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NEW SYNTHETIC ROUTE TO CARBOXYLIC ESTERS FROM GRIGNARD REAGENTS

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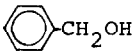
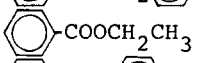
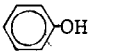
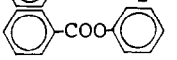
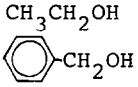
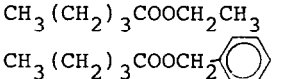
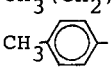
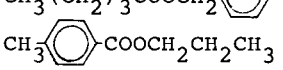
Grignard reagents are synthetically useful and many organic reactions have been reported. However, little is reported on the derivation of carboxylic esters from the reagents except by the reaction of them with diethyl carbonate.[1)]

In this letter, we wish to report a facile and useful synthetic method of carboxylic esters from Grignard reagents using pentacarbonyliron as a carbonylating reagent and hydroxy compounds.

Representative reaction procedure was as follows. To the tetrahydrofuran(THF) solution (40 ml) of phenylmagnesium bromide (22 mmol), pentacarbonyliron (3 ml, 22 mmol) was injected by syringe and the mixture was stirred for 1 hr at room temperature under nitrogen atmosphere. Then, 10 ml of a saturated solution of iodine in benzyl alcohol was added and the reaction solution was stirred further at the same reaction conditions. After 1 hr, the solution was diluted with benzene, washed three times with aqueous sodium thiosulfate to remove excess iodine, dried, and filtered, and the organic solvent was removed *in vacuo*. The residual liquid was separated by column chromatography over silica gel and purified by distillation. The product was identified as benzyl benzoate by IR, NMR, MASS, and GLC. Yield was 78% based on the Grignard reagent.

The results are shown in Table.

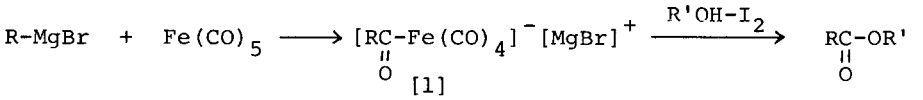
Table. Synthesis of Carboxylic Esters

RMgBr R	Hydroxy Compound	Product	Yield(%)[a]
			78
	CH_3CH_2OH		82
			63
$CH_3(CH_2)_3-$	CH_3CH_2OH	$CH_3(CH_2)_3COOCH_2CH_3$	(89)
$CH_3(CH_2)_3-$		$CH_3(CH_2)_3COOCH_2$ 	73
	$CH_3CH_2CH_2OH$		71

a) Isolated yield. Yield in parenthesis was determined by GLC.

By this method, various carboxylic esters may be produced by use of various hydroxy compounds. So, the facility of the reaction procedure, mildness of the reaction conditions, and high yields of the products may make it possible to utilize this reaction for the syntheses of esters from Grignard reagents.

The reaction is assumed to proceed *via* acyltetracarbonylferrates [1] as follows.[2)]



Further studies on the utility of the present reaction are in progress.

References

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2) H. Masada, M. Mizuno, S. Suga, Y. Watanabe, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, 43, 3824 (1970); J. P. Collman, S. R. Winter, and R. G. Komoto, *J. Am. Chem. Soc.*, 95, 249 (1973); M. Yamashita and R. Suemitsu, *Tetrahedron Letters*, in press.