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REDUCTIVE COUPLING OF S-(2-PYRIDYL) ALIPHATIC THIOATES BY USE OF BIS(1,5-CYCLOOCTADIENE)NICKEL

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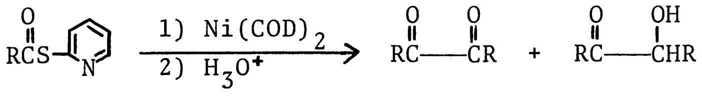
S-(2-Pyridyl) aliphatic thioates are reductively dimerized to give α-diketones and α-hydroxy ketones on treatment with bis(1,5-cyclooctadiene)nickel at 40°C.

The reductive coupling of carboxylic acid derivatives by metallic reducing reagents is one of basic organic synthetic reactions. As reducing reagents, alkali metals are often employed in the coupling such as the acyloin condensation, but there are few reports on the utilization of low valent transition metals. In the previous paper, we reported that S-(2-pyridyl) aromatic thioates are coupled by treatment with bis(1,5-cyclooctadiene)nickel(Ni(COD)$_2$) to give aromatic monoketones in good yields.$^{1)}$ In this communication, we wish to report reductive coupling of S-(2-pyridyl) aliphatic thioates(1) by treatment with Ni(COD)$_2$ which produces α-diketones(2) and α-hydroxy ketones(3).



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An N,N-dimethylformamide-toluene (10:1 v/v, 1 ml) solution$^{2)}$ of S-(2-pyridyl) dodecanethioate$^{3)}$ (1b, 0.9 mmol) was added to Ni(COD)$_2$ (1.8 mmol)$^{4)}$ under an argon atmosphere, and the mixture was stirred at 40°C for 1 h and then worked up with 2N HCl (5 ml). After extraction with Et$_2$O, the extract was dried and purified by silica gel thin layer chromatography (1:2 CHCl$_3$/hexane) to yield tetracosane-12,13-dione (2b, 56%), and 13-hydroxy-12-tetracosanone (3b, 21%).

In a similar fashion, the other dodecanoic acid derivatives such as S-(2-pyrimidyl), S-(2-benzothiazolyl), S-(2-benzoxazolyl), S-(1-methylbenzimidazol-2-yl), or S-pentachlorophenyl dodecanethioate, and 2-pyridyl dodecanoate were treated with Ni(COD)$_2$ in place of S-(2-pyridyl) dodecanethioate in the above experiment. Of the acid derivatives examined, α-diketone(2b) was obtained in low yields (10-20%) from S-(2-pyrimidyl) or S-(2-benzothiazolyl) dodecanethioate and 2-pyridyl dodecanoate, but 2b was not produced from the other thioates.

Although many experiments were tried under various reaction conditions, selective α-diketone(2b) formation was not achieved, and α-hydroxy ketone(3b) was always produced along with α-diketone(2b). The results of reductive couplings of several S-(2-pyridyl) aliphatic thioates under the same reaction conditions are summarized in Table.

Table Reductive coupling of S-(2-pyridyl) aliphatic thioates by $Ni(COD)_2$

	R	Coupling products*, 2	Yield (%) 3
a	$n-C_5H_{11}$	58	27
b	$n-C_{11}H_{23}$	56	21
c	$Ph(CH_2)_3$	45	24
d	$(CH_3)_3CCH_2$	42	30
e	$n-C_4H_9CH(C_2H_5)$	21	—
f	cyclohexyl	54	8

*The structures of all products were confirmed by elemental analysis, NMR, IR, and MS.

S-(2-Pyridyl) thioate (1e) derived from secondary acyclic carboxylic acid, i.e., 2-ethylhexanoic acid gave α-diketone in poor yield because formation of 2- and 3-heptene predominated over the coupling.[5)]

It is presumed that the present reaction proceeds via acylnickel complex which is initially formed by the reaction of 1 with $Ni(COD)_2$. The acyl part of the acylnickel complex dimerizes to give α-diketone(2) and subsequent reduction[6)] of 2 affords α-hydroxy ketone(3).

In contrast with exclusive monoketone formation from S-(2-pyridyl) aromatic thioates,[1)] monoketones were not obtained from S-(2-pyridyl) aliphatic thioates. These results indicate that coupling of the acyl part of the acylnickel complex takes place rapidly and gives α-diketone, while the aroylnickel complex readily looses CO to form arylnickel complex, which in turn produces monoketone.

It is noted that S-(2-pyridyl) aliphatic thioates readily produce α-diketones and α-hydroxy ketones in moderate yields on treatment with $Ni(COD)_2$ under mild conditions.

References and Notes

1) T. Goto, M. Onaka, and T. Mukaiyama, Chem. Lett., 1980, 51.
2) Addition of toluene (ca. 10%) to DMF was found to improve the yield of α-diketone.
3) S-(2-Pyridyl) thioates are readily prepared from carboxylic acids: M. Araki, S. Sakata, H. Takei, and T. Mukaiyama, Bull. Chem. Soc. Jpn., 47, 1777 (1974).
4) The use of one equiv. of $Ni(COD)_2$ lowered the total yield of the coupling products. The use of excess $Ni(COD)_2$ decreased the yield of α-diketone and increased that of α-hydroxy ketone.
5) A small amount of olefins were also produced from the other thioates in Table. We reported that S-(2-pyridyl) thioates derived from secondary acyclic carboxylic acids gave olefins in good yields on treatment with a catalytic amount of $NiCl_2$ and Zn powder: T. Goto, M. Onaka, and T. Mukaiyama, Chem. Lett., 1980, 709.
6) The real reducing species of 2 is not yet clear. In an independent experiment, $Ni(COD)_2$, itself, did not reduce α-diketone to α-hydroxy ketone in DMF at 40°C. However, reduction of α-diketone to α-hydroxy ketone derivatives by $Ni(CO)_4$ has been reported: N. L. Bauld, Tetrahedron Lett., 1963, 1841.

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