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A CONVENIENT METHOD FOR THE REDUCTION OF 1-(2-OXOALKYL)PYRIDINIUM SALTS

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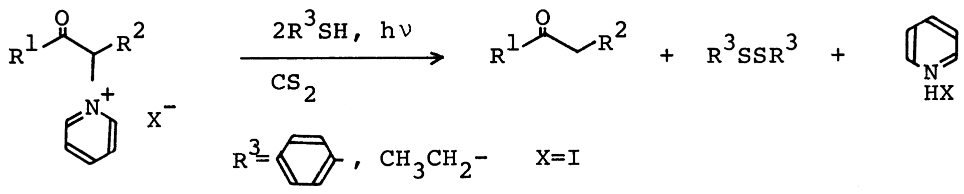
1-(2-Oxoalkyl)pyridinium salts were reduced to the corresponding ketones in high yields by the photochemical reaction with thiol in the presence of carbon disulfide.

The reduction of 1-(2-oxoalkyl)pyridinium salts to the corresponding ketones with zinc dust in acetic acid[1)] has been reported for the sake of ketone synthesis which involves the alkylation of ketopyridinium betaines. It is also reported that the dehalogenation of α-halo ketones is performed by the reduction of the corresponding pyridinium salts with sodium dithionite.[2)] Here we wish to report a new and useful method for the reduction of 1-(2-oxoalkyl)pyridinium salts by the photochemical reaction with thiol in the presence of carbon disulfide under mild conditions.

Recently we reported the facile methods for the preparation of α-diketones[3)] or α-ketocarboxylic esters[4)] by the photochemical reaction of 1-(2-oxoalkyl)-pyridinium iodides or 1-(1-ethoxycarbonylalkyl)pyridinium iodides with oxygen gas, respectively. Further study on the photochemical reaction of 1-(2-oxoalkyl)-pyridinium iodides has been achieved, and it was found that 1-(2-oxoalkyl)-pyridinium iodides were readily reduced to the corresponding ketones in high yields by the use of thiol such as benzene thiol or ethane thiol under irradiation with a high-pressure mercury lamp in the presence of carbon disulfide. It was confirmed that the present reduction did not proceed without irradiation.



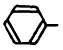
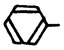
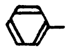
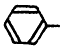
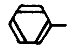
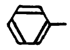
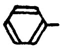
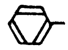
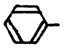
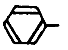
The typical reaction procedure is described for the reduction of 1-(1-benzoylpropyl)pyridinium iodide with benzene thiol; to a well degassed $CHCl_3$ (15 ml) solution of 1-(1-benzoylpropyl)pyridinium iodide (1 mmol) in a pyrex glass testtube was added benzene thiol (2.2 mmol) and carbon disulfide (5 ml) under an argon atmosphere. The reaction mixture was irradiated with a high-pressure mercury lamp for 3 hr. After the irradiation, the resulting white precipitate of pyridine hydroiodide was filtered off and the filtrate was condensed under reduced pressure.

The residue was chromatographed on silica gel and 1-phenyl-1-butanone was isolated in 86% yield.

Contrary to these results, when the present reaction procedure was applied to the pyridinium salt of α-bromo ketone such as 3-bromo-2-undecanone, the corresponding ketone was obtained only in a poor yield. This difficulity was overcome by the addition of 1.1 molar equivalents of tetra-n-butylammonium iodide in the above-mentioned reaction.

In a similar manner, various 1-(2-oxoalkyl)pyridinium salts were reduced to the corresponding ketones in high yields (see Table).

Table. The photoreduction of 1-(2-oxoalkyl)pyridinium salts.

R^1	R^2	R^3	X	Time(hr)	Yield(%)
			I	3	quant
	CH_3CH_2-		I	3	58[a]
			I	3	86
		CH_3CH_2-	Br	4	88
	CH_3-	CH_3CH_2-	Cl	2	95
CH_3-	-CH_2-	CH_3CH_2-	Br	20	95
CH_3-	$CH_3(CH_2)_9$		I	20	31
		CH_3CH_2-	I	10	95
		CH_3CH_2-	Br	20	96
CH_3-	$CH_3(CH_2)_7$	CH_3CH_2-	Br	20	92
$CH_3(CH_2)_3$	$CH_3(CH_2)_2$		I	20	38
		CH_3CH_2-	I	16	81
$(CH_2)_2CH(t\text{-}Bu)CH_2$-		CH_3CH_2-	Br	20	25[b]

a) One point one molar equivalents of thiol was used.

b) Five molar equivalents of thiol was used.

Though we have few experimental results which clarify the reaction pathway of the photochemical reaction of 1-(2-oxoalkyl)pyridinium salts with thiol at present, it should be noted that the yields of ketones depend on the nucleophilicity of the thiol and the presence of carbon disulfide is essential for the present reduction.

Further works including the mechanistic study are now in progress.

References

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