BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1566—1567 (1973)

The Selective Hydrogenation of the Knoevenagel Condensates of Acetylacetone with Aldehydes Catalyzed by Raney Nickel as a Route to 3-Substituted 2,4-Pentanediones[1]

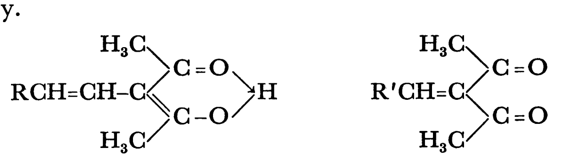
Kaku Uehara, Mitsuo Ito, and Makoto Tanaka

Department of Applied Chemistry, Faculty of Engineering, University of Osaka Prefecture, Sakai-shi, Osaka 591

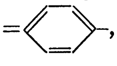
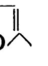
(Received October 30, 1972)

In an earlier communication,[2] it has been reported briefly that the Knoevenagel condensate of acetylacetone with butyraldehyde or propionaldehyde was hydrogenated with Raney nickel to give 3-butyl- or 3-propyl-2,4-pentanedione. In this paper, the hydrogenation of some other Knoevenagel condensates of acetylacetone with aldehydes will be described in more detail as a new general route to 3-substituted 2,4-pentanediones.

In the presence of piperidine, acetylacetone reacted with butyraldehyde, propionaldehyde, crotonaldehyde, acetaldehyde, benzaldehyde, and furfural to give the Knoevenagel condensates **1**, **2**, **3**, **4**, **5**, and **6** respectively.



1: $R=CH_3CH_2-$, **2**: $R=CH_3-$, **3**: $R'=CH_3CH=CH-$

4: $R'=CH_3-$, **5**: $R'=$ , **6**: $R'=$ 

1 and **2** exist predominantly in the enol form and give green crystalline copper(II) chelates. On the other hand, **3** to **6** have no labile hydrogen to form the enol, and therefore give no crystalline copper(II) chelate.

These condensates, **1** to **6**, were hydrogenated with Raney nickel to give 3-butyl-2,4-pentanedione (**7**), 3-propyl-2,4-pentanedione (**8**), 3-ethyl-2,4-pentanedione (**9**), 3-benzyl-2,4-pentanedione (**10**), 3-furfuryl-2,4-pentanedione (**11**), and 3-tetrahydrofurfuryl-2,4-pentanedione (**12**). These diketones are effective chelating agents and give gray crystalline copper(II) chelates. The data o the hydrogenation of **1** to **6** are shown in Table 1.

Table 1. The hydrogenation of Knoevenagel condensates

Knoevenagel condensate		Raney nickel (g)	Temp. (°C)	Time (min)	Product		Yield (%)
No.	(g)				No.	(g)	
1	20	1	70	60	**7**	17.1	86
2	20	2	70	60	**8**	16.8	83
3	15	1.5	70	455	**7**	13.2	88
4	5.5	0.3	70	150	**9**	4.0	72
5	16	1	70	150	**10**	14.1	88
6	12	1	50	30	**11**	8.6	72
6	12	1	70	70	**12**	9.0	84

In the hydrogenation of **6** at 50 °C, it was possible to interrupt the reaction to obtain **11**. The present method seems to be a general route to 3-substituted 2,4-pentanedions.

At the temperature of 100 or 120°C, a low-boiling fraction, such as 2-heptanone, benzylacetone, or tetrahydrofurfurylacetone, was produced as a by-product by the deacylation of the corresponding diketones. These monoketones remained without further hydrogenation to alcohols even at the temperature of 120 °C. This fact suggests that β-diketone modifies the hydrogenation activity of the Raney nickel in the manner described by Izumi *et al.*[3]

By the addition of **7**, the rate of the hydrogenation of 2-heptanone was decreased, resulting in a decrease in the yield of 2-heptanol. In the hydrogenation of 4-hepten-2-one, it was found that the hydrogen uptake occurred in two stages, and that the rate of the first stage was little affected by the addition of **7**. When the reaction was interrupted after the absorption of one mole equivalent of hydrogen, only 2-heptanone was formed. The additive, **7**, was recovered unchanged after the hydrogenation.

These results suggest that the activity of Raney nickel is decreased only for the carbonyl group and that, therefore, the selectivity for the C=C double bond is increased in the presence of 3-substituted 2,4-pentanedione. The modifying action of the β-diketone probably had a favorable effect on the selective hydrogenation of the Knoevenagel condensates of acetylacetone with aldehydes to 3-substituted 2,4-pentanedione.

Experimental

All the boiling points are uncorrected. The acetylacetone, aldehydes, and piperidine were of a reagent grade and were obtained from commercial sources. The Raney nickel used in this work was of the W-1 type, prepared by the ordinary method.[4] A stirring-type autoclave with a void of 100 ml was used as the reaction vessel.

Knoevenagel Condensates of Acetylacetone with Aldehydes. An equimolar mixture of acetylacetone and an aldehyde was placed in a 200-ml flask equipped with a stopper. After cooling, 0.4 mol%[5] of piperidine was added, drop by drop,

---

[1] Paper XVII in a series of "Catalytic Behavior of Metal Chelate Compounds."

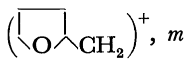
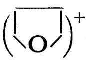
[2] K. Uehara, T. Matsumura, T. Nishi, F. Tamura, and N. Murata, *Kogyo Kagaku Zasshi*, **69**, 2027 (1966).

[3] H. Fukawa, Y. Izumi, S. Komatsu, and S. Akabori, This Bulletin, **35**, 1703 (1962).

[4] L. W. Covert and H. Adkins, *J. Amer. Chem. Soc.*, **54**, 4116 (1932).

[5] The large exess of piperidine resulted in an appreciable decrease in the yield of Knoevenagel condensates.

and the mixture was kept at 0 °C for 7 hr. The reaction mixture was then subjected to fractional distillation. 3-(1-Butenyl)-2,4-pentanedione (**1**); bp 92—95 °C/16 mmHg (lit,[6] bp 83—85.5 °C/9 mmHg), n_D^{19} 1.4839, yield, 60%. 3-(1-Propenyl)-2,4-pentanedione (**2**); bp 81—84 °C/14 mmHg, n_D^{25} 1.4845, yield, 56.8%. Found: C, 68.74; H, 8.90%, Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.90%. 3-(2-Butenylidene)-2,4-pentanedione (**3**); bp 117—120 °C/20 mmHg, n_D^{25} 1.5175, d_4^{25} 1.0120, yield, 54%. 3-Ethylidene-2,4-pentanedione (**4**); bp 90—95 °C/20 mmHg, n_D^{25} 1.4652 (lit,[7] bp 44—45°C/0.04 mmHg, n_D^{25} 1.4608), yield, 7.6%. 3-Benzylidene-2,4-pentanedione (**5**); bp 142—143 °C/4 mmHg, n_D^{25} 1.5180, yield, 44%. 3-Furfurylidene-2,4-pentanedione (**6**); bp 120—124 °C/2 mmHg (lit,[8] bp 128—129 °C/4 mmHg), n_D^{30} 1.5872.

Hydrogenation of the Knoevenagel Condensates. Each condensate, from **1** to **6**, was dissolved in 5 ml of ethanol and then hydrogenated in an atmosphere of hydrogen under an initial pressure of 100 kg/cm² at 50 to 120 °C with Raney nickel. After the theoretical amount of hydrogen had been taken up, the reaction mixture was subjected to fractional distillation. The following products were thus obtained: 3-Butyl-2,4-pentanedione (**7**); bp 99—103 °C/14 mmHg, n_D^{29} 1.4428 (lit,[9] bp 98—102 °C/16—17 mmHg, n_D^{25} 1.4442). 3-Propyl-2,4-pentanedione (**8**); bp 93—96 °C/21 mmHg (lit,[10] bp 75—77 °C/12 mmHg), n_D^{25} 1.4420. 3-Ethyl-2,4-pentanedione (**9**); bp 80—83 °C/25 mmHg, n_D^{17} 1.4399 (lit,[11] bp 80—81 °C/21 mmHg). 3-Benzyl-2,4-pentanedione (**10**); bp 90—94 °C/1 mmHg, n_D^{25} 1.5265(lit, [12] bp 115—118 °C/4 mmHg, n_D^{25} 1.5236). 3-Furfuryl-2,4-pentanedione (**11**); bp 107—108 °C/4 mmHg, n_D^{16} 1.4963; IR spectrum: 1720 (C=O), 1680 (C=C), 1600 (enol), 1070 cm⁻¹ (C–O–C). Mass spectrum: m/e 180 (parent peak), m/e 137 (P–COCH₃)⁺, m/e 81 . 3-Tetrahydrofurfuryl-2,4-pentanedione (**12**); bp 109—112 °C/2 mmHg, n_D^{17} 1.4676, IR spectrum: 1720 (C=O), 1600 (enol), 1070 cm⁻¹ (C–O–C). Mass spectrum: m/e 184 (Parent peak), m/e 141 (P–COCH₃)⁺, m/e 85 , m/e 71 .

The IR spectra of the hydrogenated products from **7** to **10** were identical with those of the authentic samples which had been prepared by the reaction of sodium acetylacetonate with alkyl halides.[13,14]

Copper(II) Chelate from 7 to 12. The copper(II) chelates from **7** to **12** were prepared by mixing an aqueous solution of cupric acetate and an ethanol solution of the hydrogenated products from **7** to **12**. They were then recrystallized from benzene–ligroin. The microanalyses were as follows: **7**, Found: C, 57.51; H, 8.24%. Calcd for $C_{18}H_{30}O_4Cu$: C, 57.80; H, 8.03%. **8**, Found: C, 55.05; H, 7.77%, Calcd for $C_{16}H_{26}O_4Cu$: C, 55.55; H, 7.58%. **9**, Found: C, 52.84; H, 7.10%, Calcd for $C_{14}H_{22}O_4Cu$: C, 52.90; H, 6.98%. **10**, Found: C, 65.04; H, 5.93%, Calcd for $C_{24}H_{26}O_4Cu$: C, 65.21; H, 5.93%. **11**, Found: C, 56.72; H, 5.25%, Calcd for $C_{20}H_{22}O_6Cu$: C, 56.92; H, 5.25%. **12**, Found: C, 55.29; H, 6.90%, Calcd for $C_{20}H_{30}O_6Cu$: C, 55.86; H, 7.03%.

Hydrogenation of 2-Heptanone or 4-Hepten-2-one. 2-Heptanone was a commercial G.R.-grade sample. 4-Hepten-2-one was prepared by the deacylation of **1** in the presence of its copper(II) chelate in methanol.[15] They were hydrogenated with 100 kg/cm² hydrogen with Raney nickel in the presence of **7** at 70 °C. In the course of the reaction, the hydrogen-uptake was followed manometrically. The fractional distillation of the reaction mixture gave 2-heptanol (bp 74—75 °C/23 mmHg) and/or 2-heptanone (bp 54—55 °C/17 mmHg).

---

[6] G. B. Payne, *J. Org. Chem.*, **24**, 1830 (1959).

[7] B. D. Wilson, *ibid.*, **28**, 314 (1963).

[8] H. Midorikawa, This Bulletin, **27**, 213 (1954).

[9] D. F. Martin, W. C. Fernelius, and M. Shamma, *J. Amer. Chem. Soc.*, **81**, 130 (1959).

[10] T. Shono, M. Tanaka, Y. Murotani, and K. Shinra, *Nippon Kagaku Zasshi*, **88**, 1068 (1967).

[11] C. R. Hauser and J. T. Adams, *J. Amer. Chem. Soc.*, **66**, 345 (1944).

[12] Y. Murakami and K. Nakamura, This Bulletin, **39**, 901 (1966).

[13] G. T. Morgan and A. E. Rawson, *J. Soc. Chem. Ind.*, **44**, 462 (1925); *Chem. Abstr.*, **20**, 192 (1926).

[14] G. T. Morgan, *J. Chem. Soc.*, **1925**, 797.

[15] K. Uehara, S. Shionoiri, M. Tanaka and N. Murata, This Bulletin, **45**, 1570 (1972).