Novel Reaction of Phosphoranes with Lactones. Formation and Thermal Ring Closure of Triphenyl(alkyl)phosphoniocarboxylate Betaines

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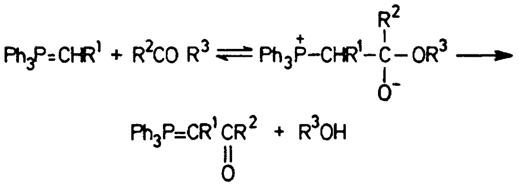
Summary The reaction of alkylidenetriphenylphosphoranes with lactones affords triphenyl(alkyl)phosphoniocarboxylate betaines, which were thermally decomposed to give triphenylphosphine and lactones with the alkylidene groups of the starting phosphoranes introduced into the ring.

It has been generally observed that the initial step in the reactions of phosphoranes with carbonyl compounds is nucleophilic addition of the ylidic carbanion to carbonyl carbon atoms to form phosphonium alkoxybetaines. In the reactions of phosphoranes with carboxylic acid esters, the betaines usually eliminate alkoxy-anions which are sufficiently basic to abstract hydrogen from the ylidic carbon atom to give keto ylides (Scheme 1).[1,2] Henrick and his co-workers[3] found that the reactions of enol lactones with alkylidenetriphenylphosphoranes also proceed by attack of the ylide on the carbonyl group to form the phosphonium enolate betaine intermediates.

We now report a novel reaction of the lactones (**1**) with methylene- or alkylidene-triphenylphosphoranes (**2**). The reaction proceeds by nucleophilic attack of the ylide carbanion on the alkyl carbon atom to form the isolable phosphoniocarboxylate betaines (**3**) (Scheme 2). Treatment of (**3**) with hydrochloric acid yielded phosphonium chlorides (**4**) and thermolysis of (**3**) gave triphenylphosphine and the lactones (**5**).



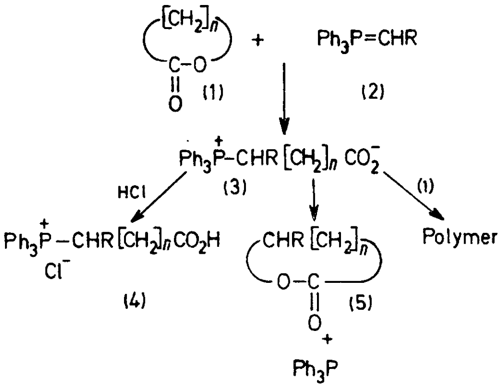
Scheme 1

A solution in ether of β-propiolactone (BPL) was added dropwise with stirring to a solution in tetrahydrofuran (THF) of the phosphorane (**2**; R=H) (prepared from $MePh_3PBr$ and $NaNH_2$ in THF) at 0 °C. After 0·5 h (**3**; $n = 2$, R = H) was obtained as a hygroscopic precipitate (yield 85%), which was converted into (**4**; $n = 2$, R = H) by treatment with excess of dilute HCl [m.p. 209—211 °C;

δ 1·72—2·20 (m, 2H), 2·70 (t, J 6 Hz, 2H), 3·20—3·50 (m, 2H), and 7·60—8·00 (m, 15H); ν_{max} 1705 (C=O), 720, 1000, 1110, and 1440 (Ph_3P^+) cm^{-1}]. Similarly the reaction of γ-butyrolactone with (**2**; R = H) afforded (**3**; n = 3, R = H) in 70% yield, and the reaction of BPL with (**2**; R = Me) yielded (**3**; n = 2, R = Me) in 75% yield. Both these phosphonium carboxylates were converted into phosphonium chlorides (**4**) and their structures were confirmed by i.r. and n.m.r. spectroscopy.

The reactions of the carbonyl-stabilized phosphoranes (**2**; R = CO_2Et and COPh) with BPL under similar conditions did not afford the equimolar adducts but small amounts of BPL polymer were obtained. The low nucleophilic reactivity of carbonyl phosphoranes may be attributed to anionic charge delocalization as is the case in Wittig reactions.[4] Since BPL polymerizes with a variety of organic base initiators, we investigated the polymerization of BPL by the phosphoranes (**2**) and found that both stabilized and non-stabilized phosphoranes were effective initiators.

Thermolysis of (**3**; n = 2, R = H) at 220 °C under nitrogen yielded triphenylphosphine and γ-butyrolactone in 74% yield. Similar reactions of (**3**, n = 3, R = H and n = 2, R = Me) afforded the corresponding lactones (**5**) in 64 and 35% yields, respectively.



SCHEME 2

The two-step reactions in Scheme 2, formation and thermolysis of (**3**), thus furnish a new method of insertion of methylene or alkylidene groups into the alkyl–oxygen bond of lactones.

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