

SODIUM 4,6-DIPHENYL-1-OXIDO-2-PYRIDONE: REAGENT FOR THE
CONVERSION OF PRIMARY HALIDES INTO ALDEHYDES^{1,2}

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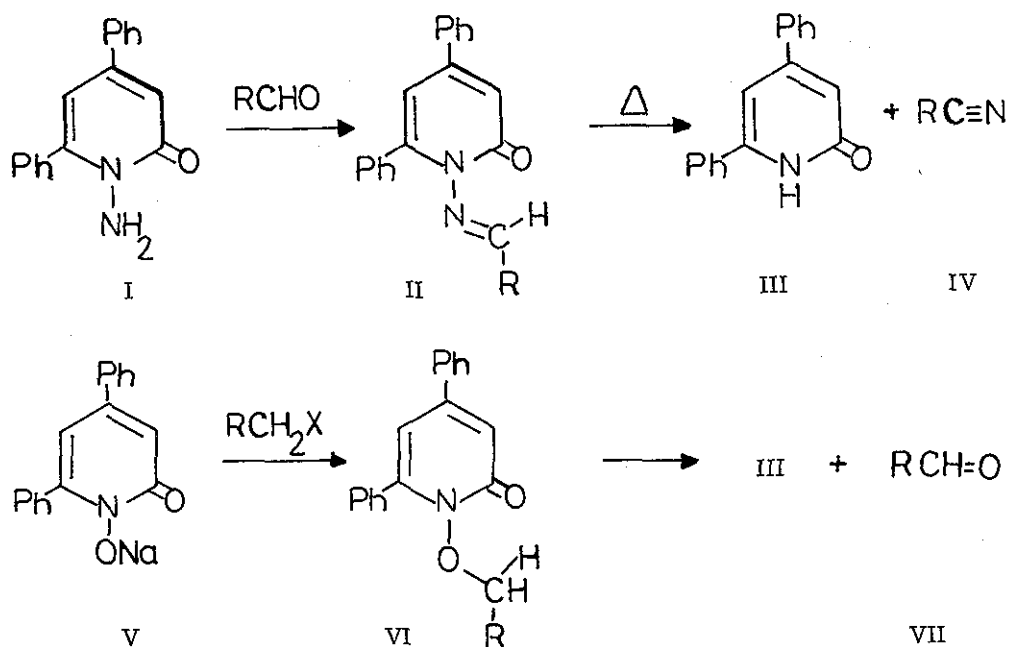
The title compound readily reacts with primary halides to yield stable 1-alkoxypyridones VI which are smoothly converted thermally to aldehydes and non-volatile 4,6-diphenylpyridone. The intermediate 1-alkoxypyridones VI form convenient crystalline derivatives for alkyl and benzyl halides.

A considerable number of methods are already available for the conversion of halides into carbonyl compounds.³ Many of these are admirable in particular circumstances but often suffer from a lack of overall generality. The most important⁴⁻¹³ are listed in Table 1, in which an attempt is made to indicate reaction conditions which could affect other functional groups, and/or the structural types to which the method cannot be applied.

Table 1: Literature methods for conversion of halides into carbonyl compounds

Reagent	Name	Ref.	Base ^{a)}	Ox ^{b)}	Bzl ^{c)}	St ^{d)}	NO ₂ ^{e)}
Me ₂ C=NO ₂ Na	Haas-Bender	4	X	-	-	-	X
Me ₂ SO, AgOTs	Kornblum	5	X	-	-	-	-
C ₅ H ₅ N, ONC ₆ H ₄ NMe ₂	Kröhnke	6	X	-	X	-	-
C ₆ H ₁₂ N ₄	Sommelet	7	-	-	X	X	X
R ₃ N ⁺ -O ⁻	-	8-10	X	-	-	-	-
Metal nitrates	-	11-13	X	X	X	-	X

The limitations are indicated as follows: a) Basic conditions. b) Sensitive groups easily oxidised. c) Reaction only goes well for benzyl halides. d) Reaction susceptible to steric hindrance. e) Reaction not suitable for nitrobenzyl halides.



Following our work on the conversion of aldehydes into nitriles by the sequence $1 \rightarrow \text{IV}^{14}$, we have investigated the conceptually similar sequence $\text{V} \rightarrow \text{VII}$, which we now wish to propose as a superior method for the conversion of halides to carbonyl compounds under neutral and non-oxidative conditions.

The anhydrous sodium salt V is a stable, crystalline material readily generated from 1-hydroxy-4,6-diphenyl-2-pyridone¹⁵ by the action of 1 equivalent of sodium methoxide in methanol under reflux for 1 hr. It reacts with a wide variety of halides to yield intermediates of type VI, usually in excellent yield (Table 2). The intermediate alkylated pyridones VI are crystalline and easily isolated. They thermolyse smoothly at ca. 180-200° to yield non-volatile 4,6-diphenyl-2-pyridone and the corresponding carbonyl compound, again usually in high yield (Table 2). The major advantage of the present method is the high yield and wide generality combined with non-basic and non-oxidising conditions. In addition to providing a method for their conversion into carbonyl compounds, the 1-alkoxy-2-pyridones VI provide useful crystalline characterisation products, particularly for benzyl halides.

In the general procedure the halide (0.8 g) and V (1.1 equiv.) in dry MeOH or EtOH (40 ml) were reacted at 0 °C or under reflux for 2-20 hr depending upon halide reactivity. The cooled solution was filtered and evaporated to dryness. The intermediate VI was separated from excess V and sodium halide by extraction into CHCl_3 , and subsequent recrystallisation from aqueous EtOH. Fragmentation to the aldehyde was achieved by vacuum thermolysis (180-200 °C: 2-4 hr) in a distillation or sublimation unit as appropriate.

The decomposition of VI (R = 2,4,6-trinitrophenyl) which is facilitated by the electron withdrawing substituents was accomplished in refluxing xylene within 4 hr. The general use of high boiling solvents for the conversion VI $\rightarrow$ VII and extension of the method for converting secondary halides into ketones are currently under investigation.

Table 2: The conversion of halides into aldehydes via sequence V $\rightarrow$ VII.

Halide	Preparation of intermediate VI			Pyrolysis of VI to aldehyde VII		
	Procedure	Yield (%) of VI	Mp	Procedure	Yield (%) of VII	Characterisation of VII
$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	a)	94	127-129°	d)	73	g), h)
$\text{o-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$	a)	92	114-116°	d)	77	g), h)
$\text{o-CNC}_6\text{H}_4\text{CH}_2\text{Br}$	a)	91	165-167°	e)	86	g), i)
$\text{o-MeOC}_6\text{H}_4\text{CH}_2\text{Br}$	a)	90	124-126°	e)	79	g), j)
$\text{m-CNC}_6\text{H}_4\text{CH}_2\text{Br}$	a)	97	140-142°	e)	70	g), i)
$\text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$	a)	99	140-141°	e)	79	g), j)
$2,4,6-(\text{NO}_2)_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$	b)	72	168-170°	f)	93	g), i)
$\text{CH}_2\text{:CHCH}_2\text{Br}$	c)	90	oil	d)	65	g), h)
$\text{CH}_3\text{CH:CHCH}_2\text{Cl}$	c)	96	86-88°	d)	59	g), h)
$\text{n-C}_4\text{H}_9\text{Br}$	c)	90	109.5-111°	d)	55	g), h)
$\text{n-C}_7\text{H}_{15}\text{Br}$	c)	97	67-69°	d)	50	g), h)

a) Treatment of halide with an equivalent of V in refluxing methanol. b) Treatment as for a) but at 0 °C. c) Treatment as for a), in refluxing ethanol. d) Vacuum distillation of thermolysis products. e) Sublimation of thermolysis products. f) Refluxed in dry xylene. g) Comparison of infrared spectrum with authentic spectrum. h) Formation of 2,4-dinitrophenylhydrazone. i) Melting point comparison. j) Recording of nmr spectrum.

FOOTNOTES AND REFERENCES

- 1 Contributed in Honour of the 60th birthday of Professor Robert B. Woodward.
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