **A** to **B**. This paper is concerned with the first evidence for an equilibrium ylid$\rightleftharpoons$phosphorane when the trapping reagent is benzoic acid.

The reaction is easily performed between −20°C and 0°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

SCHEME 1



1 δ ^{31}P 69 ppm, J_{POCH} 13.2 Hz (doublet of quadruplet) $J_{P=C-CH}$ 22,87 Hz. δ ^{1}H, CH_3—C 1.41 ppm HC—C=P 6.15 ppm J 22.87 Hz, Ph 7.39 & 7.93 ppm (CCl_4).
2 δ ^{31}P-49 ppm, J_{POCH} 14.7 Hz (doublet of quadruplet) $J_{P-C=C-H}$ 25.12 Hz (E isomer alone). δ ^{1}H, CH_3—C 1.29 ppm HC=C—P 6.57 ppm J 25.12 Hz Ph 7.39 & 7.93 ppm (CCl_4).
3 (E) δ ^{31}P 19.8 ppm $J_{P-C=CH}$ 23.5 Hz δ ^{1}H CH_3—C 1.42 et 1.57 ppm; COOMe 3.79 & 3.87 ppm. δ ^{1}HHC=CP 6.78 ppm J 22.5 Hz ($CDCl_3$), $\nu c = o$ 1740 cm^{-1}, $\nu c = c$ 1630 cm^{-1} F = 120°.
3 (Z) δ ^{31}P 19.1 ppm $J_{P-C=CH}$ 39.7 Hz δ ^{1}H CH_3—C 1.29 & 1.49 ppm COOMe 3.82 & 3.87 ppm. δ ^{1}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 ^{1}H NMR techniques especially the appearance and the disappearance of doublets for:

$$H—C—C=P,\ H—C=C—P_V \text{ and } H—C=C—P_{IV}$$

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

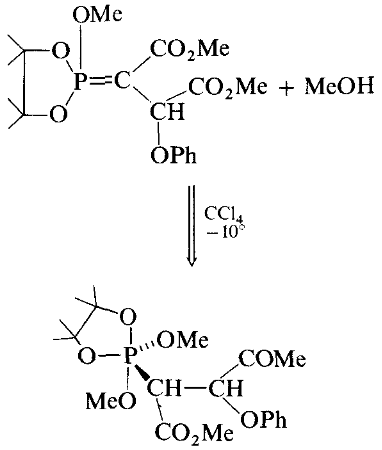
The latter readily crystallizes from an ethereal solution.

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]

$$(CH_3)_3P=CH_2 \underset{-MeOH}{\overset{+MeOH}{\rightleftharpoons}} (CH_3)_4POCH_3$$

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



To our knowledge, the present work firmly establishes the first description of the equilibrium ylid ⇌ 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.

REFERENCES

1. R. Burgada, Y. Leroux, and Y. O. El Khoshnieh, *Tetrahedron Lett.*, **21**, 925 (1980).
2. H. Schmidbaur and H. Stuhler, *Angew Chem. Int. Ed.*, **2**, 145 (1972).