A Mild, Simple, and Convenient Synthesis of Diesters from Malonyl or Succinyl Dichloride and Alcohols Catalyzed by Potassium Tetracarbonylhydridoferrate, KHFe(CO)$_4$, as a New Catalyst

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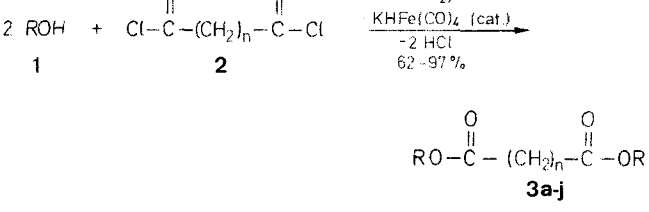
A large variety of alcohols react with acyl halides of dicarboxylic acids such as malonyl dichloride and succinyl dichloride in the presence of a catalytic amount of tetracarbonylhydridoferrate at room temperature under carbon monoxide or nitrogen to give the corresponding diesters in good yields.

Although there are many reports on diester synthesis[1-4] only few examples of the formation of dicarboxylic esters from acyl halides of dicarboxylic acids and alcohols have been described.[5] We report here a new convenient, mild, and simple synthesis of dicarboxylic esters from the acyl halide of a dicarboxylic acid **2** and alcohol **1** in the presence of potassium tetracarbonylhydridoferrate, KHFe(CO)$_4$, as catalyst. The reaction is carried out under a carbon monoxide or a nitrogen atmosphere.



The reaction of 2 molecular equivalents of alcohol **1** with one molecular equivalent of the acyl halide of a dicarboxylic acid **2** in the presence of potassium tetracarbonylhydridoferrate proceeds with immediate strong evolution of hydrogen chloride and the color of the reaction mixture changes from pale yellow to dark red. After exposure of the mixture to air oxidation,[8] careful vacuum distillation affords the diesters **3** in high yields. From the results obtained it can be seen that malonyl dichloride is more reactive than succinyl dichloride under the conditions used. It is also worthy of note that diethyl malonate is obtained in 97% yield using KHFe(CO)$_4$ as catalyst and in only 38% yield when K$_2$Fe(CO)$_4$ is used. Performance of the reaction under carbon monoxide leads to slightly higher yields than performance under nitrogen. Under the reaction conditions described here, the addition of acid-trapping agents such as *N*,*N*-dimethylaniline or pyridine is not necessary.

Potassium tetracarbonylhidridoferrate [KHFe(CO)$_4$] and dipotassium tetracarbonylferrate [K$_2$Fe(CO)$_4$] were prepared by reaction of pentacarbonyliron with ethanolic (or other alcoholic) 1 molar potassium hydroxide in molecular ratios of 1.0:3.0 and 1.0:4.0, respectively.[6,7]

Diethyl Malonate (3b); Typical Procedure:

Tetracarbonylhydridoferrate is prepared from pentacarbonyliron (0.15 ml, 1.1 mmol) and ethanolic 1 molar potassium hydroxide (3.3 ml, 3.3 mmol). To this, ethanol (1.7 ml) is added followed by the dropwise addition of malonyl dichloride (1.1 ml, 11 mmol) over 2-3 min, with stirring under a carbon monoxide atmosphere. There is an immediate vigorous evolution (almost explosively) of hydrogen chloride. The mixture is stirred at room temperature for 6 h, and then exposed to the air for oxidation for ~48 h. Filtration, concentration to a volume of ~3 ml in a rotary evaporator, and vacuum distillation affords product **3b**; yield: 1.71 g (97%); b.p. 37°C/0.41 torr.

Table. Malonic and Succinic Diesters **3** Prepared[a]

3	n	R	Yield[b] (%)	b.p. (°C)/ torr	Molecular Formula[c] or b.p. (°C)/ torr from Lit.
a	1	CH_3	68	46/1.25	180-181[1]
b	1	C_2H_5	97 38[d] 91[e]	37/0.41	198-199[3]
c	1	i-C_3H_7	96	37/0.19	$C_9H_{16}O_4$ (188.2)
d	1	n-C_4H_9	86	62/0.30	251.5[4]
e	1	n-C_5H_{11}	84	65/0.12	$C_{13}H_{25}O_4$ (245.3)
f	2	CH_3	62	31.5/0.20	121-123[1]
g	2	C_2H_5	84	42/0.18	105/15[2]
h	2	i-C_3H_7	78	43/0.13	247/1[4]
i	2	n-C_4H_9	75	53/0.16	150.5/18[4]
j	2	n-C_5H_{11}	75	82/0.14	171.5/16[4]

[a] Alcoholic 1 molar KOH (3.3 ml), Fe(CO)$_5$ (0.15 ml), Malonyl or Succinyl Dichloride (11 mmol), Alcohol (1.7 ml): r.t., 6 h, CO atmosphere.

[b] Yield of isolated product, based on amount of dichloride **2**.

[c] All products gave satisfactory microanalyses: C ±0.35, H ±0.24.

[d] K$_2$Fe(CO)$_4$ was used in place of KHFe(CO)$_4$

[e] Nitrogen was used instead of carbon monoxide.

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