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TRITYLPOTASSIUM
A NEW DEHYDROHALOGENATION REAGENT

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ABSTRACT: Ph_3CK rapidly dehydrohalogenates secondary alkyl bromides and iodides at 0^oC to give olefins in very high yield ($> 90\%$)

Dehydrohalogenation of alkyl halides is often slow. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), one of the best reagents[1], requires a temperature of 90^o for 2-bromooctane,[2] for example. In the course of other work, we found that Ph_3CK[3] is a far more effective reagent for this reaction. 2-Bromooctane reacts over a period of seconds at 0^oC to give approximately equal amounts of 1- and 2-octene (Table I, entry 4).

The experiments were carried out by adding 6.1 mmol of Ph_3CK in diglyme over 5 min. to a solution of the alkyl halide (6.0 mmol) in diglyme (10 ml). The disappearance of the red color of the organometallic reagent signals the completion of the reaction. Yields were determined by GC analysis against an internal standard (toluene or o-xylene). As will be seen in the Table, a variety of secondary alkyl halides are efficiently dehydrohalogenated to the corresponding olefins. The reaction was not particularly solvent-sensitive, DME, ether, benzene, and diglyme were all satisfactory. Ethyl dihydrocinnamate did not interfere, but the presence of cyclohexanone led to a drop in yield, presumably due to enolate formation[3] (entry 7) in the case when only one equivalent of Ph_3CK is used. The reaction failed for primary halides (entry 10) and gave poor yields for alkyl chlorides, e.g., cyclohexyl chloride (entry 9). The covalent Ph_3CLi was far less effective than the ionised Ph_3CK (entry 8).

Carbenes do not seem to be involved.[4] No evidence for the formation of cyclopropanes by attack of a carbene on a free olefin was ever observed, and cyclooctyl bromide gave cyclooctene, not [3.3.0]-bicyclooctane, an insertion product of cyclooctyl carbene.[5] We assume the reaction goes by an E2 mechanism.

$$RCHXCH_2R' + Ph_3C^- \; K^+ \xrightarrow[0^o,\ 5min.]{diglyme} RCH{=}CHR' + Ph_3CH + KX$$

$$(X = Br, I)$$

Table I

Dehydrohalogenation with Ph_3CK

1. Cyclohexyl bromide	0	Cyclohexene	98
2. Cyclopentyl bromide	0	Cyclopentene	>99
3. Cyclooctyl bromide	0	Cyclooctene	90
4. 2-bromooctane	0[b]	1-octene	47
		2-octene	53
5. Cyclohexyl iodide	0	Cyclohexene	93
6. Cyclohexyl bromide[c]	0	Cyclohexene	95
7. Cyclohexyl bromide[d]	0	Cyclohexene	5
8. Cyclohexyl bromide[e]	0	Cyclohexene	62[f]
9. Cyclohexyl chloride	80	Cyclohexene	40[g]
10. 1-bromooctane	0	1-octene	trace

a) by GC versus an internal standard.

b) product ratios essentially the same at -20° and at 90°C.

c) in the presence of ethyl dihydrocinnamate (1 equiv).

d) in the presence of cyclohexanone (1 equiv.)

e) using Ph_3CLi

f) after ½hr.

g) after 1 hr.

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