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Hydroacylation of Simple Alkyl Vinyl Ketones Using Organotetracarbonylferrates

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Alkyl vinyl ketones were hydroacylated by organotetracarbonylferrates to the corresponding 1,4-diketones in good yields in dipolar aprotic solvents such as dimethylacetamide. The addition of 18-Crown-6 made an increase of the yields.

Organotetracarbonylferrates (1) are known to react as acyl anion equivalents with various electrophiles to give carbonyl compounds including aldehydes, ketones, carboxylic esters, amides and so on.[1] But the simple Michael-type acceptors such as methyl vinyl ketone (2) have been reported to give the corresponding 1,4-diketones in poor yields,[2] although the reaction of (1) with a variety of Michael-type acceptors gave β-ketoesters, nitriles, and 3-acylcycloalkanones in good yields.

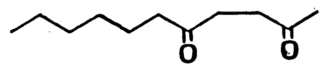
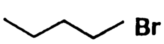
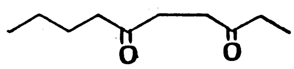
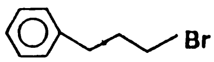
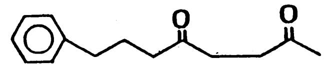
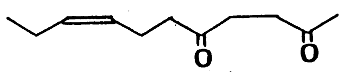
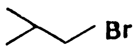
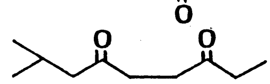
In this letter, we wish to report that 1, prepared from potassium tetracarbonylferrate[3] and bromoalkanes, were also found to react with 2 in dipolar aprotic solvents to give the diketones in good yields.[4]

$$\text{R-Br} + K_2Fe(CO)_4 \longrightarrow \underset{\underline{1}\ \ \text{L:Solvent}}{K^+[RCOFe(CO)_3L]^-} \xrightarrow{\quad \mathbf{2} \quad} RCOCH_2CH_2COCH_3$$

The results listed in Table 1 show that these reactions were dramatically affected by the solvents used. Among the solvents examined, N,N-dimethylacetamide was found to be the best for this reaction. On the other hand, no diketone was obtained when tetrahydrofuran was used. The effects of these solvents may be due to an increase of the solubility of 1, and also to an increase of the nucleophilicity by removal of the cation from a tight ion pairing situation of 1.[5]

Next, the effect of the addition of 18-crown-6 (3) was investigated. For example, the reaction of heptanoylcarbonylferrate with 2 in the presence of 3 in N-methylpyrrolidone (NMP) gave 2,5-undecanedione in 80% yield (Table 1, Run 5). Without 3, the yield was 56% in NMP. This shows that the addition of 3 brings on the increase of the yields of diketones. This effect of the cyclic ether may be due to the complete removal of potassium cation from the ferrate 1.

Table 1. Hydroacylation of methyl vinyl ketone(MVK) and ethyl vinyl ketone(EVK)

Run	R-Br	Michael acceptor	Solvent	Additive[a)]	Product	Yield/%[b)]
1		MVK	DMAA[c)]			70
2				C		84 (70)
3			DMF[d)]			64
4			NMP[e)]			56
5				C		80 (68)
6			HMPA[f)]			56
7			DMSO[g)]			40
8			THF[h)]			0
9		EVK	DMAA			73
10			NMP			63
11		MVK	DMAA			68
12				C		72
13		MVk	DMF	C		73 (55)
14			DMAA			(52)
15		EVK	DMAA			53

a)C means 18-crown-6. b)Determined by GLC. Yields in parentheses are isolated ones. c)N,N-Dimethylacetamide. d)N,N-Dimethylformamide. e)N-Methyl-2-pyrrolidone. f)Hexamethylphosphoramide. g)Dimethylsulfoxide. h)Tetrahydrofuran.

General procedure was as follows. A bromoalkane (7 mmol) was added to a solution of $K_2Fe(CO)_4$ (10 mmol) in 30 ml of a solvent under argon and the reaction mixture was stirred for 1 h at room temperature before the addition of 5.8 ml of MVK or EVK. After 20 h, 2 mol dm^{-3} hydrochloric acid was added to the reaction mixture. The solution was diluted with ether, washed three times with saturated NaCl aq, dried ($MgSO_4$), filtered, and concentrated. The residue was separated by column chromatography over silica gel.

Further applications of this hydroacylation to the synthesis of 1,4-diketones and the related compounds are in progress.

References

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