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PHOTOSENSITIZED OXYGENATION OF ALDEHYDE-AMINE MIXTURE. FACILE CARBONYL TRANSFORMATION FROM ALDEHYDE TO AMINE INVOLVING RECYCLIZATION PROCESS[1]

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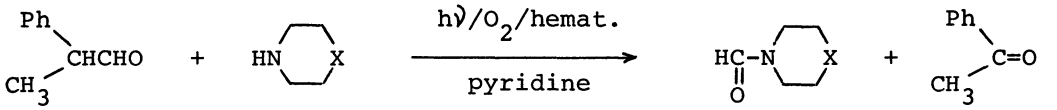
Photosensitized oxygenation of mixture of various aldehydes and morpholine(piperidine) gave N-formylmorpholine(N-formylpiperidine). When long chain non-branched aldehydes were used, the N-formylamine was obtained in more than 100% yield on the basis of aldehyde. This effective carbonyl transfer to amine includes reproduction of aldehyde.

Oxidative cleavage of carbon-carbon double bond to produce carbonyl compounds is one of the most useful synthetic methods.[2] It is well known that singlet oxygen undergoes 1,2-cycloaddition[3] to activated double bond, such as vinyl ethers,[4] vinyl sulfides,[5] and enamines[6] to give carbon-carbon cleavage products via 1,2-dioxetanes, which have been suggested as the reaction intermediates in certain cases of oxidative double bond cleavage. Especially, the reaction of aldehyde enamines with singlet oxygen affords corresponding ketones and N-formylamines as carbon-carbon cleavage products in quantitative yields.[6a)] Now we wish to report that photosensitized oxygenation of mixture of aldehyde and amine affords exclusively N-formylamine by carbonyl transformation from aldehyde to amine in good yield.

Mixture of α-phenylpropionaldehyde (I, 1 equiv.) and morpholine (II, 1.2 equiv.) in pyridine was irradiated by 500 W tungsten lamp with oxygen bubbling for 40 min. in the presence of hematoporphyrine as sensitizer. The solution took up about 1.2 equivalent of oxygen. Solvent evaporation followed by glpc analysis gave N-formylmorpholine (III) in 70% yield accompanied with acetophenone (IV, 64%). Also the reaction of (I) and piperidine (V) gave N-formylpiperidine (VI) in 68% yield on the basis of (I).

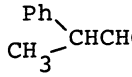
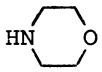
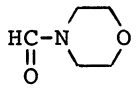
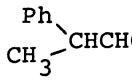
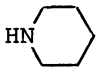
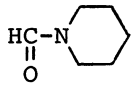
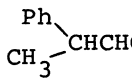
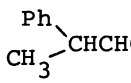
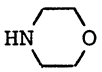
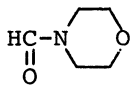
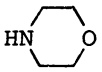
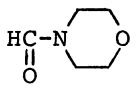
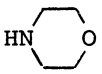


(I) (II) X= O (III) 70% (IV) 64%

(V) X= CH_2 (VI) 68% 64%

Appropriate control experiments indicated that the sensitizer, oxygen, and light were all necessary for these reactions. Products were characterized by spectroscopic and gas chromatographic comparisons with those of authentic samples. Results for various aldehyde and amine were summarized in Table I.

Table I. Yields of N-formylamines in the reactions of aldehyde-amine mixture with singlet oxygen.

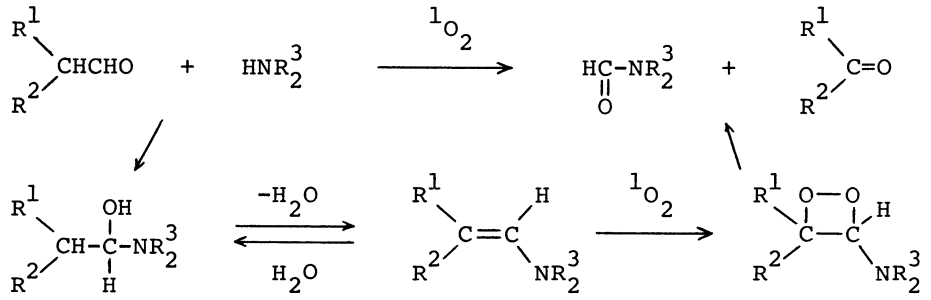
Aldehyde	Amine	N-Formylamine	Yield (%)
			70
			68
	$HN(CH_2CH_3)_2$	$HC(=O)N(CH_2CH_3)_2$	67
	$HN(CH_3)Ph$	none[a]	—
$(CH_3)_2CHCHO$			60
CH_3CHO			45
PhCHO		none[a]	—

a) Aldehyde and amine were recovered in quantitative yield.

As shown in Table I, in case of the reactions with benzaldehyde or N-methylaniline, N-formylamine was not obtained, and the starting aldehyde and amine were only recovered under the reaction conditions. It may be important that aldehydes should contain at least one α-hydrogen for these carbonyl transformation reactions.

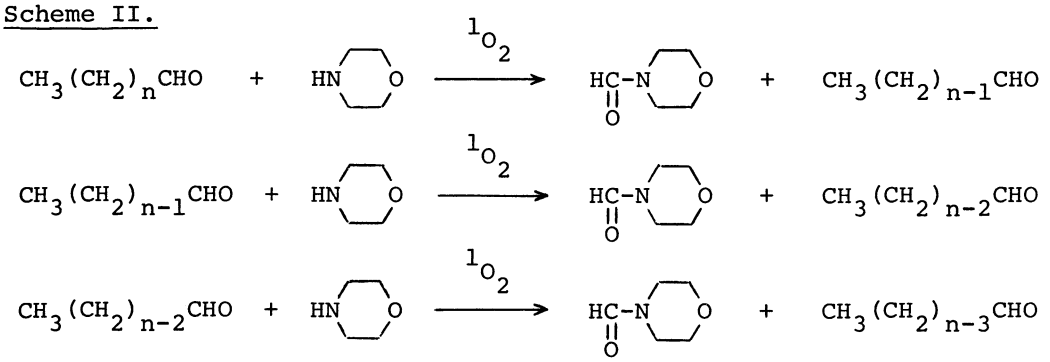
Considering that this reaction proceeded only in the combination of aldehydes containing α-hydrogen and alkylamines, the carbonyl transformation seems to involve the formation of enamine as intermediate. (Scheme I) It is significant that the N-formylamine and ketone are obtained without using enamine as reactant. Formally, the formation of N-formylamine was taken to be carbonyl transformation from aldehyde to amine by photosensitized oxygenation.

Scheme I.



In the aspect of synthetic method, the yields of N-formylation product are of much importance. When an excess of amine is used, the N-formylamine yields more than 100% on the basis of aldehyde. (Scheme II)

Scheme II.



Mixture of propionaldehyde (VII, 2.73 mmole) and morpholine (5.76 mmole) in methylene chloride was irradiated for 90 min in the presence of methylene blue. N-formylmorpholine was obtained in 103% yield on the basis of (VII), as expected. Further, mixture of propionaldehyde (2.73 mmole) and morpholine (11.52 mmole) gave N-formylmorpholine in 145% yield. When n-octylaldehyde (VIII) was used, the yield of N-formylmorpholine went up to 272% by irradiation for 240 min. (Table II.) Also the reaction of mixture of (VIII) and piperidine affords the same results. For example, N-formylpiperidine was obtained in 282% yield for 1.29 mmole of (VIII) and 20.5 mmole of (V).

Table II. Yields of N-formylmorpholine (III) in mixture of aldehyde (A) and morpholine (B).

Aldehyde (A)	Mole ratio (B)/(A)	Irrdn. time (min)	Yield of (III) (%)
CH_3CH_2CHO	1.05	90	46
CH_3CH_2CHO	2.10	90	103
CH_3CH_2CHO	4.20	90	145
CH_3CH_2CHO	6.30	180	162
$CH_3(CH_2)_2CHO$	4.90	90	109
$(CH_3)_2CHCHO$	5.20	90	35
$CH_3(CH_2)_6CHO$	8.90	90	213
$CH_3(CH_2)_6CHO$	8.90	240	272

The reaction process which includes reproduction of aldehyde can be used as a useful synthetic method of N-formylamine.

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