Convenient Preparation of β-Halovinyl Ketones under Non-Acidic Conditions

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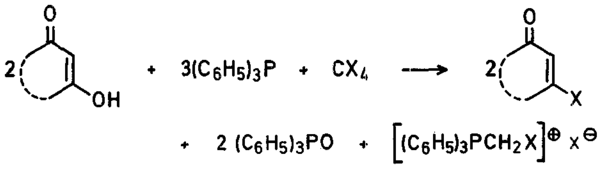
Triphenylphosphine in carbon tetrachloride represents a useful reagent[1] for the exchange of a hydroxy group with a chlorine atom[2]. Acid sensitive groups, such as acetals, etc. remain unaffected by this reagent[3] as a consequence of the essentially neutral conditions maintained throughout the reaction[4].

We have found that triphenylphosphine and carbon tetrahalides (chloride or bromide) can be used advantageously for the conversion of 1,3-diketones into β-halo-α,β-unsaturated ketones including even open chain species. In various procedures hitherto reported[5] the formation of hydrogen halide is involved and thus the preservation of acid sensitive groups is not possible. The resistence of acetals towards this reagent[3] is reflected by quantitative recovery of either 2,2-dimethoxypropane or 2,2-dimethyl-1,3-dioxolane added to the reaction mixture of triphenylphosphine, carbon tetrachloride, and 5,5-dimethylcyclohexan-1,3-dione.

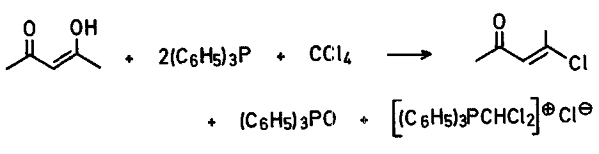
The stoichiometry of the reaction can be generally expressed by the following equation[4] (Scheme A).



1

Scheme A

In the case of open chain compounds, a different stoichiometry is valid provided that carbon tetrachloride is used as solvent (Scheme B).



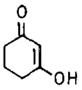
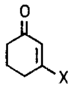
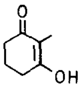
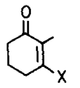
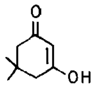
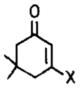
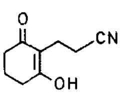
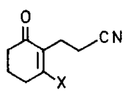
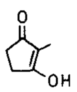
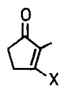
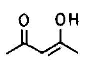
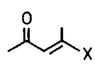
2

Scheme B

If an additional solvent is used, e.g., chloroform, which keeps the phosphonium salt (**2**) dissolved, the above stoichiometry (Scheme **A**) has to be considered even with open chain diketones.

Attempts to convert β-keto-aldehydes (2-formylcyclohexanone, benzoylacetaldehyde, *p*-bromobenzoylacetaldehyde) into the corresponding β-halovinyl ketones were unsuccesful. Under the conditions of the general procedure given below we obtained only resinous material.

Table. Reaction of β-Diketones with Triphenylphosphine and Carbon Tetrahalide

Diketone	Product	X	Yield (%)	b.p./torr
		Cl	85	74–76°/12
		Cl	81	83–85°/7
		Cl Br	82 85	92–94°/14 53–55°/1
		Cl	79	126–127°/0.5
		Cl Br	73 75	34–35°/1.5 69–70°/10
		Cl	81	44–45°/23

General Procedure for the Preparation of Chlorides:

Stoichiometric amounts of triphenylphosphine and the diketone were dissolved (or suspended) in dry carbon tetrachloride (1.5 ml per g of phosphine) and heated at 50–55° with stirring. In about 15 min the mixture became turbid and the salt **1** began to separate in crystalline form. The reaction was complete in 3–4 hours. The phosphonium salt **1** (80–97%) was filtered off and the carbon tetrachloride removed on a rotatory evaporator, leaving a semicrystalline residue which was triturated with pentane. Insoluble triphenylphosphine oxide (90–100%) was filtered off and the solvent evaporated to give the crude product (90–100%) which, after fractionation, afforded analytically pure material.

General Procedure for the Preparation of Bromides:

To the solution or suspension of diketone (2 mol-equiv) and triphenylphosphine (3 mol-equiv) in chloroform (1.5 ml per g of phosphine) stirred at 45°, a solution of carbon tetrabromide (1 mol-equiv) in chloroform (1 ml per g) was added. After 3 hours the chloroform was removed by rotary evaporation and the residue extracted with pentane followed by work up as described above.

Received: August 8, 1975

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[1] L. F. Fieser, M. Fieser, *Reagents for Organic Synthesis*, Vol. 1, Wiley, New York, 1968, p. 1247.

[2] J. B. Lee, T. J. Nolan, *Tetrahedron* **23**, 2789 (1967).

[3] J. B. Lee, T. J. Nolan, *Can. J. Chem.* **44**, 1331 (1966).

[4] I. Tömösközi, L. Gruber, L. Radics, *Tetrahedron Lett.* **1975**, 2473.

[5] R. D. Clark, C. H. Heathcock, *Synthesis* **1974**, 47.