A New Preparative Method of 1,6-Diketones from Fatty Acids and Vinylmagnesium Chloride

SHOJI WATANABE, KYOICHI SUGA, TSUTOMU FUJITA, AND YUKIO TAKAHASHI

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan 280

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The reaction of vinylmagnesium chloride with a fatty acid or its ester in the presence of cuprous chloride gives a 1,6-diketone. From *n*-valeric acid, *n*-tetradecane-5,10-dione is obtained in 53% yield. From methyl *n*-valerate, a mixture of *n*-tetradecane-5,10-dione (33%) and 5-oxo-1-nonene (34%) is obtained.

La réaction du chlorure de vinyle magnésium avec les acides gras et leurs esters, en présence de chlorure cuivreux, donne une dicétone-1,6. A partir de l'acide *n*-valérique, on obtient la *n*-tétradécanedione-5,10 avec un rendement de 53%. A partir du *n*-valérate de méthyle, on obtient un mélange de *n*-tétradécanedione-5,10 (33%) et d'oxo-5 nonène-1. [Traduit par le journal]

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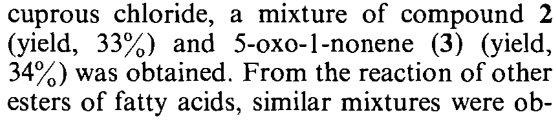
Various preparative methods of diketones are known (1). However, a direct synthesis of 1,6-diketones from a fatty acid or its ester has not been known. These authors reported that the reaction of vinylmagnesium chloride with benzoic acid gave 5-oxo-5-phenyl-1-pentene (2). We have found that such a reaction in the presence of cuprous chloride with fatty acids gives 1,6-diketones, and that with methyl esters leads to a mixture of 1,6-diketones and vinyl ketones.

Thus, vinylmagnesium chloride (0.2 mol) in tetrahydrofuran was added to a mixture of *n*-valeric acid (**1**) (0.05 mol) and cuprous chloride (0.05 mol), the reaction mixture was agitated for 8 h, and allowed to stand overnight. Decomposition of excess Grignard reagent with saturated ammonium chloride solution, and work-up gave *n*-tetradecane-5,10-dione (**2**) in 53% yield. Various 1,6-diketones were prepared from fatty acids and the results are listed in Table 1.

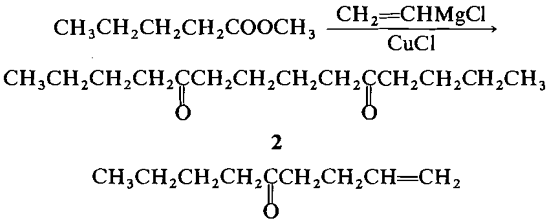


$$\underset{\mathbf{1}}{CH_3CH_2CH_2CH_2COOH} \xrightarrow[CuCl]{CH_2{=}CHMgCl}$$

$$CH_3CH_2CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2CH_3$$

2

From the reaction of methyl *n*-valerate with vinylmagnesium chloride in the presence of cuprous chloride, a mixture of compound **2** (yield, 33%) and 5-oxo-1-nonene (**3**) (yield, 34%) was obtained. From the reaction of other esters of fatty acids, similar mixtures were obtained (Table 1). However, the reaction of benzoic acid gave 1,6-diphenyl-1,6-hexanedione in poor yield.



$$CH_3CH_2CH_2CH_2COOCH_3 \xrightarrow[CuCl]{CH_2{=}CHMgCl}$$

$$CH_3CH_2CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2CH_3$$

2

$$CH_3CH_2CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2CH{=}CH_2$$

3

This procedure for the synthesis of 1,6-diketones from fatty acids or their esters and vinylmagnesium chloride is a new useful method.

Experimental

Reaction of Vinylmagnesium Chloride with n-Valeric Acid (1)

A solution of vinylmagnesium chloride (0.2 mol) in tetrahydrofuran was prepared from magnesium and gaseous vinylchloride as reported previously (3, 4). The solution was then added to a mixture of *n*-valeric acid (5.1 g, 0.05 mol) and cuprous chloride (4.95 g, 0.05 mol) at room temperature. The reaction mixture was agitated for 10 h at room temperature and worked-up with aqueous ammonium chloride. The mixture was repeatedly extracted with isopropylether, the extract dried, solvent removed, and the residue distilled *in vacuo* to give 3.0 g of compound **2**; b.p. 120°/5 Torr; m.p. 57°; i.r. (cm^{-1}): 1700 ($>C{=}O$); n.m.r. (δ, p.p.m.): 1.4 (6H, triplet, CH_3—), 1.9 (12H, multiplet, —CH_2—), 2.3 (8H, triplet, —CH_2—CO—CH_2—).

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.30; H, 11.58. Found: C, 74.29; H, 11.53.

The same technique was used on the reaction of vinylmagnesium chloride with other carboxylic acids. These products are listed in Table 1. The physical constants of these compounds are as follows.

TABLE 1. Reaction of fatty acids or their esters with vinylmagnesium chloride

Acid or Ester	Product	Yield (%)
Propionic acid	3,8-Decadione ①[*]	1
n-Butyric acid	4,9-Dodecadione ②[*]	2
iso-Butyric acid	2,9-Dimethyl-3,8-decadione ③[*]	24
n-Valeric acid	5,10-*n*-Tetradecadione ④[*]	53
n-Caproic acid	6,11-*n*-Hexadecadione ⑤[*]	20
Methyl propionate	3,8-Decanedione ①[*]	5
	5-Oxo-1-heptene ⑥[†]	17
Methyl *n*-butyrate	4,9-Dodecadione ②[*]	19
	5-Oxo-1-octene ⑦[†]	47
Methyl *iso*-butyrate	2,9-Dimethyl-3,8-decadione ③[*]	22
	6-Methyl-5-oxo-1-heptene ⑧[†]	31
Methyl *n*-valerate	5,10-*n*-Tetradecadione ④[*]	33
	5-Oxo-1-nonene ⑨[†]	34
Methyl *n*-caproate	6,11-*n*-Hexadecadione ⑤[*]	6
	5-Oxo-1-decene ⑩[†]	40
Methyl enanthate	7,12-Octadecanedione ⑫[*]	5
	5-Oxo-1-undecene ⑪[†]	22
Methyl *n*-caprylate	8,13-Eicosanedione ⑭[*]	7
	5,Oxo-1-dodecene ⑬[†]	28
Methyl pelargonate	9,14-*n*-Docosanedione ⑯[*]	11
	5-Oxo-1-tridecene ⑮[†]	17
Methyl *n*-caprate	10,15-*n*-Tetracosanedione ⑱[*]	6
	5-Oxo-1-tetradecene ⑰[†]	24
Methyl benzoate	1,6-Diphenyl-1,6-hexanedione ⑳[*]	5
	5-Phenyl-5-oxo-1-pentene ⑲[†]	6

[*] Elementary analyses (carbon and hydrogen) agreed with the calculated data.
[†] Identified by comparison of i.r., n.m.r., and gas chromatography with those of authentic samples (5).

4,9-Dodecanedione: m.p. 57°, b.p. 87°/10 Torr; 2,9-dimethyl-3,8-decanedione: b.p. 80°/5 Torr; n_D^{27} 1.4425; 6,11-*n*-hexadecanedione: m.p. 71°, b.p. 160°/5 Torr; 7,12-octadecanedione: m.p. 80°; 8,13-eicosanedione: m.p. 83°; 9,14-docosanedione: m.p. 88°; 10,15-*n*-tetracosanedione: m.p. 92°; 1,6-diphenyl-1,6-hexanedione: m.p. 105°; u.v. (MeOH) λ_{max} 243 (ε 25 800), 279 mμ (ε 8650).

Reaction of Vinylmagnesium Chloride with Methyl n-Valerate

Vinylmagnesium chloride (0.4 mol) in tetrahydrofuran was added to a mixture of methyl *n*-valerate (11.6 g, 0.1 mol) and cuprous chloride (9.9 g, 0.1 mol) in tetrahydrofuran (50 ml) at 0° under nitrogen. The reaction mixture was agitated for 7 h at room temperature and worked-up in the usual manner to give 3.7 g (yield 33%) of compound 3 (b.p. 86°/7 Torr) and 4.8 g (yield 34%) of the compound 2 (b.p. 138°/7 Torr). The same technique was used on the other esters. The products are listed in Table 1.

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