Organomanganese(II) Reagents; X[1]. A Convenient Preparation of Various Acetoxyketones, Keto-nitriles, Keto-esters, Keto-acids, Diketones, and Heterocyclic Ketones (Acylheterocycles) via Acylation of Organomanganese(II) Reagents

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We have previously reported the preparation of various halo-, alkoxy-, and alkylthio-ketones by acylation of organomanganese reagents with functionally substituted carboxylic acid chlorides or symmetrical anhydrides[1]. We now describe some applications of this new synthetic method to the preparation of ketones, containing other functional groups.

The following acylations are performed with carboxylic acid chlorides (Method A) or mixed carboxylic carbonic anhydrides (acyl carbonates; Method B) in ether. It should be noted that a large variety of acylating agents or solvents can be used in these reactions[2]. Organomanganese iodides (**1**) are easily and quantitatively prepared from the corresponding organolithium or organomagnesium derivatives[1].

$$R^1Li\ (or\ R^1\text{—}MgBr) + MnJ_2 \xrightarrow{ether} R^1\text{—}MnJ + LiJ\ (or\ MgBrJ)$$

1

Reagents **1** react selectively with acetoxy-substituted carboxylic acid chlorides or alkanedioic monoester chlorides (**2**) to give acetoxy-substituted ketones (**3**) or oxoalkanoic esters (**4**), respectively. The reaction may also be performed with acyl carbonates (e.g., **2'**) in place of the acid chlorides **2**.

$$R^1\text{—}MnJ + R^2\text{—}C(=O)Cl \longrightarrow R^1\text{—}C(=O)\text{—}R^2$$

1 **2**

3a-h $R^2 = -(CH_2)_n-OAc$,

4a-d $R^2 = -(CH_2)_n-COOR$

$$n\text{-}C_4H_9\text{—}MnJ + C_2H_5O\text{—}C(=O)\text{—}O\text{—}C(=O)\text{—}(CH_2)_6\text{—}COOC_2H_5 \longrightarrow$$

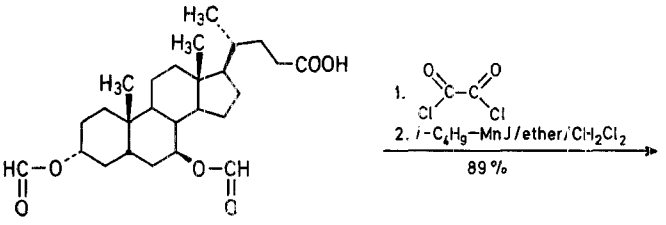
2'

$$n\text{-}C_4H_9\text{—}C(=O)\text{—}(CH_2)_6\text{—}COOC_2H_5$$

4c

Ketones **3,4** are obtained in generally high yields, even in the cases **3a, b** in which α-acetoxycarboxylic chlorides are used. A main limitation of the present method is observed in the attempted preparation of α-ketoesters from ethoxalyl chloride; α-ketoesters are too reactive so that they react readily with the organomanganese reagents, even in the presence of ethoxalyl chloride, and only low yields of α-ketoesters are the result.

This method has been used in the synthesis of some functionally substituted ketosteroids[3]. Thus, the hydroxy groups in a dihydroxysteroid-24-acid were protected against organomanganese reagents by acylation. Thus, acetoxy- and also the analogous formyloxysteroid acids (e.g., **5**) were converted into the acid chlorides with oxalyl chloride, and the acid chlorides were submitted to the reaction with isobutylmanganese(II) iodide to give the ketone (e.g., **6**) in high yields. In this context it should be recalled that formic esters are more reactive than acetic esters and can react with organomanganese reagents[4].



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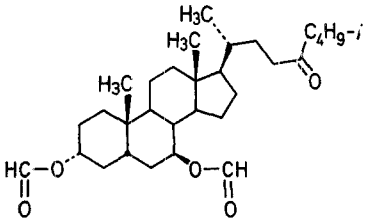

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Ketoacids (**8**) can be obtained by hydrolysis of ketoesters **4**. Some ketoacids (**8**) can also be obtained in moderate to good yields by reaction or organomanganese(II) compounds (**1**) with alkanedioic anhydrides (**7**) (Method C).

$$R^1\text{—}MnJ + \text{(cyclic anhydride)} \longrightarrow R^1\text{—}C(=O)\text{—}(CH_2)_n\text{—}COOH$$

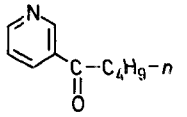
1 **7** **8**

n = 2,3

In general, the use of solvents or ligands bearing an amino substituent is known to decrease drastically the yields of ketones[2]. Similar drawbacks are encountered with amino-carboxylic acid chlorides or mixed and symmetrical anhydrides; therefore, aminoketones cannot be prepared from these amino compounds. However, when *N*-heterocyclic acid anhydrides are used, the influence of the amino function is lowered; thus, the 3-pyridyl ketone **10** is obtained in fair yield from ethyl 3-pyridylcarbonyl carbonate (**9**) and butylmanganese(II) iodide.

$$n\text{-}C_4H_9\text{—}MnJ + \text{(3-pyridyl-C(=O)-O-C(=O)-OC}_2H_5) \xrightarrow{38\%}$$

9



10

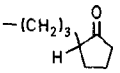
Not all nitrogen derivatives show this detrimental effect. Thus, ketonitriles (**12**) are obtained in high yields from carboxylic chlorides (**11**) containing a cyano group. Furthermore acetonitrile has been successfully used as solvent[2].

$$R^1\text{—}MnJ + R^2\text{—}C(=O)Cl \longrightarrow R^1\text{—}C(=O)\text{—}R^2$$

1 **11** **12**

$R^2 = -(CH_2)_4-CN$, 

Table 1. Preparation of Functionally Substituted Ketones **3**, **4**, **8**, **12**, **16**, and **20** from Organomanganese Reagents (**1**) and Acylating Agents **2**, **7**, **11**, **15**, and **19**

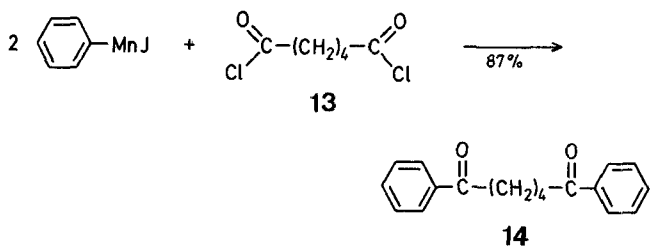
Product	R^1	R^2	Method[a]	Yield [%]	m.p. [°C] or b.p. [°C]/torr	n_D^{20}	Molecular Formula[b] or Lit. Data
3a	n-C_4H_9	$-CH(OAc)-CH_3$	A	87	b.p. 92°/12	1.4235	$C_9H_{16}O_3$ (172.2)
3b	n-C_4H_9-C≡C-	$-CH(OAc)-CH_3$	A	68	b.p. 70°/0.01	1.4537	$C_{11}H_{16}O_3$ (196.25)
3c	n-C_4H_9	$-(CH_2)_5-OAc$	A	95	b.p. 113°/0.8	1.4380	$C_{12}H_{22}O_3$ (214.3)
3d	$(H_3C)_2C=CH-$	$-(CH_2)_5-OAc$	A	89	b.p. 83°/0.01	1.4630	$C_{12}H_{20}O_3$ (212.3)
3e	n-C_4H_9-C≡C-	$-(CH_2)_5-OAc$	A	80	b.p. 149°/0.5	1.4610	$C_{14}H_{22}O_3$ (238.3)
3f	n-C_4H_9		A	58	b.p. 113°/0.5	1.5055	b.p. 100°/1[7] n_D^{20}: 1.5085[7]
3g	n-C_4H_9		A	96	b.p. 135°/0.2	1.5140	$C_{13}H_{16}O_3$ (220.3)
3h	H_3CO-		A	82	m.p. 110°		$C_{16}H_{14}O_4$ (270.3)
4a	n-C_7H_{15}	$-CH_2-CH_2-COOCH_3$	A	85	b.p. 151°/15	1.4385	b.p. 110–112°/0.6[5]
4b	n-C_4H_9	$-CH_2-CH_2-COOCH_3$	A	87	b.p. 119–120°/18	1.4323	b.p. 111°/15[8]
4c	n-C_4H_9	$-(CH_2)_6-COOC_2H_5$	A	97	b.p. 125–126°/0.15	1.4405	$C_{14}H_{26}O_3$ (242.35)
			B	91			
4d	$(H_3C)_2C=CH-$	$-(CH_2)_6-COOC_2H_5$	A	92	b.p. 107–109°/0.03	1.4620	$C_{14}H_{24}O_3$ (240.35)
8a	n-C_7H_{15}	$-CH_2-CH_2-COOH$	C	72.5	m.p. 75°		m.p. 78°[9]
8b	n-C_4H_9	$-(CH_2)_3-COOH$	C	55	m.p. 42°		m.p. 40°[10]
12a	n-C_4H_9	$-(CH_2)_4-CN$	A	86	b.p. 91°/0.3	1.4430	$C_{10}H_{17}NO$ (167.25)
12b	n-C_4H_9		A	84	b.p. 128–130°/0.02 m.p. 49°		$C_{12}H_{13}NO$ (187.25)
16a	n-C_4H_9	$-(CH_2)_4-C(=O)-C_4H_9$-n	A	79	m.p. 67°		m.p. 65°[11]
16b	C_2H_5	$-(CH_2)_4-C(=O)-C_4H_9$-n	A	90	b.p. 93°/0.1 m.p. 48°		m.p. 47°[12]
16c	C_2H_5	$-(CH_2)_6-C(=O)-C_4H_9$-n	A	87	m.p. 56–57°		$C_{14}H_{26}O_2$ (226.35)
20	n-C_4H_9		A	77[c]	b.p. 100°/0.05	1.4641	$C_{13}H_{22}O_2$ (210.3)

[a] Acylating components in Method A: acyl chlorides, Method B: acyl ethyl carbonates, Method C: alkanedioic anhydrides.

[b] The microanalyses were in good agreement with the calculated values: C ±0.21, H ±0.24.

[c] Partial decomposition occurs during distillation, the yield refers to chromatographed product (silica gel; hexane/ethyl acetate 90/10).

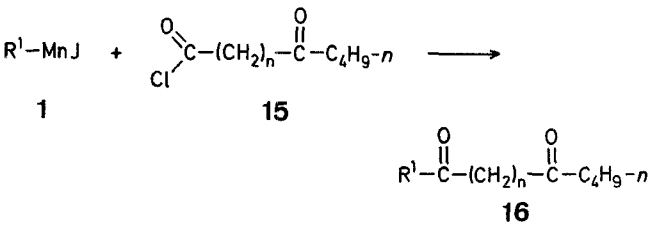
The preparation of diketone **14** via alkanedioic acid dichloride **13** has already been described[5].



13

14

While the above route leads only to symmetric diketones, the reaction of organomanganese(II) iodides (**1**) with oxoalkanoyl chlorides (**15**) can be used for the preparation of unsymmetric diketones (**16**) in high yields.



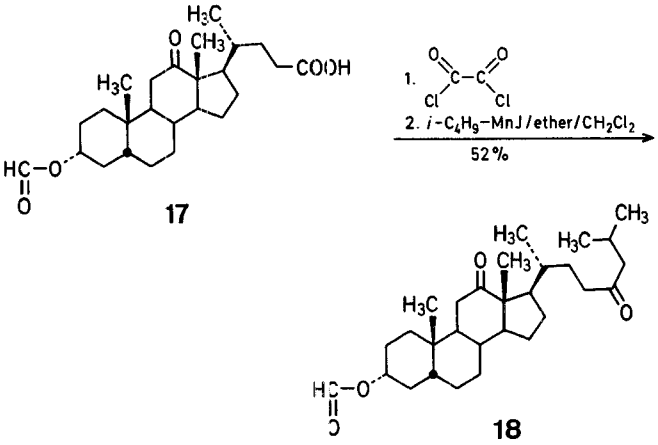
The selective attack of the organomanganese reagent on the chlorocarbonyl group of **15** is surprising since organomanganese(II) compounds react readily with ketones even at −50 °C[4a,6]. One exception to this chemoselectivity has been previously described in the field of steroids when the acid chloride of **17** was used[3]. In this special case, a fair yield of ketone **18** is obtained because of the partial attack of the carbonyl group.

Table 2. Preparation of Heteroaryl Ketones **10**, **23**, and **24** from Organomanganese Reagents **1** and Acylating Agents **9**, **21**, and **22**

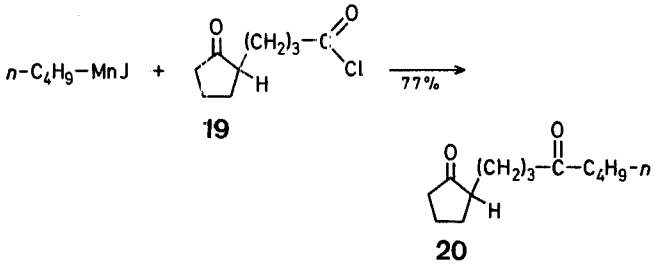
Product	R^1	Heterocyclic Group	Method[a]	Yield [%]	m.p. [°C] or b.p. [°C]/torr	n_D^{20}	Molecular Formula or Lit. Data
10	n-C_4H_9		B	38	b.p. 86°/0.5	1.5020	b.p. 106–112°/3.5[17] n_D^{20}: 1.5118[17]
23a	n-C_4H_9		A B	87 79	b.p. 97–98°/12	1.4895	b.p. 108–109°/16[13]
23b	n-C_4H_9		A	91	b.p. 95–96°/12	1.4750	b.p. 98°/12[14]
23c	$-CH=C(CH_3)_2$		A	72	b.p. 118°/15 m.p. 27,5°		b.p. 47–48°/0.04[15]
23d	$-C\equiv C-C_4H_9$-n		A	43[b]	b.p. 97°/0.7	1.5285	$C_{11}H_{12}O_2$ (176.2)
24	n-C_4H_9		A	96	b.p. 91–92°/1	1.5300	b.p. 141°/25[16] n_D^{18}: 1.5376

[a] See Table 1.

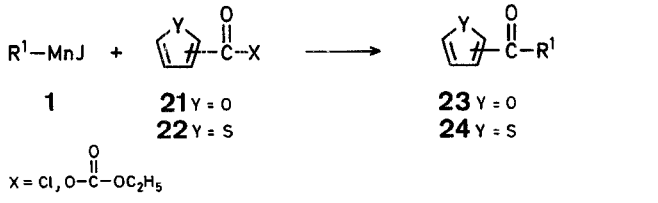
[b] Unstable product which partially decomposes during distillation. No microanalysis performed.



This result, however, cannot be explained by a weak difference in reactivity between the 12-oxo and the chlorocarbonyl groups. Indeed, the ketoacid chloride **19** affords the diketone **20** in good yield in spite of a similar competition. The present problem certainly results from the proximity of the two functions concerned during reaction with the organomangane reagent.



Contrary to *N*-heterocyclic ketones, furyl and thienyl ketones **(23, 24)** can be prepared in high yields from the corresponding acid chlorides **(21,22)** and organomanganese(II) iodides (Table 2).



All reactions are performed with equimolecular amounts of organomanganese reagents (**1**) and acylating agents.

As regards the synthesis of ketones, in particular, functionally substituted ketones, the use of organomanganese reagents is often superior over that of other organometallic compounds (cf. Ref.[1]).

The keto-steroids **6** and **18** have already been described[3]. The preparation of acid chlorides is performed by classical methods [$SOCl_2$[18], $SOCl_2$/DMF[18,19], $(COCl)_2$[18]]. Mixed carboxylic carbonic anhydrides (acyl carbonates) are quantitatively prepared according to Ref.[20]; they are used without previous purification.

The preparation of manganese iodide and of organomanganese(II) iodides **1** have been described earlier[1].

Ketones from Organomanganese(II) Reagents (1) and Carboxylic Acid Chlorides (2,11, 13, 15, 19, 21, 22) (Method A) or Acyl Ethyl Carbonates (2', 9, 21') (Method B); General Procedure:

A solution of the carboxylic acid chloride (50 mmol) or acyl ethyl carbonate (carboxylic-carbonic anhydride, 50 mmol) in anhydrous ether (30 ml) is added to a stirred ethereal suspension or solution of the organomanganese iodide **1** (52 mmol) at −10 °C under nitrogen (for ketoacid chlorides **15** and **20**, the addition is performed at −50 °C, then stirring is continued for 15 min). The mixture is then allowed to warm to room temperature, stirred for 2 h (for **4h** when R—C≡C—MnJ is used as component **1**), and hydrolyzed at 0 °C with 0.5 normal hydrochloric acid (60 ml) [hydrolysis can also be performed with aqueous sodium hydrogen carbonate (or sodium carbonate); in this case, the manganese(II) salt precipitates and can be filtered off]. The aqueous layer is decanted and extracted with hexane or ether (2 × 50 ml). The combined organic layers are washed with aqueous sodium hydrogen sulfite or thiosulfate (30 ml), if a small amount of iodine is present, then with saturated sodium hydrogen carbonate solution (50 ml), and are dried with magnesium sulfate. The solvent is removed under vacuum and the product is isolated by crystallization **(3h, 16a)**, liquid column chromatography **(16c, 20)** or more generally by distillation (Tables 1 and 2).

Oxoalkanoic Acids (8) from Dicarboxylic Anhydrides (7) (Method C):

The pure solid cyclic anhydride **7** (50 mmol) is added in one portion to the stirred ethereal solution or suspension of the organomanganese reagent **1** (52 mmol) at 0 °C. The mixture is then allowed to warm to room temperature, stirred for 8 h, and hydrolysed at 0 °C with normal hydrochloric acid (80 ml). The aqueous layer is decanted and extracted with ether (3 × 50 ml). The combined organic layers are washed with an acidified solution of sodium hydrogen sulfite (30 ml), if a small amount of iodine is present, then with water (50 ml), and are dried with magnesium sulfate. The solvent is re-

Table 3. Spectral Data of the Ketonic Compounds prepared

Compound	I.R. (neat) ν [cm^{-1}]	^{1}H-N.M.R. (CCl_4/TMS_{int})[a] δ [ppm]
3a	1740 (C=O)	5.00 (q, 1H, O—CH—C=O); 2.45 (t, 2H, CH_2—C=O); 2.05 (s, 3H, O—CO—CH_3); 1.34 (d, 3H, CH—CH_3); 0.92 (t, 3H, H_3C—CH_2)
3b	1690 (C=O); 1740 (COO); 2210 (C≡C)	4.98 (q, 1H, O—CH—C=O); 2.42 (t, 2H, CH_2—C≡C); 2.06 (s, 3H, O—CO—CH_3); 1.42 (d, 3H, CH—CH_3); 0.95 (t, 3H, H_3C—CH_2)
3c	1715 (C=O); 1740 (COO); 1620 (C=C)	3.98 (t, 2H, CH_2—O); 2.37 (t, 4H, CH_2—C=O); 1.96 (s, 3H, O—CO—CH_3); 0.90 (t, 3H, H_3C—CH_2)
3d	1690 (C=O); 1740 (COO)	5.96 (s, 1H, C=CH); 3.96 (t, 2H, CH_2—O); 2.32 (t, 2H, CH_2—C=O); 2.10 (s, 3H, *cis*-H_3 C—C=C—C=O); 1.97 (s, 3H, O—CO—CH_3); 1.86 (s, 3H, *trans*-H_3C—C=C—C=O)
3e	1625 (C=O); 1740 (COO); 2220 (C≡C)	3.98 (t, 2H, CH_2—O); 2.47 (t, 2H, CH_2—C=O); 2.35 (t, 2H, CH_2—C≡C); 1.95 (s, 3H, O—CO—CH_3); 0.95 (t, 3H, H_3C—CH_2)
3f	1690 (C=O); 1775 (COO); 1450; 1485; 1605 (C_6H_4)	7.72 (d, 1H, *o*-C_6H_4—C=O); 7.38 (dd, 1H, *p*-C_6H_4—OAc); 7.25 (dd, 1H, *p*-C_6H_4—C=O); 7.05 (d, 1H, *o*-C_6H_4—OAc); 2.78 (t, 2H, CH_2—C=O); 2.22 (s, 3H, O—CO—CH_3); 0.92 (t, 3H, H_3C—CH_2)
3g	1685 (C=O); 1765 (COO); 1500; 1600 (C_6H_4)	7.87 (d, 2H, *o*-C_6H_4—C=O); 7.06 (d, 2H, *o*-C_6H_4—OAc); 2.84 (t, 2H, CH_2—C=O); 2.18 (s, 3H, O—CO—CH_3); 0.92 (t, 3H, H_3C—CH_2)
3h	1645 (C=O); 1760 (COO); 1510; 1605 (C_6H_4)	7.82 (m, 4H, *m*-C_6H_4—OCH_3 + *m*-C_6H_4—OAc); 7.20 (d, 2H, *o*-C_6H_4—OAc); 6.97 (d, 2H, *o*-C_6H_4—OCH_3); 3.87 (s, 3H, OCH_3); 2.32 (s, 3H, O—CO—CH_3)
4a	1715 (C=O); 1735 (COO)	3.62 (s, 3H, OCH_3); 2.5 (m, 6H, CH_2—CO—CH_2 + CH_2—COO); 0.90 (t, 3H, H_3C—CH_2)
4b	1715 (C=O); 1740 (COO)	4.60 (s, 3H, OCH_3); 2.52 (m, 6H, CH_2—CO—CH_2 + CH_2—COO); 0.90 (t, 3H, H_3C—CH_2)
4c	1715 (C=O); 1740 (COO)	4.03 (q, 2H, CH_2—O); 2.33 (t, 4H, CH_2—CO—CH_2); 2.20 (t, 2H, CH_2—COO); 1.22 (t, 3H, O—CH_2—CH_3); 0.90 (t, 3H, H_3C—CH_2)
4d	1690 (C=O); 1620 (C=C); 1740 (COO)	5.98 (s, 1H, C=CH); 4.03 (q, 2H, CH_2—O); 2.34 (t, 2H, CH_2—C=O); 2.22 (t, 2H, CH_2—COO); 2.10 (s, 3H, *cis*-H_3C—C=C—C=O); 1.86 (s, 3H, *trans*-H_3C—C=C—C=O); 1.22 (t, 3H, O—CH_2—CH_3)
8a	1710 (C=O) 3000 (OH)	10.86 (s, 1H, COOH); 2.67 (t, 4H, CO—CH_2—CH_2—COOH); 2.46 (t, 2H, C_6H_{13}—CH_2—CO); 1.70–1.15 (m, 10H, H_3C—CH_2—CH_2—CH_2—CH_2—CH_2); 0.90 (t, 3H, CH_3)
8b	1815 (C=O); 3100 (OH)	2.6–2.3 (m, 6H, CH_2—CO—CH_2—CH_2—CH_2—COOH); 1.87 (m, 2H, CH_2—CH_2—COOH); 1.75–1.14 (m, 4H, H_3C—CH_2—CH_2); 0.93 (t, 3H, CH_3)
10	1690 (C=O); 705; 1420; 1468 1575; 1588 (pyridyl)	9.08 (s, 1H, 2-H); 8.67 (d, 1H, 6-H); 8.15 (d, 1H, 4-H); 7.36 (dd, 1H, 5-H); 2.95 (t, 2H, CH_2—CO); 1.8–1.2 (m, 4H, CH_2—CH_2—CH_3); 0.95 (t, 3H, CH_3)
12a	1710 (C=O); 2250 (C≡N)	2.42 (m, 6H, CH_2—CO—CH_2 + CH_2—CN); 0.92 (t, 3H, CH_3)
12b	1690 (C=O); 2240 (C≡N); 1580; 1600 (C_6H_4)	8.25 (s, 1H, *o*-C_6H_4—CN + C=O); 8.22 (s, 1H, *p*-C_6H_4—C=O); 7.86 (d, 1H, *p*-C_6H_4—CN); 7.68 (dd, 1H, *m*-C_6H_4—CN); 3.00 (t, 2H, CH_2—C=O); 0.98 (t, 3H, CH_3)
16a	1700 (C=O)	2.35 (t, 8H, CH_2—CO—CH_2); 1.8–1.1 (m, 12H, CH_2); 0.88 (t, 6H, CH_3)
16b	1705 (C=O)	2.60–2.25 (m, 8H, CH_2—CO—CH_2); 1.80–1.15 (m, 8H, CH_2); 1.02 (t, 3H, H_3C—CH_2—C=O); 0.90 (t, 3H, CH_2—CH_2—CH_3)
16c	1705 (C=O)	2.37 (m, 8H, CH_2—CO—CH_2); 1.75–1.15 (m, 12H, CH_2); 1.05 (t, 3H, H_3C—CH_2—C=O); 0.90 (t, 3H, CH_2—CH_2—CH_3)
20[b]	1710 (C=O); 1740 (cyclic C=O)	2.6–1.1 (m, 19H); 0.94 (t, 3H, CH_3)
23a	1680 (C=O); 3140; 1570; 880 (furyl)	7.56 (d, 1H, 5-H); 7.10 (d, 1H, 3-H); 6.48 (dd, 1H, 4-H); 2.76 (t, 2H, CH_2—CO); 1.8–1.2 (m, 4H, CH_2—CH_2—CH_3); 0.94 (t, 3H, CH_3)
23b	1680 (C=O); 3140; 1565; 1510; 875 (furyl)	8.10 (s, 1H, 2-H); 7.42 (d, 1H, 5-H); 6.70 (d, 1H, 4-H); 2.72 (t, 2H, CH_2—CO); 1.85–1.15 (m, 4H, CH_2—CH_2—CH_3); 0.94 (t, 3H, CH_3)
23c	1660 (C=O); 1620 (C=C); 3130; 880 (furyl)	7.57 (d, 1H, 5-H); 7.12 (d, 1H, 3-H); 6.65 (s, 1H, C=CH—CO); 6.46 (dd, 1H, 4-H); 2.24 (s, 3H, *cis*-H_3C—C=C—CO); 1.94 (s, 3H, *trans*-H_3C—C=C—CO)
23d[c]	1640 (C=O); 2210 (C≡C); 3140; 1570; 880 (furyl)	7.76 (d, 1H, 5-H); 7.32 (d, 1H, 3-H); 6.63 (dd, 1H, 4-H); 2.48 (t, 2H, CH_2—C≡C); 1.85–1.25 (m, 4H, CH_2—CH_2—CH_3); 0.96 (t, 3H, CH_3)
24	1660 (C=O); 3100; 1520; 720 (thienyl)	7.68 (m, 2H, 3-H + 5-H); 7.06 (dd, 1H, 4-H); 2.85 (t, 2H, CH_2—CO); 1.85–1.20 (m, 4H, —CH_2—CH_2—CH_3); 0.92 (t, 3H, CH_3)

[a] Recorded on a Jeol MH-100 spectrometer at 100 MHz.

[b] ^{13}C-N.M.R. ($CDCl_3$/TMS_{int}): δ = 220.65 (C=O, cyclopentane); 210.65 (CH_2—CO—CH_2); 49.00 (C-2, cyclopentane); 42.55 (CH_2—CO—CH_2); 38.05 (C-5, cyclopentane); 29.55 (C-3, cyclopentane); 29.30 (C_4H_9—CO—CH_2—CH_2—CH_2); 25.95 (H_3C—CH_2—CH_2); 22.40 (H_3C—CH_2); 21.80 (C_4H_9—CO—CH_2—CH_2); 20.75 (C-4, cyclopentane); 13.90 ppm (CH_3); this spectrum was recorded on a Jeol FX 90Q spectrometer at 22.5 MHz.

[c] ^{13}C-N.M.R. ($CDCl_3$/TMS_{int}): δ = 164.90 (C=O); 153.30 (C-2, furyl); 147.70 (C-5, furyl); 120.65 (C-3, furyl); 112.50 (C-4, furyl); 95.40 (C≡C—CO); 79.00 (C≡C—CO); 29.80 (H_3C—CH_2—CH_2); 22.00 (H_3C—CH_2); 18.85 (CH_2—C≡C); 13.50 ppm (CH_3); this spectrum was recorded on a Jeol FX 90Q spectrometer at 22.5 MHz.

moved under vacuum and the crude ketoacid **8** is dissolved in 0.5 normal potassium hydroxide (130 ml); this aqueous solution is washed with ether (3 × 30 ml), carefully acidified with 6 normal sulfuric acid, then extracted with ether (3 × 50 ml). The ethereal solution is dried with magnesium sulfate and evaporated in vacuum to give the almost pure ketoacid **8** (sometimes as a mixture with its cyclic hemiacetalic form). The product is recrystallized only when analytical purity is required.

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