Condensation of Propiolactones with Phosphorus Ylides: a Convenient Synthesis of α,β-Ethylenic Ketones

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δ-Hydroxy-β-ketophosphoranes have been obtained by condensation of propionolactones with ylides and afforded α,β-unsaturated ketones on heating.

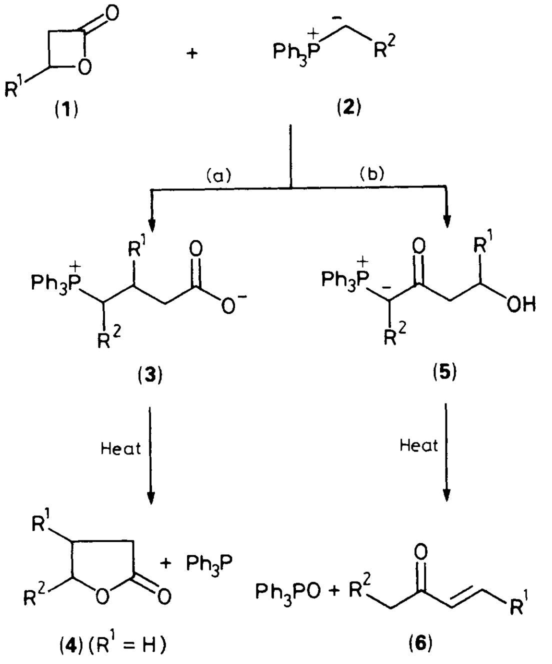
Kise and co-workers[1] found that the reaction of β-propionolactones (**1**) with alkylidenetriphenylphosphoranes (**2**) proceeds by attack of the ylide on the alkyl carbon atom to form the phosphonium carboxylate betaines (**3**). Thermolysis of (**3**) gives lactones (**4**) [Scheme 1, pathway (a)].

In contrast with these results, we now report that, under different conditions, lactones (**1**; R^1 = H or Me) give ketophosphoranes (**5**) by attack of the ylide carbanion on the carbonyl group [pathway (b)]. Thus, a solution in toluene of propionolactone was added dropwise to a stirred solution in

Table 1. Preparation of (**5**) and (**6**).

			Ylide (**5**)		Ketone (**6**)[a]		
	R^1	R^2	% Yield[b]	M.p., *t*/°C	% Yield[c]	B.p., *t*/°C (*p*/mmHg)	[Lit. data]
a	H	H	56	146—148	40[d]	35(135)	[36.5(145)[g]]
b	Me	H	68	145—147	76[e]	120—121(760)	[121—122(760)[h]]
c	Me	Me	55	115	70[e]	60(15)	[61(18)[i]]
d	Me	Pr^n	50	95—97	58[e]	78(13)	[67(10)[h]]
e	Me	Ph	50	122—125	60[f]	72(17)	—[j]
f	Me	4-MeOC$_6$H$_4$	55	173—174	73[f]	75(2)	—[j]

[a] All products gave satisfactory spectroscopic and/or analytical data. [b] Yields are given for pure ylides: (**5a—d**) following treatment with HCl and NaOH; (**5e—f**) dissolved in the minimum amount of CH_2Cl_2 and then dilution with hexane to give the ylide. [c] Yields are given for pure ketones. Crude yields, based on Ph_3PO exceed 90%. [d] Unoptimized yield. [e] Ketones purified by distillation. [f] Ketones purified by chromatography on silica gel (ether–pentane, 90:10) before distillation. [g] Ref. 3. [h] Ref. 4. [i] Ref. 5. [j] Ref. 6.



(a) Ylide (**2**) prepared from phosphonium bromide and $NaNH_2$ in tetrahydrofuran.

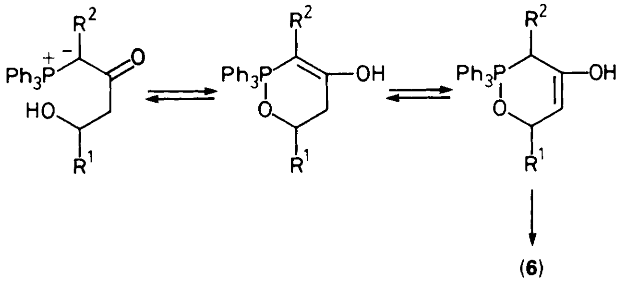
(b) Ylide (**2**) prepared from the same salts and Bu^{t}OK in toluene.

Scheme 1

toluene of the phosphorane (**2**) at 40 °C. After 2–4 h, (**5**) was obtained (yields 50–68% after purification). Table 1 gives the results.

Thermolysis of pure (**5**) for 20–30 min at 150–170 °C under reduced pressure (2—230 mmHg) affords α,β-unsaturated ketones (**6**) and triphenylphosphine oxide.

The mechanism of this new extrusion reaction of triphenylphosphine oxide probably involves the generation of an oxaphosphinine as an intermediate (Scheme 2).†



Scheme 2

The elimination is stereoselective and affords only (*E*)-unsaturated ketones. Butyrolactone gives the same product from path (b)[2] but it does not extrude triphenylphosphine oxide on heating.

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† To our knowledge, no oxaphosphinine has been previously reported.