CHEMISTRY LETTERS, pp. 2167-2168, 1987.

Preparation of Enamides via Reductive Acylation of N-Acetoxyimino Compounds by Use of $Fe_3(CO)_{12}$

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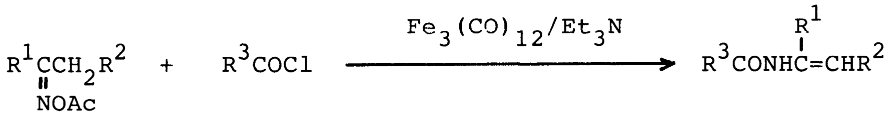
Treatment of N-acetoxyimino compounds with $Fe_3(CO)_{12}$ in the presence of acyl halides and triethylamine gave enamides in good yields.

The reductive fission of N-O bond in organic compounds induced by iron carbonyl complexes is useful methodology in organic synthesis.[1-5] We now report that N-acetoxyimino compounds can be converted into enamides in good yields upon treatment with $Fe_3(CO)_{12}$ in the presence of acyl halides and triethylamine.



$$\underset{\text{NOAc}}{\underset{\|}{R^1C}}H_2R^2 + R^3COCl \xrightarrow{Fe_3(CO)_{12}/Et_3N} R^3CONH\overset{R^1}{\overset{|}{C}}=CHR^2$$

1a-d **2a-i**

A mixture of acetoxy(2-chloro-1-phenylethylidene)azane **1a** (2.0 mmol), $Fe_3(CO)_{12}$ (1.0 mmol) and trietylamine (5.0 mmol) in THF (15 cm^3) was stirred at room temperature for 3-5 h. During this period the mixture changed from green to dark brown. Benzoyl chloride (3.0 mmol) was added, and the resulting mixture was further stirred for 5 h. After removal of the solvent under reduced pressure, the residue was extracted with benzene (30 cm^3). The extract was chromatographed on silica gel with benzene/ethyl acetate (9/1), giving N-(2-chloro-1-phenylethenyl)benzamide **2a** in 84% yield. Similar treatments of the imino compounds (**1b-d**) gave the corresponding enamides (**2b-f**). The structures of the products were confirmed on the basis of their spectral data[6] and elemental analyses. The results are given in Table 1.

The stereoconfiguration of the enamides depended upon the structure of the starting imino compounds. When substituent R^2 in **1** was phenyl group, the Z-isomers of **2** were exclusively produced. However, from the halogen-containing imino compounds, a mixture of the Z- and E-isomers was obtained, and the formation of the Z-isomers predominated. No enamides were obtained from alkylideneazanes such as acetoxy(1-methylpentylidene)azane and acetoxycyclohexylideneazane.

Enamides have been prepared from oximes by two methods. One is the thermolysis in acetic anhydride-pyridine and the other is the reductive acylation by

Table 1. Formation of enamides

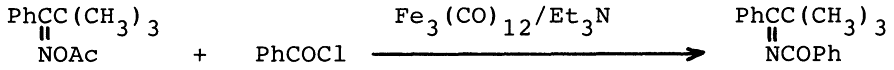
Imino compound			Acyl halide	Enamide			
1	R^1	R^2	R^3	**2**	Mp/°C	Yield/%[a)]	Z:E[b)]
1a	C_6H_5	Cl	C_6H_5	**2a**	168-169[c)]	84	67:33
1a	C_6H_5	Cl	CH_3	**2b**	66-67.5[c)]	14	57:43
1a	C_6H_5	Cl	$(CH_3)_2CBr$	**2c**	81-82[c)]	55	69:31
1b	C_6H_5	Br	C_6H_5	**2d**	169-170[c)]	48	81:19
1b	C_6H_5	Br	CH_3	**2e**	oil	33	77:23
1c	C_6H_5	C_6H_5	C_6H_5	**2f**	175-175.5	56	100
1c	C_6H_5	C_6H_5	$(CH_3)_2CBr$	**2g**	121-122	98	100
1c	C_6H_5	C_6H_5	CCl_3	**2h**	122-125	95	100
1d	CH_3	C_6H_5	C_6H_5	**2i**	65-67	37	100

a) Isolated yields based on imino compounds used. b) The isomer ratios were determined by GLC analyses of the reaction mixtures, and the structures of the respective isomers were confirmed by their NMR spectra. c) The mp's of Z-isomers.

use of Cr(II) and Ti(III) salts.[7)] The advantage of the present method over the above methods is that the reaction is applicable to the preparation of halogen-containing enamides. Dehalogenation usually occurs when Cr(II) and Ti(III) salts are used as reducing agents.[8)] Under thermolysis conditions, the halogen-containing imino compounds gave complex mixtures.

The reactivity of iron carbonyl complexes for the reductive acylation decreased in the order: $Fe_3(CO)_{12} \gg Et_3NH[HFe_3(CO)_{11}] \sim Fe_2(CO)_9$. The mononuclear complexes such as $Fe(CO)_5$ and $Na_2Fe(CO)_4$ were uneffective.

The N-acetoxyimino compound having no active hydrogen such as **1e** afforded the corresponding N-benzoylimino compound **3a** instead of enamide.



$$\begin{array}{c}\mathrm{Ph\underset{\|}{C}C(CH_3)_3}\\ \mathrm{NOAc}\end{array} + \mathrm{PhCOCl} \xrightarrow{\mathrm{Fe_3(CO)_{12}/Et_3N}} \begin{array}{c}\mathrm{Ph\underset{\|}{C}C(CH_3)_3}\\ \mathrm{NCOPh}\end{array}$$

1e **3a** Yield: 77%

References

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(Received August 7, 1987)