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A NEW METHOD FOR THE PREPARATION OF α-DIKETONES BY THE PHOTO-OXIDATION OF β-KETOALKYLPYRIDINIUM IODIDES

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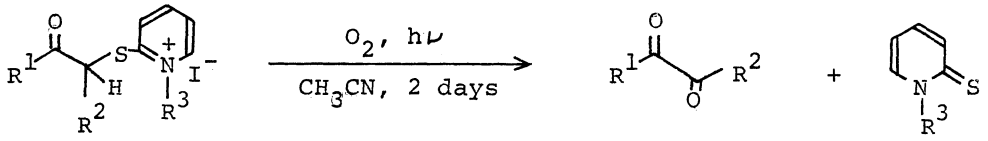
α-Diketones were obtained in good yields by the photo-oxidation of β-ketoalkylpyridinium iodides in the presence of tetra-n-butylammonium iodide.

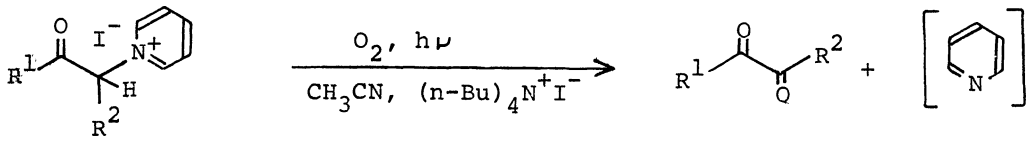
In the course of our study on the reaction of pyridinium salts, it was found that the photo-oxidation of N-alkyl-2-(β-ketoalkylthio)-pyridinium iodides(I) took place smoothly to afford the corresponding α-diketones (II) and N-alkyl-2-pyridothione (III) in fairly good yields. It was confirmed that the present oxidation reaction did not proceed without light.



(I) (II) (III)

R^1=Me, R^2=$PhCH_2$, R^3=Me 42% 43%

Further it was established that the photo-oxidation of β-ketoalkylpyridinium iodides (IV) in the presence of tetra-n-butylammonium iodide proceeded very rapidly at room temperature to afford α-diketones under irradiation with a high pressure mercury lamp.



(IV) (II)

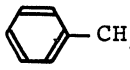
The following procedure is representative. A solution of ω-ethylphenacylpyridinium iodide (1.0 mmol) and tetra-n-butylammonium iodide (1.5 mmol) in CH_3CN (20 ml) was irradiated with the high pressure mercury lamp while oxygen was bubbled through. After the irradiation (30 min), the reaction mixture was poured into an aqueous Na_2SO_3 solution, and the mixture was shaken until a red color of iodine disappeared. An organic layer was extracted with ether and the extract was condensed under reduced pressure. The residue was chromatographed on silica gel and 1-phenyl-1,2-butanedione was isolated in 80% yield.

Similarly, various pyridinium iodides were oxidized to give the corresponding α-diketones in good yields as shown in the Table.

The photo-oxidation of the pyridinium iodides also took place in a slightly basic aqueous solution. For example, a solution of ω-ethylphenacylpyridinium iodide (1.0 mmol), tetra-n-butylammonium iodide (0.73 mmol) and $NaHCO_3$ (1.0 mmol) in H_2O (10 ml)-CH_3CN (10 ml) was treated according to the manner described in the case of the oxidation in an organic solution to afford 1-phenyl-1,2-butanedione in 81% yield. While, in the cases of the pyridinium salts derived from α-iodo-dialkylketones, the corresponding α-diketones were obtained in insufficient yields (20-60%).

On the other hand, α-diketones were not obtained under acidic (0.1N HCl -CH_3CN) or neutral (pH 7 phosphate buffer - CH_3CN) condition and the unreacted pyridinium salts were detected on tlc. The α-diketone also was not produced when K_2CO_3, which is commonly employed for the generation of stable pyridinium ylids, was used as a base. These results indicate that the present oxidation in aqueous solution proceeds only under limited pH values.

Table. The photo-oxidation of β-ketoalkylpyridinium iodides.

R^1	R^2	non-aqueous medium time(min)	yield(%)	aqueaus medium time(min)	yield(%)
	C_2H_5-	30	80	10	81
	CH_3-	30	78	10	72
		15	95	10	84
CH_3-	CH_3-(-CH_2-)$_5$	30	70	30	56
CH_3-	CH_3-(-CH_2-)$_9$	60	70	30	60
CH_3-(-CH_2-)$_3$	CH_3-(-CH_2-)$_2$	60	64	30	54
-$C(CH_3)(n\text{-}C_4H_9)$-(-CH_2-)$_3$		15	71	10	35
CH_3-				10	20

In the chemistry of pyridinium salts and pyridinium ylids, it is one of the most important problems to eliminate pyridine moiety from the pyridinium salt to yield the desired product. Concerning the reductive elimination of pyridine moiety of the pyridinium salts, several methods[1] are already known. On the other hand, few studies about the oxidative cleavage of C-N bond of the pyridinium salts were reported.[2]

According to the present method, oxygenated products are obtained in good yields under mild conditions by the oxidative fission of C-N bond of the pyridinium iodides. Therefore, it would provide a useful synthetic route in the chemistry of pyridinium salts.

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