Conversion of Aldehydes and Ketones into Chloro-olefins and Acetylenes Using Chloroiodomethane as a Chloromethylene Source

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Summary Chloroiodomethane smoothly reacts with triphenylphosphine to yield chloromethyltriphenylphosphonium iodide (**1**), which in turn can be utilized for the conversion of aldehydes and ketones into chloro-olefins and acetylenes upon treatment with potassium t-butoxide.

Wittig chloromethylenation of carbonyl compounds has been reported using chloromethylenetriphenylphosphorane (**2**),[1,2] but the preparation of the requisite precursor chloromethyltriphenylphosphonium salts is rather complicated. We report here a convenient method for the synthesis of the phosphonium iodide (**1**) and its use for chloromethylenation (Scheme 1).†

$$\begin{tikzcd}
CH_2ClI + Ph_3P \arrow[r, "THF"] & \overset{+}{Ph_3P}CH_2Cl\ I^-\ \text{(1)} \arrow[d, "Bu^tOK"', "Bu^tOH"] \\
R^1R^2C{=}CHCl\ \text{(3)} & Ph_3P{=}CHCl\ \text{(2)} \arrow[l, "R^1R^2C{=}O"']
\end{tikzcd}$$

Scheme 1

The phosphonium iodide (**1**) was obtained as a white precipitate in 60—70% yield by heating a solution in tetrahydrofuran (THF) of triphenylphosphine and chloroiodomethane[3] (slight excess) under reflux for *ca.* 10 h [m.p. BPh_4^- salt 190—193 °C (decomp.)[1]].‡ Potassium t-butoxide seemed to be the most suitable base for the deprotonation of (**1**) to give (**2**), the formation of which was shown by the appearance of a characteristic orange-red colour. Addition of an aldehyde or a ketone led to conversion into the corresponding chloro-olefin (**3**) in reasonable yield (Table), after purification by preparative g.l.c.

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† Recently another method for the preparation of chloromethyltriphenylphosphonium chloride has appeared: R. Appel and W. Morbach, *Synthesis*, 1977, 699.

‡ Satisfactory elemental analyses were obtained for all compounds.

TABLE

Chloromethylenation of aldehydes and ketones (Scheme 1).[a]

R^1	R^2	Yield/%[b] of (**3**)	$E:Z$ ratio
$-[CH_2]_5-$		94	
$-[CH_2]_6-$		86[c]	
$-[CH_2]_4CHMe-$		89	92 : 8
Ph	Me	75	56 : 44[d]
p-ClC_6H_4	Me	59	52 : 48
p-MeC_6H_4	Me	65	57 : 43
Ph	H	81	46 : 54
p-ClC_6H_4	H	68	37 : 63
$Me[CH_2]_7$	H	45	44 : 56

[a] Compound (**1**) (25 mmol) was treated with Bu^{t}OK (30 mmol) in 50 ml of Bu^{t}OH for 1·5 h at ambient temperature, the carbonyl compound $R^1R^2C{=}O$ (20 mmol) was added, and the mixture was kept for 4 h under nitrogen. In the case of acetophenones, the olefin $R^1R^2C{=}CH_2$ was also detected in 10—15% yield. [b] G.l.c. yield based on $R^1R^2C{=}O$. [c] 10 mmol of R^1R^2-$C{=}O$. [d] Z-isomer: δ(CCl_4) 2·00 (3H, d, Me), 5·96 (1H, q, =CClH), and 7·18 (5H, s, Ph); E-isomer: δ 2·11 (3H, d, Me), 6·15 (1H, q, =CClH), and 7·15 (5H, s, Ph).

In the presence of excess of potassium t-butoxide (2·5 equiv.), prolonged reaction of aromatic aldehydes (8 h) gave phenylacetylenes, the procedure giving a route for the one-step conversion of the formyl group into an acetylenic function[4] (Scheme 2).

$$\mathrm{ArCHO}\xrightarrow[\text{excess Bu}^t\text{Ok}]{(\mathbf{2})}\mathrm{ArC{\equiv}CH}$$

Ar	Yield/%
Ph	91
p-MeC_6H_4	63
o-ClC_6H_4	49
p-ClC_6H_4	37

SCHEME 2

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