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TRAPPING OF CARBANIONIC SPECIES
SYNTHESIS OF NEW SALT-FREE YLIDS AND PHOSPHORANES

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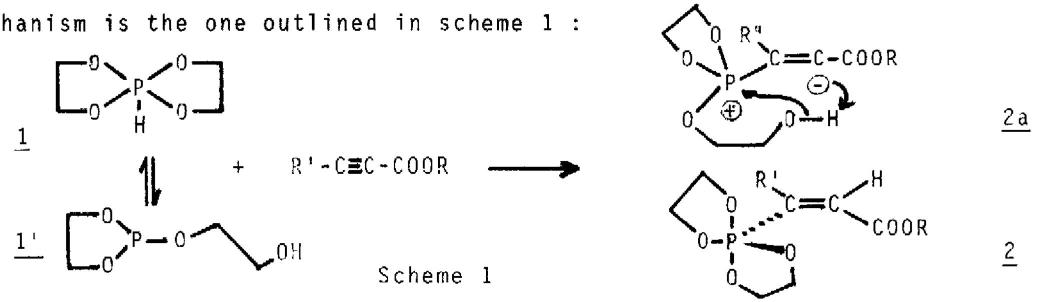
Summary - Syntheses of new salt-free ylids and phosphoranes by addition of a trivalent phosphorus compound with dimethylacetylene dicarboxylate in presence of a trapping reagent are described. The results are consistent with trapping of carbanionic species.

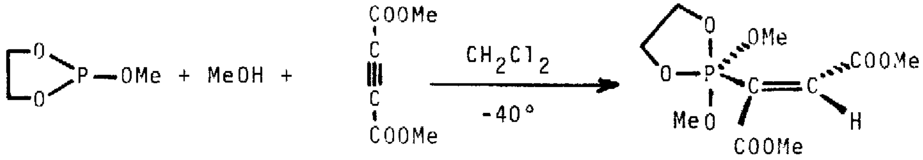
In a previous note (1), we reported the synthesis of new vinylphosphoranes obtained from an addition reaction between spirophosphoranes which present a P-H bond and mono and dicarbonyl acetylenic compounds. The most likely mechanism is the one outlined in scheme 1 :



Scheme 1

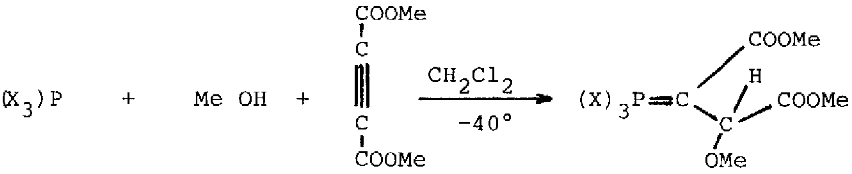
Spirophosphorane 1 reacts in its tricoordinated tautomeric form 1' leading to a *carbanionic quasi-phosphonium* species 2a. 2a stabilizes itself by protonation and formation of the phosphorane 2. The tricoordinated tautomeric form 1' includes both the P III $\left[{}^{O}_{O}\right>$P-O-structure and a protic nucleophilic group-OH. Therefore, in order to extend the scope of this reaction, we have examined the reaction of $\left[{}^{O}_{O}\right>$ P-OMe with MeOH and noted that it provides a novel and direct route to the synthesis of the monocyclic phosphoranes 3 and 4 in a nearly quantitative yield (Table I).

A



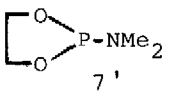
The reaction A gives rise to an ylid if it is performed with another tricoordinated phosphorus compound namely $P(OMe)_3$ or $P(NMe)_3$: reaction B.

B

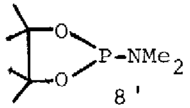


5 X = OMe 6 X = NMe$_2$

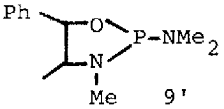
On the basis of these results it is clear that the course of the reacting species leading to an ylid or to a phosphorane is controlled by the structure of the trivalent phosphorus compound. This assumption was proved by the following studies. We investigated several reactions using tricoordinated compounds 7'-10', following the same experimental conditions :



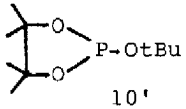
7'



8'

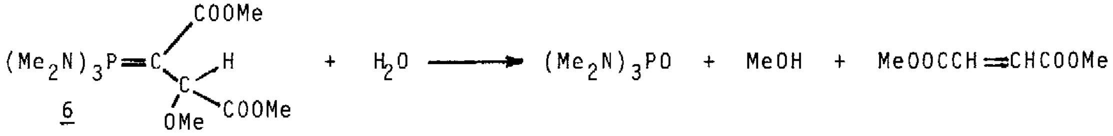


9'



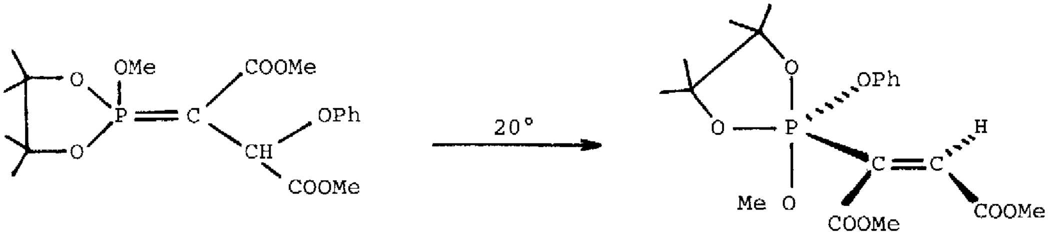
10'

All of them led to an ylid analogous to 5 and 6 (Table II). Structure proofs are based on the NMR (^{1}H, ^{31}P) spectra analysis (see Table I and II), the IR spectra, combustion analysis and a chemical reaction : hydrolysis. For instance



In presence of methanol, ylids 5-10 can undergo an addition reaction analogous to that described by Schmidbaur (3) to give a phosphorane.

When the trapping reagent used in reaction A is phenol, we obtain a quantitative yield of ylid. Between 0° and 20° this ylid undergoes a complete rearrangement leading to a phosphorane (path c, scheme 2)



δ^{31}P 70.5 ppm

δ^{31}P-52 ppm $J_{HC=CP}$ 23.2Hz
(E configuration)

The carbanionic species 11 (scheme 2) can be trapped with other reagents. For instance, carbon dioxide and phthalimide work well.

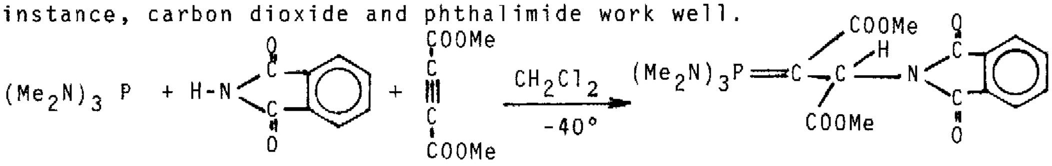
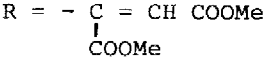
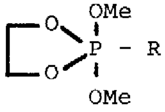
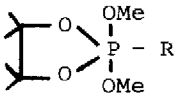


TABLE I PHOSPHORANES



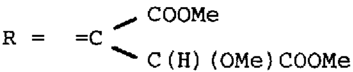
$R = -C(COOMe) = CH\ COOMe$

N°		$\delta^{31}P$ ppm	MeOP		HC=C-P		Me-C	CH_2O	COOMe
			δ	J_{HCOP}	δ	J	δ	δ	δ
3		-36	3.42	12.75	6.22	45.6	–	3.84 3.73	3.69 3.73
4		-50	3.45	13.12	6.24	43.5	1.2	–	3.65 3.66

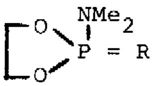
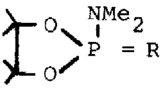
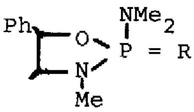
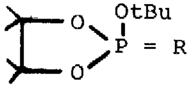
The coupling constant $J_{HC=CP} \simeq 45$ Hz supports the Z configuration

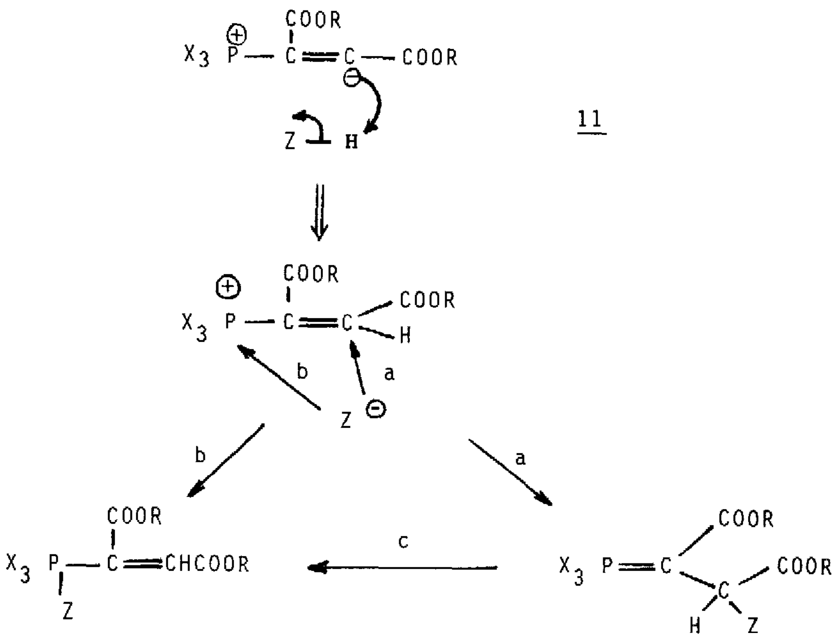
This structural relationship is in good agreement with the coupling constants of vinylphosphonates (7).

TABLE II YLIDS



$R = {=}C(COOMe)C(H)(OMe)COOMe$

N°		$\delta^{31}P$ ppm	HCC = P		COOMe	OMe	$PNMe_2$	
			δ	J	δ	δ	δ	J
5	$(MeO)_3P = R$	52	4.8	30	3.5 3.7	3.3	–	–
6	$(Me_2N)_3P = R$	66	4.5	25.5	3.27 3.48	3.6	2.64	10.5
7		78.5	4.6	27.7	3.5 3.6	3.3	2.76	10.5
8		64.5	4.65	26	3.45 3.54	3.21	2.73	10.5
9		67	4.65	18	3.55 3.63	3.46	2.85	10.5
10		57	4.50	24	3.48 3.63	3.24	–	–



Scheme 2

During our study, we never observed the Arbuzov reaction which would be the reaction of $Z^{\ominus}$ with X_3 (X=OMe). This reaction occurs when the carbanionic intermediate 11 is formed in the absence of trapping reagent (2).

The unstable ylid 10 (Table II) decomposes quickly at room temperature to give a phosphonate.

Reactions of trivalent phosphorous compounds (essentially Ph_3P) with dimethylacetylene dicarboxylate have been the object of intensive study in recent years (4-6). To our knowledge, the ylids and phosphoranes are new (Table I and II). Further studies are in progress to investigate the reactivities of these novel ylids, involving new trapping reagents with synthetic potentialities.

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