YLIDS WITH A P-H BOND
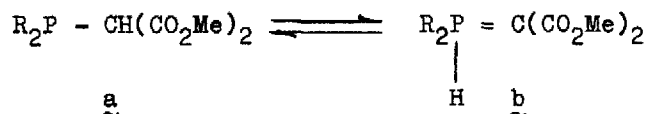
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Summary: Tertiary bis(methoxycarbonyl)methyl phosphines are reversibly isomerized to ylids with a P-H bond. The phosphine- P-H ylid equilibrium depends on the solvent nature, on the concentration, temperature and substituents at the phosphorus atom.

Compounds of trivalent phosphorus with a labile α - hydrogen (R_2P-CHX_2) possess interesting chemical properties.[1,2] Formerly we have managed to convert them into ylids of some new types with Cl, Br, R_2P, RS, Me_3Si, RNH etc substituents at the phosphorus atom.[1-4]

In this paper it is shown that tertiary bis(methoxycarbonyl)methyl phosphines are reversibly isomerized to ylids with a P-H bond.

$$R_2P - CH(CO_2Me)_2 \rightleftharpoons R_2P = C(CO_2Me)_2$$

$$\underset{\underset{\sim}{a}}{} \qquad \qquad \underset{\underset{H}{\quad \underset{\sim}{b}}}{}$$

The phosphine-ylid equilibrium $\underset{\sim}{a} \rightleftharpoons \underset{\sim}{b}$ is a genuine tautomeric process connected with a redox conversion of two prototropic isomers and reversible change in the valency of phosphorus and a formation of a P=C bond.

The tautomeric system $\underset{\sim}{a} \rightleftharpoons \underset{\sim}{b}$ has been investigated by spectral methods. The compounds $\underset{\sim}{5},\underset{\sim}{6}$ (Tables 1 and 2) exist in the crystalline state in the form of P-H ylids $\underset{\sim}{b}$. The IR spectra obtained in nujol show only bands of the ylid structure $\underset{\sim}{b}$: 1085(P=C),1310,1590,1670(=C-C=O),2400 cm^{-1}(P-H). However, in solution and on melting of compounds $\underset{\sim}{5},\underset{\sim}{6}$ the P-H ylid tautomeric form $\underset{\sim}{b}$ is in equilibrium with the phosphine form $\underset{\sim}{a}$. The integration of NMR signals and IR bands allows the proportion of the tautomeric forms $\underset{\sim}{a},\underset{\sim}{b}$ and the equilibrium constant K_T to be determined (Table 1).

Table 1. Tautomeric composition of compounds 1-6

$$K_T = \frac{[b]}{[a]}$$

$$RR'P-CH(CO_2Me)_2 \rightleftharpoons RR'P=C(CO_2Me)_2$$
$$\underset{a}{} \qquad \overset{H}{\underset{b}{}}$$
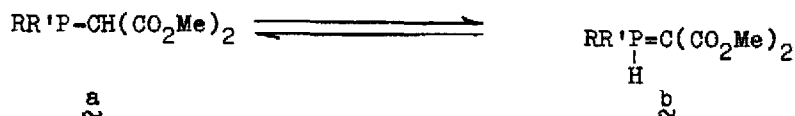
COMPOUND	R,R'	% a	% b	K_T	SOLVENT, 20°C, c=0.2 mol/l
1	R = R' = i-Pr	70	30	0.43	$CHCl_3$
2	R = R' = n-Bu	85	15	0.18	$CHCl_3$
3	R = t-Bu,R'=n-Bu	65	35	0.54	$CHCl_3$
4	R = t-Bu,R'=i-Bu	67	33	0.49	$CHCl_3$
5	R = t-Bu,R'=s-Bu	35	65	1.85	$CHCl_3$
6	R = t-Bu,R'=i-Pr	~90	~10	–	C_6H_{12}
		85	15	0.18	THF
		75	25	0.33	C_6H_6
		60	40	0.67	CH_2Cl_2
		39	61	1.56	$CHCl_3$

Compound 5. IR ($CHCl_3$, $\vee$, cm^{-1}):1730,1750 (C=O) – form a;1085(P=C),1325, 1598,1672 (=C-C=O),2360 (P-H) – form b. ^{1}H-NMR ($CDCl_3$, δ ,ppm):4.08(s,CH_3O) – form a; 4.17 (s,CH_3O), 6.5 (d,^{1}J(PH) 440 Hz,P-H) – form b. ^{31}P-NMR ($CHCl_3$, δ , ppm): 29.2, s – form a; 32 (d,^{1}J(PH) 440 Hz), 35 (d,^{1}J(PH) 440 Hz) – signals of diastereomers due to asymmetrical phosphorus and carbon atoms – form b.

Compound 6. IR ($CHCl_3$, $\vee$, cm^{-1}): 1725,1750 (C=O) – form a;1088(P=C),1330, 1600,1675 (=C-C=O), 2360 (P-H) – form b. ^{1}H-NMR ($CDCl_3$, δ .ppm):4.03(s,CH_3O),3.7 (d,^{2}J(PH) 2 Hz,P-CH) – form a;4.12(s,CH_3O), 6.5(d,^{1}J(PH) 460 Hz,P-H) – form b; ^{31}P-NMR($CHCl_3$, δ ,ppm):35.5, s – form a; 40,d,^{1}J(PH) 460 Hz – form b.

Compounds 1-4 are liquids and their spectral characteristics are similar to those of 5 and 6. In the absence of solvent, in pure liquid compounds 1-4 the content of the P-H ylid is small ($\sim$ 5-15%). In chloroform it is higher.

The position of the equilibrium a $\rightleftharpoons$ b depends strongly on the solvents

used, on the concentration, temperature and substituent at the phosphorus atom
(Table 1). In the solvent sequence $C_6H_{12} <$ THF $< C_6H_6 < CH_2Cl_2 < CHCl_3$ the
tautomeric equilibrium shifts towards the P-H ylid b. On heating the equilib-
rium shifts reversibly towards the phosphine form a, on cooling - towards the
P-H ylid b. The dependence of an equilibrium constant K_T on the temperature
($\Delta G = -RT\ln K_T$) allows thermodynamic parameters of the prototropic equilibrium
a $\rightleftharpoons$ b to be determined. For compound 6 at concentration 0.2 mol/l in chloro-
form, in the temperature interval 10-50°C values of enthalpy difference
ΔH -2.4$\pm$0.2 kcal/mol, entropy ΔS -7.4$\pm$0.7 e.u., are found. Consequently the
P-H ylid form b is more advantageous energetically, whereas the phosphine
form a is preferable from a structural view-point.
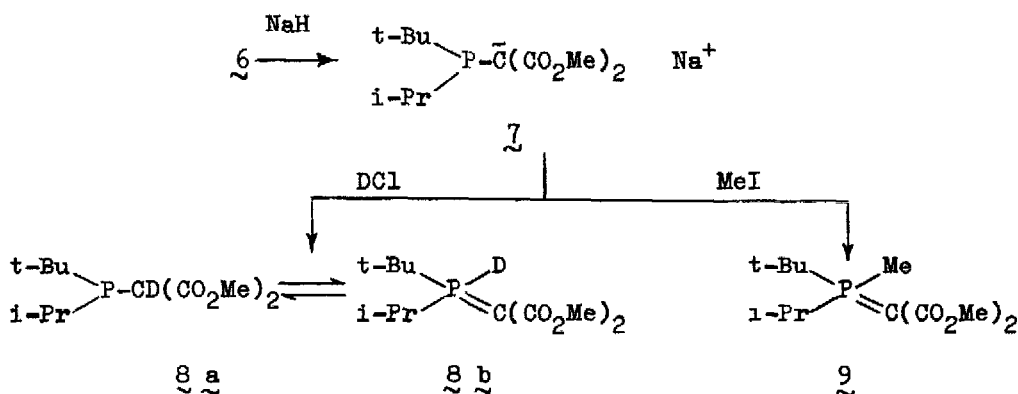
From Table 1 one may see that sterically bulky alkyl substituents t-Bu,
s-Bu,i-Pr stabilize the P-H ylid form b and shift the tautomeric equilibrium
towards this form. Introduction of a bulky substituent at the phosphorus atom
in compounds 1-6 destabilizes the phosphine form and gives space advantage to
the formation of the P-H ylid form; this may be seen from Stuart-Briegleb mo-
lecular models. Bulky alkyl substituents increase the C-P-C valency bond
angles of the trivalent form, their values being close to those of the penta-
valent state; this effect should favour the formation of the P-H ylid form. As
is known, for pentavalent phosphorus compounds typical angle values are 105-
110°, whereas for trivalent ones these are 95-100°.

Compounds 1-6 (Table 2) were prepared by the reaction of dialkylchloro-
phosphines with a suspension of a sodio-malonic ester in diethyl ether. Details
the synthesis of these compounds are given in ref [1,2]

Table 2. Dialkyl bis(methoxycarbonyl)methyl phosphines 1-6

COMPOUND	YIELD, %	B.P.(0.06 mm Hg)	M.P.	n_D^{20}	δp(ppm,form a)
1	55	95°C	-	1.4845	19.7
2	50	110°	-	1.4800	-
3	60	103°	-	1.4800	14
4	65	95°	-	1.4789	10.5
5	70	98°	71°C	-	29.2
6	50	95°	59°	-	34.8

Compounds 1-6 are stable liquids distilled in vacuo, or crystalline mate-
rials. Their chemical properties are similar to those of trivalent phosphorus
compounds. They are easily oxidized, alkylated with methyl iodide and add
sulphur [2]. The labile hydrogen of these compounds may be easily substituted
with sodium upon treatment with sodium hydride in tetrahydrofuran. Interac-
tion of the sodium derivative of 7 with deuterium chloride gives the deute-
rated compound 8, and reaction with methyl iodide proceeds at the phosphorus
atom to form the ylid 9[5] (an "ylid" modification of the Michaelis-Becker
reaction).

$$6 \xrightarrow{\text{NaH}} \underset{\text{i-Pr}}{\overset{\text{t-Bu}}{>}} P-\bar{C}(CO_2Me)_2 \quad Na^+$$

7

DCl   MeI

$$\underset{\text{i-Pr}}{\overset{\text{t-Bu}}{>}}P-CD(CO_2Me)_2 \rightleftharpoons \underset{\text{i-Pr}}{\overset{\text{t-Bu}}{>}}\overset{D}{\underset{}{P}}=C(CO_2Me)_2 \qquad \underset{\text{i-Pr}}{\overset{\text{t-Bu}}{>}}\overset{Me}{\underset{}{P}}=C(CO_2Me)_2$$

8 a   8 b   9

The ^{31}P-NMR spectrum of 8 exhibited a singlet at 35 ppm, (form 8 a) and
a doublet at 40 ppm, ^1J (PD) 70 Hz (form 8 b) [7]

References

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2. O.I.Kolodiazhnyi, Zh.Obshch.Khim., in press.

3. O.I.Kolodiazhnyi, V.P.Kukhar, International Conference on Phosphorus
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5. Ylid 9: Yield 50%, m.p.92°C (from $Et_2O+C_6H_{12}$). IR(KBr,ν,cm^{-1});1078(P=C),
   1307,1605,1670(=C-C=O).PMR(CCl$_4$,δ): 2 ppm,d,J(PH) 12 Hz(CH$_3$P).δ_P 40.6 ppm.

6. Positive chemical shifts are downfield from 85% H_3PO_4 used as an external
   standard.

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