Lithiotriphenylphosphinioacetonide, a New Type of 1, 3-Dianion

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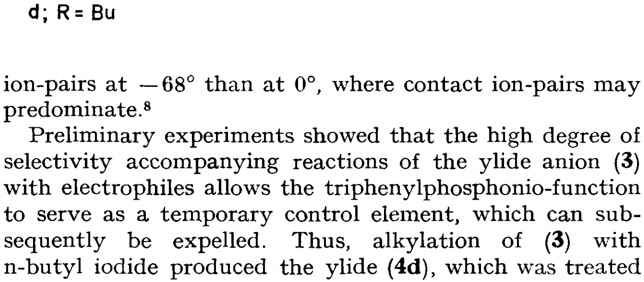
Summary Triphenylphosphinioacetonide (**2**) undergoes selective metallation with n-butyl-lithium to afford the novel 1,3-dianion (**3**) as evidenced by deuteriation and condensations with electrophiles.

Certain β-ketophosphonium salts containing α-hydrogens react with basic reagents to form stable β-ketophosphonium ylids.[1–6] We now report a new reaction of β-ketophosphonium salts in which sequential, twofold ionization of acetonyltriphenylphosphonium chloride (**1**)[1] gives lithiotriphenylphosphinioacetonide (**3**). Such 1,3-di-ionization of a β-ketophosphonium salt has not been reported previously, although the secondary ionization of triphenylphosphinioacetophenonide has.[7]

Conversion of (**1**) into (**3**) was accomplished as follows. Treatment of the phosphonium salt (**1**) with 5% aqueous potasium hydroxide at room temperature afforded the ylide (**2**)[1] (60—70%). Dropwise addition of n-butyl-lithium (0·018 mol) in hexane to a solution of (**2**) (0·016 mol) in THF (200 ml), at −68° under nitrogen, gave the soluble, ylide anion (**3**). After 20 min the reaction mixture was quenched with deuterium oxide to regenerate the ylide (**2**) containing 0·9 deuterium at the methyl carbon as shown by n.m.r. analysis. Treatment of (**3**) with benzyl bromide (0·01 mol) for 1 h at −68°, followed by 30 min at 25°, resulted in selective terminal alkylation to afford (**4a**)[3] (44%). Similarly allyl bromide gave (4b)‡ (52%), m.p. 94—96·5°. Condensation of (**3**) with benzophenone afforded the alcohol (4c) (65%),‡ m.p. 175—177°. Alkylations of (**3**) at 0° consistently led to reduced yields of (**4a**—**b**). Since deuteriation experiments established that this did not arise from more extensive decomposition of (**3**) at higher temperature, these results are tentatively attributed to the existence of a greater fraction of (**3**) as solvent-separated ion-pairs at −68° than at 0°, where contact ion-pairs may predominate.[8]



$[\mathrm{Ph_3\overset{+}{P}CH_2{\cdot}CO{\cdot}Me}]\mathrm{Cl}^-$ (1)

$\mathrm{Ph_3\overset{+}{P}-\overset{-}{C}H{\cdot}CO{\cdot}Me}$ (2)

$[\mathrm{Ph_3\overset{+}{P}\text{-}\overset{-}{C}H{\cdot}CO{\cdot}\overset{-}{C}H_2}]\mathrm{Li}^+$ (3)

$\mathrm{Ph_3\overset{+}{P}-\overset{-}{C}H{\cdot}CO{\cdot}CH_2R}$

(4)a; $\mathrm{R = CH_2Ph}$
b; $\mathrm{R = CH_2CH{=}CH_2}$
c; $\mathrm{R = \underset{OH}{\underset{|}{C}}Ph_2}$
d; $\mathrm{R = Bu}$

$\mathrm{R^1CH{=}CH{\cdot}CO{\cdot}CH_2R^2}$

(5)a; $\mathrm{R^1 = Ph,\ R^2 = Bu}$
b; $\mathrm{R^1 = 3,4\text{-}Cl_2C_6H_3,\ R^2 = CH_2CH{=}CH_2}$

Preliminary experiments showed that the high degree of selectivity accompanying reactions of the ylide anion (**3**) with electrophiles allows the triphenylphosphonio-function to serve as a temporary control element, which can subsequently be expelled. Thus, alkylation of (**3**) with n-butyl iodide produced the ylide (**4d**), which was treated with benzaldehyde in $\mathrm{Me_2SO}$ at 55° for 18 h to afford $\alpha\beta$-

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‡ Satisfactory analytical and spectral data were obtained for this compound.

unsaturated ketone (**5a**)[9] [40% yield from (**3**)]. Similarly, the ketone (**5b**)‡ was prepared from (**3**) (49%) by sequential reactions with allyl bromide and 3,4-dichlorobenzaldehyde.

The present results involving the ylide anion (**3**) contrast with previously reported reactions of the less nucleophilic ylide (**2**) with alkyl halides and ketones; the former gave rise to exclusive *O*-alkylation, while the latter failed to yield isolable amounts of condensation products.[1]

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