

Formic Acid as a Hydride Donor : Reduction of Acid Chlorides to Aldehydes

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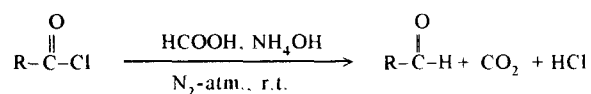
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Abstract : Chlorides of a variety of acids : primary, secondary, tertiary, long chain aliphatic and $\alpha\beta$ -unsaturated have been converted into aldehydes by reduction with formic acid at pH 9-10 at room temperature in high yields. © 1998 Elsevier Science Ltd. All rights reserved.

We wish to report here a new and convenient method for the preparation of aldehydes from acid chlorides. In the past, the Rosenmund reduction¹ used to be the method of choice for the conversion of acid chlorides to aldehydes. Numerous methods have been developed since to carry out this conversion^{2,3,4,5}. The majority of these reactions involve the use of expensive reagents and stringent experimental conditions, for example, rigorous exclusion of moisture, use of low temperatures etc.

Commonly acid anhydrides are the expected products when salts of acid and acid chlorides react with one another. Formic acid possessing the dual characteristics of an aldehyde and an acid behaves differently from other acids in its reducing character. It has been reported to effect reduction by hydride transfer⁶ and among the substrates reduced are pyridine⁷, Schiff's bases⁸, enamines⁹ and pyridinium salts¹⁰. It was, postulated that by using formic acid as a hydride donor acid chlorides could be reduced to aldehydes. We have now found this reaction to be feasible (Scheme I) and have succeeded in preparing several aldehydes (Table I).



(Scheme I)

Table I

R	Time (min)	Yield %	R	Time (min)	Yield %	R	Time (min)	Yield %
C ₂ H ₅	35-40	79	PhCH ₂	45-50	80	(CH ₃) ₂ C=CH	40-45	86
n-C ₃ H ₇	25-30	90	Cl-CH ₂	40-45	82	Ph-CH=CH	40-45	90
C ₁₁ H ₂₃	20-25	96	CH ₃ -CHCl	40-45	79	PhC≡C	35-40	79
C ₁₅ H ₃₁	15-20	95	Cl ₃ C	40-45	76	iso-C ₃ H ₇	20-25	86
C ₁₇ H ₃₅	15-20	94	$\Delta^{10}\text{C}_{10}\text{H}_{19}$	30-35	91	(CH ₃) ₃ C	15-20	85
Ph	30-35	79	$\Delta^9\text{C}_{17}\text{H}_{33}$	25-30	91			

Our results show that chlorides of a variety of acids: primary, secondary, tertiary, long chain aliphatic, aromatic, $\alpha\beta$ -unsaturated and $\alpha\beta$ -acetylenic can be successfully reduced to aldehydes by this method. Additionally, the presence of isolated double bonds and halogens does not hamper the reaction.

The acid chloride, was dissolved in chloroform/ether and treated with ammonium hydroxide to which was gradually added formic acid (excess: three fold over acid chloride). A thin stream of N_2 was bubbled through the mixture during the course of the reaction to minimise aerobic oxidation of the aldehyde. Stirring was continued at ambient temperature. After completion of the reaction, the organic layer was separated and the solvent removed to yield the aldehyde. Ether was used to facilitate the isolation of the aldehydes with low boiling points.

In all cases, the formation of aldehydes were confirmed by testing with Fehling's, Benedict's and Tollens' reagents and identified by determination of refractive index as well as by derivatisation. Homogeneity of the prepared aldehydes were confirmed by GLC/TLC.

This method involves the use of inexpensive and easily accessible reagents and is extremely simple. The time required for this conversion is uniformly less than an hour. The reaction requires no heating or cooling and work up of the reaction mixture is very simple. The products obtained are pure and require no further purification. This method, hence, holds the promise of evolving into a general method for the preparation of aldehydes.

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