

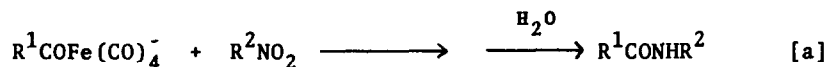
REACTION OF ACYL CARBOXYLFERRATE(O) WITH NITRO COMPOUND.
A NEW SYNTHETIC ROUTE TO AMIDE

Masakazu Yamashita, Yoshihisa Watanabe, Take-aki Mitsudo,
and Yoshinobu Takegami

Department of Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan

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In recent years, acyl tetracarboxylferrates(0) have been shown to be a useful starting reagent for the preparation of aldehydes,¹⁻³⁾ ketones,⁴⁾ and carboxylic acid derivatives.⁵⁾ In this letter, we wish to report that the acyl carboxylferrates react with nitro compounds to give carboxylic amides in excellent yields; the ferrates act as a reducing and acylating reagent in this reaction.⁶⁾



General procedure was as follows. The acyl carboxylferrates were prepared by three methods, A, B, and C. The method A involves a reaction between acid chlorides and disodium tetracarboxylferrate, $Na_2Fe(CO)_4[I]$.²⁾ In the method B, carboxylic anhydrides are treated with $[I]$.³⁾ Addition of a Grignard reagent to pentacarboxyliron is employed as the method C. To 11 mmol of the acyl ferrate in THF, prepared *in situ* as described above, an equimolar nitro compound was added at room temperature under an argon atmosphere. The reaction proceeded vigorously and exothermally with an evolution of carbon dioxide. Thirty minutes later, the reaction mixture was poured into water and extracted with diethyl ether or chloroform. After removal of the solvent, products were separated by column chromatography over silica gel and purified by recrystallization. The products were identified by means of ir, nmr, elemental analyses

Table 1. Reaction of acyl tetracarbonylferrates with nitro compounds

$\begin{matrix} R^1 \\ \text{COFe}(\text{CO})_4 \\ R^1 \end{matrix}$	Method	Nitro Compound	Product	Yield ^{a)} (%)
CH_3	A	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{CH}_3\text{CONHC}_6\text{H}_5$	86
CH_3	A	CH_3NO_2	$\text{CH}_3\text{CONHCH}_3$	71
CH_3CH_2	B	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{CH}_3\text{CH}_2\text{CONHC}_6\text{H}_5$	83
C_6H_5	B	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{C}_6\text{H}_5\text{CONHC}_6\text{H}_5$	78
$\text{CH}_3(\text{CH}_2)_4$	C	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{CH}_3(\text{CH}_2)_4\text{CONHC}_6\text{H}_5$	68
$\text{CH}_3(\text{CH}_2)_5$	C	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{CH}_3(\text{CH}_2)_5\text{CONHC}_6\text{H}_5$	71

a) Isolated yield based on an amount of nitro compounds.

and glpc. The typical results are shown in Table 1. In these reactions, by-products formed were only a small amount of amines, R^1NHR^2 (R^1, R^2 ; see equation [a]).

The facility of the reaction procedure, mildness of the reaction conditions and the excellent yields of the products may make it possible to utilize this reaction for the syntheses of amides from nitro compounds. Further studies on the mechanistic aspect and development of this reaction are underway.

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