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SYNTHESIS OF OLEFINS BY NICKEL-CATALYZED DECARBONYLATION OF S-(2-PYRIDYL) THIOATES

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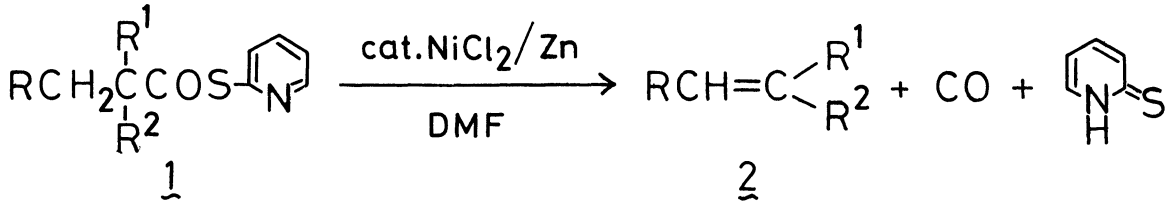
S-(2-Pyridyl) thioates, especially derived from secondary and tertiary carboxylic acids, are decarbonylated by use of a catalytic amount of nickel chloride and zinc powder to give olefins in good yields.

It has been reported that zero valent nickel complexes are oxidatively inserted into CO-O bond of carboxylic esters to afford alkyl metal complexes with decarbonylation under mild conditions.[1] In the previous paper, we reported that S-(2-pyridyl) aromatic thioates readily underwent decarbonylation with bis(1,5-cyclooctadiene)nickel [$Ni(COD)_2$] to give aromatic monoketones in good yields.[2]

Recently, we have found that the decarbonylation of S-(2-pyridyl) thioates also takes place smoothly in the presence of a catalytic amount of nickel chloride and activated zinc powder instead of using an equimolecular amount of $Ni(COD)_2$. In this communication, we wish to report a new and convenient method for the preparation of olefins from S-(2-pyridyl) thioates having a β-hydrogen by way of the nickel-catalyzed decarbonylation as depicted in the following equation.

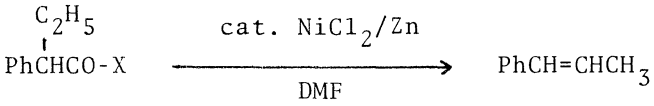


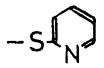
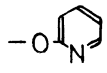
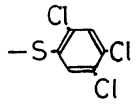
1 2

The typical procedure for the preparation of β-methylstyrene is as follows: Under an argon atmosphere, a mixture of S-(2-pyridyl) 2-phenylpropanethioate [1 mmol], anhydrous nickel chloride [0.05 mmol], activated zinc powder[3] [2 mmol] and N,N-dimethylformamide [1.5 ml] was stirred at 60°C for 3 h, and then extracted with pentane. The extract was washed with water and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography to give β-methylstyrene in 83% yield. It is noted that this reaction does not proceed in the absence of nickel chloride.

The results of the reaction of several 2-phenylpropionic acid derivatives with nickel chloride and zinc powder are shown in Table 1. It is shown that S-(2-pyridyl) 2-phenylpropanethioate gave β-methylstyrene in the best yield among

Table 1. Reaction of carboxylic acid derivatives with nickel catalyst[a)]



X	Conditions °C	h	Yield(%)[b)]
	100	3	83
	110	5	5
—Cl	100	8	0
	100	5	0

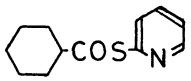
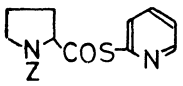
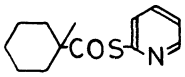
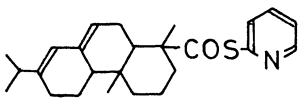
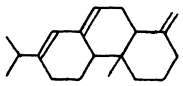
a) Molar ratios of $NiCl_2$ and Zn to acid derivatives were 0.05 and 2.0, respectively.
b) Yield was based on acid derivative.

the acid derivatives examined. This result indicates that S-(2-pyridyl) thioate is more susceptible to reduction by low valent nickel species to be decarbonylated than the other acid derivatives such as acyl halide, 2-pyridyl carboxylate and S-(2,4,5-trichlorophenyl) thioate.

The results of the decarbonylation of various S-(2-pyridyl) thioates having a β-hydrogen are shown in Table 2. S-(2-Pyridyl) thioates derived from acyclic secondary and tertiary carboxylic acids gave the corresponding olefins in high yields, while satisfactory yields of olefins were not given when thioates derived from primary and cyclic carboxylic acids were used.

There have been reported several methods for the decarbonylation reaction of various carboxylic acid derivatives, i.e., the decarbonylation by transition metals such as rhodium, palladium, cobalt and other metals,[4)] and the oxidative decarboxylation by lead tetraacetate[5)] or N-chlorosuccinimide.[6)] The efficient method for olefin formation by decarbonylation of acyl halides using a catalytic amount of rhodium complexes requires high reaction temperature in most cases.[7)] On the contrary, according to the present method, the decarbonylation of S-(2-pyridyl) thioates proceeds under rather milder conditions at 130°C or lower temperature. The oxidative decarboxylation of carboxylic acids having a phenyl

Table 2. Decarbonylation reaction of S-(2-pyridyl) thioates

Entry	R	1 R¹	R²	Conditions °C	h	2 (isomer ratio)[a]		Yield(%)[b]
1	$CH_3(CH_2)_8$	H	H	130	2	$CH_3(CH_2)_8CH=CH_2$		23
2	Ph	H	H	130	0.6	$PhCH=CH_2$		60
3	H	Ph	H	70	0.6	$PhCH=CH_2$		85[c]
4	CH_3	Ph	H	70	3	$PhCH\overset{t}{=}CHCH_3$		83
5	H	PhO	H	70	3	$PhOCH=CH_2$		87
6	$CH_3(CH_2)_2$	C_2H_5	H	100	3	$CH_3(CH_2)_3CH\overset{t}{=}CHCH_3$	(62)	81
						$CH_3(CH_2)_3CH\overset{c}{=}CHCH_3$	(19)	
						$CH_3(CH_2)_2CH\overset{t}{=}CHCH_2CH_3$	(19)	
7				100	8			17
8		d)		100	1.5		d)	82
9	$PhCH_2$	CH_3	CH_3	100	7	$PhCH_2CH_2\overset{CH_3}{\overset{\vert}{C}}=CH_2$	(85)	76
						$PhCH_2CH=C(CH_3)_2$	(15)	
10				100	8		(73)	45
							(27)	
11				100	25			29[c]

a) The ratio of olefin isomers was determined by NMR spectrum and gas chromatogram.
b) Yield was based on S-(2-pyridyl) thioate.
c) Dioxane was used as a solvent.
d) Z=$PhCH_2OCO$

group at the α position using lead tetraacetate affords acetoxyl derivatives as a major product.[8] In contrast, the present nickel-catalyzed decarbonylation of S-(2-pyridyl) thioates derived from those carboxylic acids produces olefins in good yields as shown in entry 3 and 4. In addition, the present method is superior

to the oxidative decarboxylation in isomer ratio of the produced olefins as shown in entry 6 and 9. For example, the decarboxylation of 2,2-dimethylpentanoic acid by lead tetraacetate gave an isomeric mixture of 2-methylpent-1-ene (64%) and 2-methylpent-2-ene (36%).[9]

We assume that, in the present reaction, an alkyl nickel complex is initially formed through the oxidative addition of S-(2-pyridyl) thioate to low valent nickel species followed by loss of CO, and then is converted to an olefin with elimination of a β-hydrogen.

It is noteworthy that the starting materials, S-(2-pyridyl) thioates, are readily prepared from free carboxylic acids by use of dipyridyl disulfide and triphenylphosphine,[10] and the thioates are decarbonylated to give corresponding olefins in good yields under mild conditions using a catalytic amount of nickel chloride and zinc powder. The combination of these two reactions provides a convenient method for the conversion of a free carboxylic acid to the corresponding olefin.

References

1) a) J. Ishizu, T. Yamamoto, and A. Yamamoto, Chem. Lett., 1976, 1091.
b) T. Kohara, S. Komiya, T. Yamamoto, and A. Yamamoto, ibid., 1979, 1513.
2) T. Goto, M. Onaka, and T. Mukaiyama, Chem. Lett., 1980, 51.
3) Org. Synth., Coll. Vol. III, 408 (1955).
4) I. Wender and P. Pino, Ed., "Organic Syntheses via Metal Carbonyls", Vol. 2, John Wiley and sons, Inc., New York (1977), p.595.
5) R. A. Sheldon and J. K. Kochi, Org. React., 19, 279.
6) B. M. Trost, M. J. Crimmin, and D. Butler, J. Org. Chem., 43, 4549 (1978).
7) K. Ohno and J. Tsuji, J. Am. Chem. Soc., 90, 99 (1968).
8) J. D. Bacha and J. K. Kochi, J. Org. Chem., 33, 83 (1968).
9) J. K. Kochi, J. D. Bacha, and T. W. Bethea III, J. Am. Chem. Soc., 89, 6538 (1967).
10) M. Araki, S. Sakata, H. Takei, and T. Mukaiyama, Bull. Chem. Soc. Jpn., 47, 1777 (1974).

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