Polish J. Chem., **78**, 299–302 (2004)

Catalytic Ketonisation Over Oxide Catalysts. Part IX*. Single Step Synthesis of Aliphatic Saturated and Unsaturated $C_{11} – C_{13}$ Ketones from Carboxylic Acids

by M. Gliński[1] and J. Gibka[2]**

[1]*Warsaw University of Technology (Politechnika), Faculty of Chemistry,*
Laboratory of Catalytic Synthesis, Noakowskiego 3, 00-664 Warsaw, Poland
[2]*Institute of General Food Chemistry, Technical University of Łódź,*
90-924 Łódź, Stefanowskiego 4/10, Poland

(Received September 25th, 2003; revised manuscript October 30th, 2003)

Metameric undecan-x-ones (x = 2–6), dodecan-y-ones (y = 2–5), tridecan-z-ones (z = 4–7) and two unsaturated aliphatic ketones were prepared by vapor phase ketonisation of the appropriate monocarboxylic acids in the presence of 20 wt% MnO_2/Al_2O_3 catalyst under flow conditions. The ketones were obtained in yields between 48 and 89% in a multigram scale (80–250 g). Their physical and spectral data have been determined.

Key words: direct synthesis of ketones from carboxylic acids, MnO_2/Al_2O_3 catalyst

Various aliphatic ketones are of great use in organic synthesis and many synthetic methods have been developed for their preparation. One of these methods is the vapor phase catalytic ketonisation of carboxylic acids [1]. The reaction is performed in a continuous mode under flow conditions in the presence of a solid catalyst. Many metal oxides deposited on the surface of inorganic supports are active in the ketonisation of acids [2–4]. The most active are those, which contain oxides of manganese, cerium, zirconium, thorium and lanthanum [2–4]. A valuable modification of the method presented above is the usage of simple alkyl esters as precursors of acids, when the application of pure acids is not feasible or not advantageous. This method ensures the preparation of phenylalkanones [5], unsymmetric aliphatic ketones [6] and few cycloalkanones [7–9] with good or moderate yields.

Since 1997 we have been studying the relation between the structure of organic compounds and their odor properties [10]. Recently, we examined this relation in the family of straight-chain $C_9 – C_{13}$ alkanones, $C_9 – C_{13}$ alkanols and their simple derivatives, ethylene and propylene acetals, and also acetates. This work is focused on the synthesis of ketones substrates for the preparation of a whole group of these compounds.

---

[*] Part VIII – Gliński M. and Kaszubski M., *React. Kinet. Catal. Lett.* (submitted).
[**] To whom correspondence should be addressed (e-mail: marekg@ch.pw.edu.pl).

EXPERIMENTAL

Catalyst: 20 wt% MnO_2/Al_2O_3 catalyst was prepared by the impregnation of Al_2O_3 extrudates (2–3 mm diameter) (Alumina C, Degussa, $S_{BET} = 104\ m^2/g$) with a solution of $Mn(NO_3)_2 \cdot 4H_2O$ (Fluka, purum p.a.) in distilled water, drying at 393 K for 24 h and heating in a stream of air at 723 K for 3 h. During calcination manganese nitrate decomposes according to:

$$Mn(NO_3)_2 \cdot 4H_2O \rightarrow MnO_2 + 2NO_2 + 4H_2O$$

Reagents: The following monocarboxylic acids were used: ethanoic (POCH Gliwice, p.a), propanoic (BDH, pure), butanoic (Aldrich, 99+%), pentanoic (Aldrich, 99%), hexanoic (Aldrich, 99%), heptanoic (Aldrich, 96%), octanoic (Aldrich, 98+%), nonanoic (Aldrich, 96%), decanoic (BDH, pure), undecanoic (Fluka, pure) and 10-undecenoic (Aldrich, 98%). Prior to use the acids were distilled under normal/reduced pressure. Nitrogen (99.5% purity) was supplied from a cylinder and was dried by passing through a silica gel tower.

Analytical, physicochemical and spectral determinations: The composition of the reaction products was analyzed by gc (Tracer wax capillary column, 15 m long, 0.25 mm, FID, chromatograph KONIK HRGC 4000 B, Spain) and identified by gc-ms (Hewlett-Packard 5971). Samples for gc analysis were treated with saturated aqueous K_2CO_3 solution and dried over anhydrous $MgSO_4$. Each sample was titrated with a standard 0.1 M KOH solution in the presence of phenolphthalein with the aim of determining the conversions of acids.

The ^{1}H NMR spectra were recorded on a Bruker 250 DPX spectrometer in $CDCl_3$. Chemical shifts were recorded in ppm (δ) relative to TMS as internal standard. J values are given in Hz. The IR spectra were measured by using a Specord M 80 spectrometer. Microanalyses were performed on a Perkin Elmer 2400 B CHN elemental analyser.

General procedure for synthesis of ketones: *The preparation of ketones should be performed under a hood. Otherwise, large scale operations (2–10 moles) with monocarboxylic acids, which possess unpleasant or evil smelling odor can hardly be carried out. In addition, the formation of low boiling unsaturated compounds with sharp penetrating unpleasant odor and evolution of small amounts of carbon monoxide during the synthesis has been also observed.*

In a tubular quartz reactor (i.d. 30 mm), heated by an electric furnace, 50 g of 20 wt% MnO_2/Al_2O_3 catalyst was placed, then 20 g of fused quartz (3–5 mm diameter) to serve as a preheater. The reactor was connected with a double jacketed glass condenser and a round bottomed two neck flask for liquid products. A glass tube in the side neck of the flask was connected with scrubber with glass fritter immersed in acetone to catch traces of products escaping in the gas stream. A dropping funnel, containing a mixture of acids, equipped with an equalizing tube and a nitrogen inlet was mounted on the top of reactor. A stream of nitrogen (4 dm^3/h) was passed through the catalyst, which was slowly heated to the reaction temperature, usually 673–698 K (thermocouple located on the external wall of the reactor). The mixture of substrates was introduced into the reactor chamber, one drop per 4–7 seconds. After completing the reaction, the acetone solution from the scrubber was concentrated in a rotatory evaporator and the residue was added to the main portion of products. The water layer was separated from the reaction products and the organic layer was washed carefully with 5% $NaHCO_3$ solution, then with brine and dried over anhydrous $MgSO_4$. The final separation was achieved by fractional distillation under normal/reduced pressure. For general separation purposes, 50 cm in length of a vacuum jacketed glass Vigreux column was satisfactorily applied.

RESULTS AND DISCUSSION

Catalytic ketonisation of monocarboxylic acid in vapor phase over 20 wt% MnO_2/Al_2O_3 catalyst proceeds according to:

$$2RCOOH \rightarrow RCOR + H_2O + CO_2$$

A symmetric ketone is formed as a product of the main reaction. Small amounts of other ketones with the general formula CH_3-$(CH_2)_n$-CO-$(CH_2)_m$-CH_3, where n = const, m = 0, 1, 2, …..(n-1) were also found. The ketonisation of a mixture of two acids (3:1 molar ratio) proceeds according to:

$$3RCOOH + R^1COOH \rightarrow (1+y)\ RCOR + x\ RCOR^1 + y\ R^1COR^1 + 2H_2O + 2CO_2$$

where: x + 2y = 1. Two symmetric ketones and one unsymmetric ketone were formed. As side products various ketones and unsaturated compounds were found. The details of the preparation of 15 aliphatic ketones containing 11–13 carbon atoms, as well as their analytical data, are collected in Tables 1 and 2.

Table 1. Ketones obtained in the catalytic ketonisation of various carboxylic acids.

Mixture of acids	Molar ratio of acids	Ketone	Yield[a] [%]	n_D^{20} [exp]	Bp [°C/mm Hg]
$C_2 : C_{10}$	5.15	CH_3-CO-$(CH_2)_8$-CH_3 (11–2)	70[d]	1.4262	67–69/0.4
$C_3 : C_9$	4.79	CH_3-CH_2-CO-$(CH_2)_7$-CH_3 (11–3)	68[d]	1.4271	70–2/0.6
$C_4 : C_8$	4.00	CH_3-$(CH_2)_2$-CO-$(CH_2)_6$-CH_3 (11–4)	66[d]	1.4269	69–73/0.4
$C_5 : C_7$	3.97	CH_3-$(CH_2)_3$-CO-$(CH_2)_5$-CH_3 (11–5)	61[d]	1.4276	70–1/0.4
C_6	–	CH_3-$(CH_2)_4$-CO-$(CH_2)_4$-CH_3 (11–6)	87[f]	1.4268	78–80/1.0
$C_2 : C_{11}$	4.45	CH_3-CO-$(CH_2)_9$-CH_3 (12–2)	68[d]	1.4326	95–6/0.8
$C_3 : C_{10}$	5.57	CH_3-CH_2-CO-$(CH_2)_8$-CH_3 (12–3)	65[e]	1.4385	89–90/0.7
$C_4 : C_9$	2.98	CH_3-$(CH_2)_2$-CO-$(CH_2)_7$-CH_3 (12–4)	60[d]	1.4360	88–91/0.8
$C_5 : C_8$	3.80	CH_3-$(CH_2)_3$-CO-$(CH_2)_6$-CH_3 (12–5)	67[d]	1.4367	93–6/0.9
$C_4 : C_{10}$	3.99	CH_3-$(CH_2)_2$-CO-$(CH_2)_8$-CH_3 (13–4)	69[e]	1.4339	86–8/0.6
$C_5 : C_9$	3.88	CH_3-$(CH_2)_3$-CO-$(CH_2)_7$-CH_3 (13–5)	64[d]	1.4351	66–9/0.3
$C_6 : C_8$	3.24	CH_3-$(CH_2)_4$-CO-$(CH_2)_6$-CH_3 (13–6)	60[d]	1.4342	69–71/0.2
C_7	–	CH_3-$(CH_2)_5$-CO-$(CH_2)_5$-CH_3 (13–7)	89[f]	–[b]	70–2/0.2
$C_2 : C_{11}^{=c}$	3.84	CH_3-CO-$(CH_2)_8$-CH=CH_2 (12–2^{11})	48[d]	1.4458	92–4/0.7
$C_3 : C_{11}^{=c}$	4.03	CH_3-CH_2-CO-$(CH_2)_8$-CH=CH_2 (13–3^{12})	51[d]	1.4490	69–73/0.2

[a] – the yields are based on isolated products, yields of other ketones are omitted; [b] – m.p. 29°C; [c] – 10-undecenoic acid; [d] – 80–100 g; [e] – 120–140 g; [f] – 220–250 g of ketone.

The yields of two symmetric ketones were in the range of 87–89%. The yields of most of unsymmetric ketones were in the range of 60–70%, depending on the molar ratio of acids, the differences in boiling points of the ketones formed, and the scale of synthesis. Lower yields of dodec-11-en-2-one (12-2^{11}) and tridec-12-en-3-one (13-3^{12}) were caused by their partial decomposition and the formation of a coke deposit on the surface of the catalyst, which was quickly deactivated.

Table 2. Analytical data for the obtained ketones.

Ketone	GC purity [%]	IR [cm^{-1}]	^{1}H NMR [δ ppm]
11–2	99.9	2950, 2875, 1725, 1470, 1360	0.85 (3H, t, J = 6.5); 1.26 (12H, m); 1.55 (2H, t, J = 7.0); 2.15 (3H, s); 2.39 (2H, t, J = 7.5).
11–3	97.8	3000, 2850, 1730, 1490, 1330	0.85 (3H, t, J = 6.6); 1.05 (3H, t, J = 7.35); 1.30 (10H, m); 1.56 (2H, tt, J = 7.2); 2.41 (4H, m).
11–4	99.0	3000, 2800, 1720, 1480, 1350	0.85 (6H, 2t, J = 7.3); 1.15 (8H, m); 1.53 (4H, m); 2.30 (4H, tt, J = 7.50, J = 7.25).
11–5	99.8	3000, 2800, 1720, 1480, 1350	0.89 (6H, 2t, J = 7.0); 1.29 (8H, m); 1.55 (4H, m); 2.38 (4H, tt, J = 7.5).
11–6	99.9	2950, 2875, 1725, 1480, 1350	0.89 (6H, t, J = 7.5); 1.30 (8H, m); 1.57 (4H, m); 2.39 (4H, tt, J = 7.5).
12–2	98.3	2900, 2855, 1725, 1470, 1360	0.89 (3H, t, J = 6.9); 1.27 (14H, s); 1.59 (2H, t, J = 7.1); 2.12 (3H, s); 2.48 (2H, t, J = 7.4).
12–3	97.7	3000, 2850, 1720, 1480, 1350	0.86 (3H, t, J = 6.8); 1.15 (3H, t, J = 7.0); 1.35 (12H, m); 1.56 (2H, tt, J = 7.0); 2.40 (4H, m).
12–4	97.8	2950, 2850, 1725, 1480, 1350	0.86 (6H, 2t, J = 7.3); 1.20 (10H, m); 1.55 (4H, m); 2.32 (4H, tt, J = 7.50, J = 7.20).
12–5	98.7	2950, 2850, 1720, 1480, 1350	0.89 (6H, 2t, J = 7.5); 1.30 (10H, m); 1.55 (4H, m); 2.36 (4H, tt, J = 7.50).
12–2[11]	97.0	2950, 2850, 1725, 1645, 1460, 1370, 920	1.33 (14H, m); 2.13 (3H, s); 2.40 (2H, t, J = 7.4); 4.96 (2H, m); 5.81 (1H, m).
13–4	99.6	3000, 2900, 1725, 1470, 1380	0.91 (6H, m), 1.26 (12H, m), 1.59 (4H, m), 2.37 (4H, m).
13–5	97.8	3000, 2850, 1720, 1470, 1370	0.89 (6H, m), 1.32 (12H, m), 1.55 (4H, m), 2.39 (4H, t, J = 7.4).
13–6	96.2	3000, 2850, 1720, 1480, 1370	0.81 (6H, 2t, J = 6.0), 1.29 (12H, m), 1.49 (4H, m), 3.11 (4H, t, J = 7.5).
13–7	99.4	2940, 2880, 1720, 1470, 1370	0.81 (6H, t, J = 7.5), 1.20 (12H, m), 1.50 (4H, t,t, J = 6.6), 2.31 (4H, t, J = 7.5).
13–3[12]	96.9	2950, 2850, 1725, 1645, 1470, 1380, 915	0.93 (3H, t, J = 7.4); 1.21 (12H, m); 1.48 (2H, m); 2.30 (4H, q, t); 4.84 (2H, m); 5.67 (1H, m).

Acknowledgment

Financial support from the Polish State Committee for Scientific Research (KBN Grant No. 7T09B 049 20) is gratefully acknowledged.

REFERENCES

1. Squibb E., *J. Am. Chem. Soc*., **17**, 187 (1895).
2. Gliński M., Kijeński J. and Jakubowski A., *Appl. Catal. A: Gen*., **128**, 209 (1995).
3. Gliński M. and Kijeński J., *Appl. Catal. A: Gen.*, **190**, 87 (2000).
4. Gliński M. and Kijeński J., *React. Kinet. Catal. Lett.*, **69**, 123 (2000).
5. Gliński M. and Szudybill J., *React. Kinet. Catal. Lett*., **77**, 335 (2002).
6. Gliński M., Szymański W. and Łomot D., *Polish J. Chem*., **77**, 1033 (2003).
7. Gliński M. and Kaszubski M., *React. Kinet. Catal. Lett.*, **70**, 271 (2001).
8. Gliński M. and Kaszubski M., *Polish J. Chem.*, **76**, 1037 (2002).
9. Gliński M. and Kaszubski M., *React. Kinet. Catal. Lett.*, (submitted).
10. Gibka J., Góra J., Gliński M. and Kijeński J., *Perfumer & Flavorist*, **24**, 19 (1999).