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A NEW METHOD FOR THE PREPARATION OF SYMMETRICAL AROMATIC KETONES FROM AROMATIC CARBOXYLIC ACIDS

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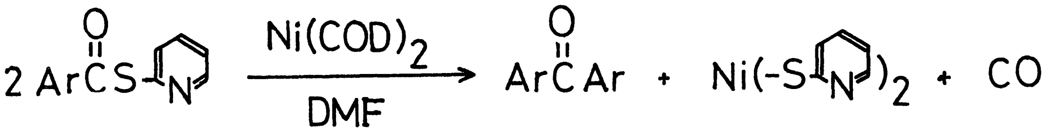
Treatment of S-(2-pyridyl) aromatic thioates, readily derived from aromatic carboxylic acids, with bis(1,5-cyclooctadiene)nickel [Ni(COD)$_2$] under mild conditions afforded symmetrical aromatic ketones in good yields.

In the previous papers, we reported that the reaction of S-(2-pyridyl) thioates or 2-pyridyl carboxylates with Grignard reagents$^{1)}$ or π-allylnickel complexes$^{2)}$ afforded corresponding ketones selectively. In this communication, we wish to report a new and convenient method for the preparation of symmetrical aromatic ketones from aromatic carboxylic acids via S-(2-pyridyl) aromatic thioates. It was found that the reductive homo-coupling of S-(2-pyridyl) aromatic thioates took place by the treatment with Ni(COD)$_2$ smoothly at 50°C, and afforded symmetrical aromatic ketones in good yields, along with nickel salt and CO as depicted in the following equation. The starting materials, S-(2-pyridyl) aromatic thioates, are readily prepared from aromatic carboxylic acids, 2,2'-bipyridyl disulfide, and triphenylphosphine in good yields.$^{1)}$



There have been reported several methods for the preparation of aromatic ketones, which include the Friedel-Crafts acylation of aromatic compounds,$^{3)}$ the reaction of aromatic acyl halides with organometallic compounds,$^{4)}$ and the oxidation of diarylmethanols.$^{5)}$ In contrast with these reactions, according to the present method, symmetrical aromatic ketone is prepared from a single starting material, i.e. S-(2-pyridyl) aromatic thioate.

A typical procedure for the preparation of p,p'-dichlorobenzophenone is as follows: Under argon atmosphere, an oxygen-free N,N-dimethylformamide(DMF, 1.5 ml) solution of S-(2-pyridyl) p-chlorobenzothioate (1.0 mmol) was added to Ni(COD)$_2$ (1.1 mmol) at room temperature. The reaction mixture was stirred at 50°C for 3 h, and then worked up with 5%aq. HCl (15 ml), and extracted with ether (60 ml). The ether layer was washed three times with water (50 ml) to remove DMF, and dried over Na_2SO_4. After removal of the solvent, p,p'-dichlorobenzophenone was isolated in 92% yield by silica gel chromatography. p,p'-Dichlorobenzil or p,p'-dichloro-

Table. The reaction of S-(2-pyridyl) thioate with $Ni(COD)_2$

Ar	Temp.(°C)	Time(h)	Ketone	Yield(%)
Ph	50	6	Ph_2CO	74 6)
m-chloro-C_6H_4	50	4	(m-chloro-$C_6H_4)_2CO$	90
p-chloro-C_6H_4	50	3	(p-chloro-$C_6H_4)_2CO$	92
m-tolyl	50	6	(m-tolyl)$_2$CO	72
p-tolyl	r.t.	15	(p-tolyl)$_2$CO	81
o-methoxy-C_6H_4	50	3	(o-methoxy-$C_6H_4)_2CO$	80
m-methoxy-C_6H_4	r.t.	15	(m-methoxy-$C_6H_4)_2CO$	69
p-methoxy-C_6H_4	50	3	(p-methoxy-$C_6H_4)_2CO$	62
p-cyano-C_6H_4	50	4	(p-cyano-$C_6H_4)_2CO$	78
2-thienyl	50	3	(2-thienyl)$_2$CO	71
cinnamyl	50	3	(cinnamyl)$_2$CO	63

biphenyl was hardly produced in this reaction. The table shows the results of the treatment of various S-(2-pyridyl) aromatic thioates with $Ni(COD)_2$.

It should be noted that benzil derivatives or biphenyl derivatives are scarecely produced by the homo-coupling of aroyl moiety or aromatic ring moiety of S-(2-pyridyl) aromatic thioates. It was also noteworthy that the aromatic ketones such as m,m'-dichlorobenzophenone, m,m'-dimethylbenzophenone, and o,o'-and m,m'-dimethoxybenzophenones are prepared in good yields by the present reaction. The preparation of these aromatic ketones is difficult by a conventional method as the Friedel-Crafts reaction.

The mechanism of the present reaction has not been made clear. However, we assume that aroyl nickel complex is initially formed through the oxidative addition of S-(2-pyridyl) aromatic thioate to $Ni(COD)_2$, and then is transformed to arylnickel complex with the loss of CO. The arylnickel complex then couples with another S-(2-pyridyl) aromatic thioate to afford aromatic ketone.

The detailed mechanism of the present reaction is under investigation.

References and Note

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2) M. Onaka, T. Goto, and T. Mukaiyama, Chem. Lett., 1979, 1483.

3) N. V. Veber and I. P. Tsukervanik, Zh. Org. Khim., 5, 116 (1969).

4) D. A. Shirley, Org. React., Vol. 8, 28 (1954).

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6) When 2-pyridyl benzoate was employed in place of S-(2-pyridyl) benzothioate, benzophenone was obtained in 23% yield under the same reaction conditions.

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