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.

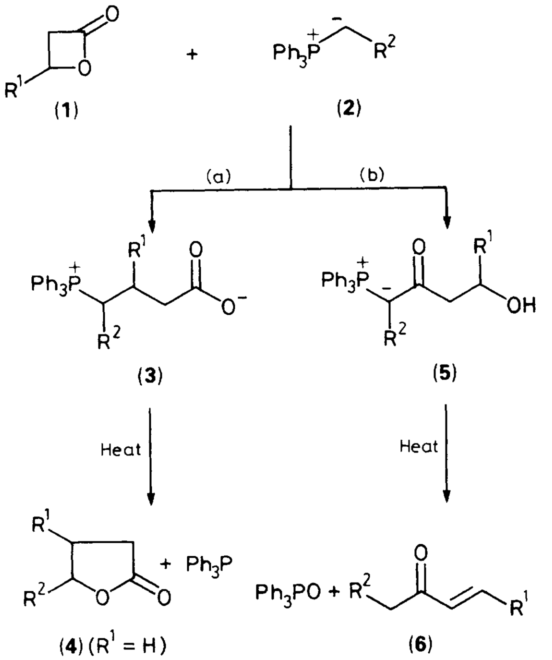
Kise and co-workers[1] found that the reaction of β-propionolactones (**1**) with alkylidenetriphenylphosphoranes (**2**) proceeds by attack of the ylide on the alkyl carbon atom to form the phosphonium carboxylate betaines (**3**). Thermolysis of (**3**) gives lactones (**4**) [Scheme 1, pathway (a)].

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-$MeOC_6H_4$	55	173—174	73[f]	75(2)	—[j]

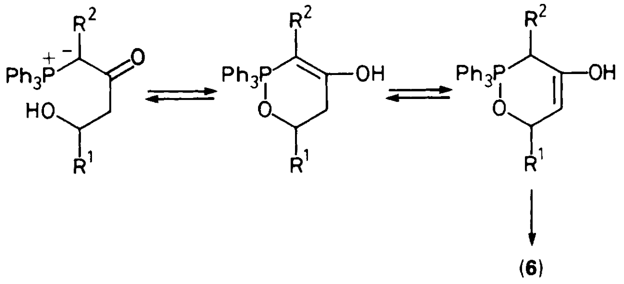
[a] All products gave satisfactory spectroscopic and/or analytical data. [b] Yields are given for pure ylides: (**5a**—**d**) following treatment with HCl and NaOH; (**5e**—**f**) dissolved in the minimum amount of CH_2Cl_2 and then dilution with hexane to give the ylide. [c] Yields are given for pure 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^tOK in toluene.

Scheme 1



Scheme 2

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).†

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.