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MILD REDUCTION OF α-HALO KETONES TO KETONES PROMOTED BY PI_3 OR P_2I_4

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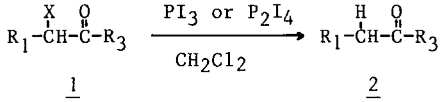
PI_3 and P_2I_4 cleanly reduce α-bromo and α-iodo ketones to ketones

We are currently investigating [1] the behaviour of PI_3 and P_2I_4, two inorganic reagents which have been only scarcely used in the past and which we found valuable as reducing agents[2].

We now find that these readily available reagents [3] reduce α-iodo and α-bromo ketones to ketones (P_2I_4:0,55 mmol ; PI_3:1,1 mmol). The reactions occur readily (1-8hrs) in CH_2Cl_2, usually at room temperature and require stoicheiometric amount of phosphorus derivative. Moreover, the organic phosphorus by products formed during the reactions are water soluble and are easily discarded from the desired ketone. As expected α-iodo ketones are much faster reduced than their bromo analogues. The reaction works particularly well in case of aliphatic ketones,which usually require more drastic conditions [4] than the aryl ones.

SCHEME I



$$R_1\text{-}\overset{X}{C}H\text{-}\overset{O}{\overset{\|}{C}}\text{-}R_3 \xrightarrow[CH_2Cl_2]{PI_3 \text{ or } P_2I_4} R_1\text{-}\overset{H}{C}H\text{-}\overset{O}{\overset{\|}{C}}\text{-}R_3$$

1 2

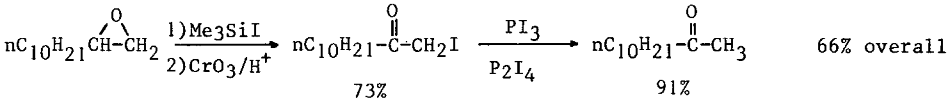
X = Br,I

The methods proposed can be advantageously compared to the ones already described[4-7]

The mechanism of this reaction is not clear at present. The transformation can be explained by direct attack of the phosphorus atom on the halide of 1 (a process already described for the reaction of triphenylphosphine with α-halo ketones [7]) or by interaction of the oxygen of the carbonyl group with the phosphorus atom and further attack of the iodine ion released on the halogen.Both mechanisms should produce an enolate. Recent reactions which use sodium iodide in connection with an acid[4] or chlorotrimethylsilane [6] have been proposed to work via the latter mechanism. These results and others suggest the possible direct conversion of α-hydroxyketones[8] and α-halo acetals[9] to ketones. We are currently investigating such reactions.

Finally, this reaction coupled with the one we describe in the previous paper allows the high yield "two pots" conversion of epoxides to ketones. To our knowledge, this is an unusual transformation.

SCHEME II



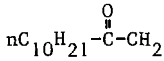
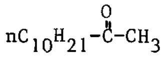
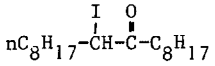
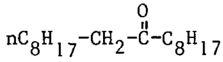
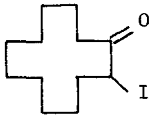
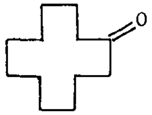
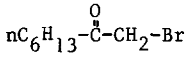
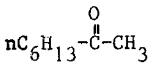
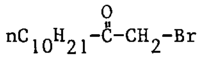
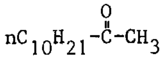
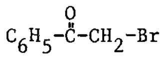
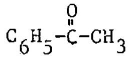
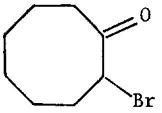
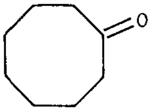
$$nC_{10}H_{21}CH\overset{O}{\text{-}}CH_2 \xrightarrow[2)CrO_3/H^+]{1)Me_3SiI} nC_{10}H_{21}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2I \xrightarrow[P_2I_4]{PI_3} nC_{10}H_{21}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

73% 91% 66% overall

Epoxides can be converted to carbonyl compounds [10] in acidic media. The reaction usually implies skeleton rearrangements and in the case of terminal epoxides leads to an aldehyde whereas

TABLE

Reduction of α-halo ketones with PI_3 *and* P_2I_4

Substrate 1	Reagent	Ketone 2	t,h/temp.	Yield (%)
 $nC_{10}H_{21}-\overset{O}{\overset{\|}{C}}-CH_2I$	P_2I_4 PI_3	 $nC_{10}H_{21}-\overset{O}{\overset{\|}{C}}-CH_3$	1.0/25° 1.0/25°	91 89
 $nC_8H_{17}-\overset{I}{\overset{\mid}{C}}H-\overset{O}{\overset{\|}{C}}-C_8H_{17}$	PI_3	 $nC_8H_{17}-CH_2-\overset{O}{\overset{\|}{C}}-C_8H_{17}$	1.0/25°	97
	P_2I_4		1.0/25°	92
 $nC_6H_{13}-\overset{O}{\overset{\|}{C}}-CH_2-Br$	P_2I_4 PI_3	 $nC_6H_{13}-\overset{O}{\overset{\|}{C}}-CH_3$	4.5/25° 4.5/25°	82 75
 $nC_{10}H_{21}-\overset{O}{\overset{\|}{C}}-CH_2-Br$	P_2I_4	 $nC_{10}H_{21}-\overset{O}{\overset{\|}{C}}-CH_3$	5.0/25°	87
 $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-Br$	P_2I_4	 $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$	6.5/25° 8.0/50°	54 91
	P_2I_4		7.0/25°	91

we obtain exclusively the methyl ketone by our procedure.

References and notes

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