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REACTION OF MIXED CARBOXYLIC ANHYDRIDES WITH GRIGNARD REAGENTS

APPLICATION TO THE PREPARATION OF KETO ESTERS; SCOPE AND LIMITATIONS

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Abstract—The low-temperature Grignard reaction of mixed carboxylic anhydrides derived from acid chlorides and *o*-anisic acid to the general synthesis of keto esters is demonstrated for compounds **1–6**, although, some limitations on substrate and Grignard reagent species are also encountered; attempts in the oxa series **2** are unsuccessful, and reaction with ω-phenylpropyl Grignard species for **1** and **4** shows a drastic decrease in yields of the keto esters for *m*-methoxy analogues. Anomalous behaviour may be associated with an alternative type of specific metal-coordination complex which includes the ether oxygen atom properly situated in the substrate or the reagent.

During the course of our synthetic work on saturated heterocycles, we have studied the conversion of ester acid chlorides **1** and **2** to keto esters **7** and **8**, which has hitherto been achieved using organocadmium reagents.[1] We have sought alternative procedures for accomplishing this transformation without reagents containing heavy metals.

Recently, Mukaiyama *et al.*[2] reported a convenient method for preparing ketones and diketones from carboxylic acids, which involved the low temperature *in situ* reaction of mixed carboxylic anhydrides with Grignard reagents. A main feature of this reaction is preferential approach of the reagent to the anhydride carbonyls through a favorable intermediate 6-membered chelate complex and regioselective attack from the less hindered side in a desired sense. Thus, a 1,4-diketone such as 2,5-dioxoundecane was synthesized in good yields via the mixed carboxylic anhydrides with a hindered *o*-substituted benzoic acid from levulinic acid by one-step procedure without protection of its keto group.

We have now found that this method is also successfully applied to the general synthesis of keto esters from carboxylic acids. We describe herein applicability of the present procedure with scope and limitations and its utility with a variety of alkyl Grignard reagents.

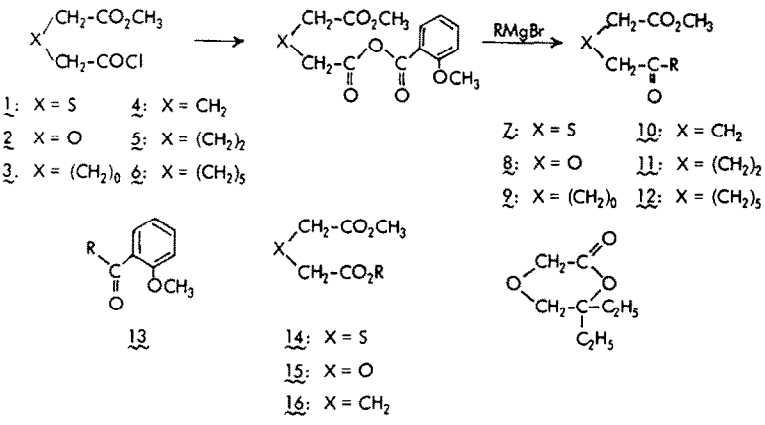
RESULTS AND DISCUSSION

In order to test the feasibility of this method, preliminary studies were carried out on a small scale in cases **1** and **4**, from which the mixed carboxylic anhydrides were prepared *in situ* by utilizing *o*-anisic acid followed by dropwise addition of Grignard reagent solutions essentially according to the original procedure.

To find the best conditions, variation in temperature and amounts of the reagents were examined. These results are summarized in Table 1. When methyl-, ethyl-, propyl- and benzyl-magnesium bromides were used, most of experiments gave invariably keto esters **7** and **10** as major products. Optimum results were obtained when the Grignard reagent was reacted below −70°. Higher reaction temperature resulted in decreased yields of **7** and **10** with a diminished degree of regioselectivity and instead increased formation of a few side products, **13** and **14**† or **16**.† Other unidentified materials were also obtained as most polar fractions of by-products. They were produced increasingly when excess Grignard reagents were used, presumably owing to overalkylation. The steric bulk of alkyl group in the Grignard species appeared to effect to some extent lowering in yields of **7** in changing from methyl to ethyl and benzyl successively. It is noteworthy that the reaction with benzylmagnesium bromide starting with **1** led to only a rearranged keto ester. The *o*-rearranged structure of **7d'** (not **7d**) was established by spectral data, especially based on the aromatic signal pattern in its NMR spectrum resembling very closely to that of *o*-methylacetophenone. The exclusive *o*-migration in the benzyl group may be rationalized by assuming the situation of an initially formed chelate complex in the intermediate, as depicted in Fig. 1. Then, a maximum possible overlap between π-orbital of the carbonyls and reacting orbital of the incipient benzyl anion would occur most favorably at the *o*-position on the benzene ring based on a conjugation effect. In other words, this finding seems to give a validity for the intermediate complex postulated by Mukaiyama *et al.*[2]

Encouraged by the above results, we undertook duplicate runs on a large scale using the foregoing optimum conditions. Furthermore, we applied this synthetic technique to other various acid chlorides to extend the scope. Fortunately, reasonable yields of keto esters could be realized in most cases as listed in Table 2. For example, methyl 6-oxooctanoate **11b** and methyl 9-oxodecanoate **12a** were obtained from the corresponding ester acid chlorides in 72 and 67% yields, respectively. Similarly, this procedure proved useful also in the succinic acid series **9a**. The keto esters were, in practice, easily isolated by rough column chromatography followed by distillation, or occasionally by direct fractional distillation. The method, in our hand, also

†The production of diesters **14** or **15** (or **16**), including the unsymmetrical and symmetrical ones, is at a first glance interesting. These compounds tend to produce increasingly when the normal reaction does not go well, particularly in the hetero series. ROMgX, first generated in the Grignard solution, may react with the anhydrides to yield the unsymmetrical diesters, while CH_3OMgX, newly generated from interaction between the reagent and the methyl ester function of the substrate, may be responsible for formation of the symmetrical dimethyl esters.



1: X = S 4: X = CH_2
2: X = O 5: X = $(CH_2)_2$
3: X = $(CH_2)_0$ 6: X = $(CH_2)_5$

7: X = S 10: X = CH_2
8: X = O 11: X = $(CH_2)_2$
9: X = $(CH_2)_0$ 12: X = $(CH_2)_5$

13

14: X = S
15: X = O
16: X = CH_2

a: R = CH_3, b: R = C_2H_5, c: R = n-C_3H_7, d: R = $C_6H_5CH_2$
e: R = $C_6H_5(CH_2)_2$, f: R = m-CH_3O-$C_6H_4(CH_2)_2$, g: R = $C_6H_5(CH_2)_3$, h: R = m-CH_3O-$C_6H_4(CH_2)_3$, i: R = p-CH_3O-$C_6H_4(CH_2)_3$.

Table 1. Grignard reaction of mixed carboxylic anhydrides from 1 and 4[a]

Substrate	RMgBr (eq.)	Temp °C	Product[b] (%, isolated) 13	14 or 16	7[f] or 10[f]	Others[c]	7 or 10/13
1	CH_3(1.1)	-75	13a[d](2.8)	14a[d](16.9)	7a (72.9)	(7.5)	26.0
	CH_3(1.1)	-35	13a (5.0)	14a (28.6)	7a (53.8)	(12.6)	10.8
	CH_3(1.1)	0	13a (10.1)	14a (39.8)	7a (36.3)	(13.8)	3.6
	CH_3(2.5)	-75	13a (1.2)	14a (14.8)	7a (38.6)	(45.4)	32.2
	C_2H_5(1.1)	-75	13b[e](4.5)	14a (17.2) 14b[f](9.2)	7b (61.2)	(7.9)	13.6
	n-C_3H_7(1.1)	-75	13c[e](5.5)	14a (14.6) 14c[f](9.6)	7c (64.7)	(5.6)	11.8
	$C_6H_5CH_2$(1.1)	-75	13d[g](12.7)	14a (12.5)	7d[g](38.0)	(37.7)*	3.0
4	CH_3(1.1)	-75	13a (5.7)	16a[d](7.7)	10a (82.1)	(4.5)	14.4
	CH_3(1.1)	-35	13a (7.6)	16a (12.0)	10a (65.0)	(15.4)	8.6
	CH_3(1.1)	0	13a (9.0)	16a (22.9)	10a (58.2)	(9.8)	6.5

[a] All reactions were run on a 0.01-mol scale at given temperatures according to the general procedure described in Experimental.

[b] The products, given in % weight, were separated by preparative TLC (9:1 C_6H_6-EtOAc) in decreasing order of Rf value from left to right and, if necessary, their purities and contents were checked and estimated by GLC (5% Carbowax 20 M).

[c] Sum of unidentified materials; the asterisk mark (*) comprizes 19.8% of least polar components.

[d] The structures were identified based on their IR and/or NMR spectra recorded in "The Aldrich Library of Infrared and NMR Spectra."

[e] The structures were established by comparing their IR and NMR spectra with those of **13a** and its analogue.

[f] The structures were confirmed by comparison with the authentic samples on basis of their physical constants and IR and NMR spectra (see Experimental).

[g] The *o*-rearranged structure was established by NMR comparison with *o*-methylacetophenone[d] (see Experimental).

advantageously permitted, if required, recovering and recycling *o*-anisic acid as an accessory agent used.

In spite of our efforts, application to the oxa series **2** has proven to be disappointing and unpromising, regardless of Grignard reagent species and reaction conditions. Whenever the mixed anhydride from **2** was treated with each of several Grignard reagents in varying amounts at temperatures ranging from 0° to −70°, none of the objective corresponding keto esters were detected in the reaction products. On examining the reaction products when conducted at −30 to −60° using ethylmagnesium bromide, there were formed only undesired compounds, e.g. **13b** (5%), **15a** (30%), **15b** (30%) and further a lactone (20%), tentatively assigned structure **17**, on the basis of the spectral data.

To gain further insight into this limitation, we surveyed the present reaction with other systems such as **18**, **19** and **20**.

The reaction with an equimolar amount of methylmagnesium bromide proceeded normally at −70° in both cases of **19** and **20**, giving alkoxy ketones **22** and **23** in over 50% yields. In contrast, we found that the similar

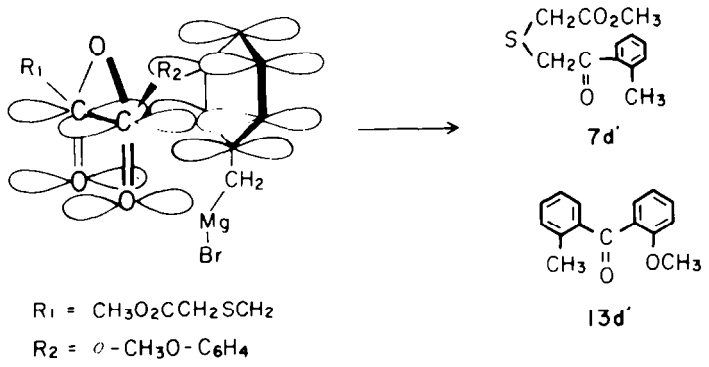


Fig. 1.

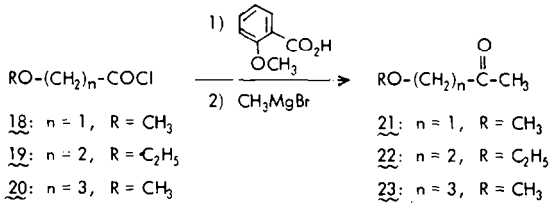
Table 2. Synthetic keto esters[a]

Compound	Isolated yield[b] %	B.p. °C (mm)
7a	63.2	82-85 (0.6)
7b	68.7	80-83 (0.4)
7c	58.7	85-89 (0.3)
7d'	46.3	151-152(0.7)
7e	51.2 (63.7)	146-148(0.35)
7f	55.3 (63.0)	163-165(0.5)
7g	64.7 (82.0)	145-147(0.35)
7h	(2.1)	150 (0.5)
7i	23.2 (34.1)	161-164(0.25)
9a	57.6	94-95.5(20)
10a	52.6	95-96((13)
10h	8.6 (12.1)	160-162(0.5)
10i	58.5 (67.4)	157-160(0.35)
11b	71.8	122-123(16)
12a	67.2	151-153(16)

[a] See Experimental.

[b] The yields refer to distilled products. The yields given in parentheses are based on GLC.

reaction† for **18** produced no expected ketone **21** but surprisingly, more than 50% of the unreacted anhydride of **18**, accompanied by **13a** and other polar substances in about 5% combined yield.



Based upon the above observation, it has become apparent that the failure in the oxa series **2** as well as in **18** should be eventually attributed to the unusual reactivity common to a type of α-alkoxyacetic acid derivatives. The crucial element responsible for the anomaly, although not clear, might be associated with a particular metal complex which would alternately be generated between the ether oxygen atom situated α to the carbonyl of the substrate and the reagent, and interfere specifically with the normal reaction proceeding through the original chelate complex.

Some structural limitations of the Grignard reagent are also included in Table 2; in the reaction with a series of ω-phenylpropylmagnesium bromides for **1** and **4**, only substitution of a methoxy group at the *m*-position on the phenyl ring drastically decreased yields of the corresponding keto esters. This was not the case for the ω-phenylethyl Grignard species. This intriguing phenomenon could not be accounted for by mere steric influence of the alkyl chain in the Grignard reagent. It may be due to stereochemical aspects, probably involving a metal-coordination complex interrupted by such a hetero function suitably attached to the phenyl ring.

Although further extension may also add limitations, this procedure is now available as a generally useful method for preparing keto esters. The operational simplicity and high efficiency of the method will provide an alternative to the well-known dialkylcadmium procedure in certain cases.

EXPERIMENTAL

All b.ps are uncorrected. IR spectra were recoded on a Jasco DS-403G spectrometer. NMR spectra were taken on a Varian A-60 instrument using TMS as the internal standard. Silica gel columns used the 0.05–0.2 mm silica gel manufactured "for column chromatography" by E. Merck & Co., Darmstadt, Germany. Preparative thin layer chromatography (preparative TLC) was carried out on 20 × 20 × 0.2 cm glass plates precoated with silica gel GF_{254} (E. Merck & Co.). Gas-liquid phase chromatographic (GLC) analyses were determined on Shimazu GC-4APF chromatograph. All analytical GLC was conducted on a column packed with 1, 5, or 20% carbowax 20 M.

Materials. Methyl 2-(chloroformylmethylthio)acetate **1**[1] (b.p. 129–130°/17 mm), methyl 2-(chloroformylmethoxy)acetate **2**[1] (b.p.

†According to L. P. Hammett, Physical Organic Chemistry, McGraw-Hill Book, Co., Inc., New York, 1940, p. 211, alkaline hydrolysis of acetic esters in H_2O at 25° is known to be accelerated 20 times by introduction of an α-methoxy group as an electron-attracting substituent. The same trend probably holds for the addition of Grignard reagent to the esters. Accordingly, the Grignard reaction of the mixed anhydride from **18** would be expected to facilitate further conversion to the overalkylated carbinol. Nevertheless, careful GLC analysis of the reaction product revealed only minor formation of **13a** (1.8%), methyl methoxyacetate (0.7%), and the methyl carbinol of **21** (2.9%), in addition to recovered methoxyacetic acid anhydride (54%). Even if excess reagent was used, the result was not significantly altered, suggesting that the normal reaction was extraordinarily retarded or prevented by a somewhat different mechanism.

123–126°/24 mm), methyl 3-chloroformylpropionate **3** (b.p. 80–83°/13 mm) and methyl 4-chloroformylbutyrate **4** (b.p. 103–105°/19 mm) were prepared readily from the corresponding cyclic anhydrides and methyl 5-chloroformylpentanoate **5** (b.p. 118–118.5°/17 mm) and methyl 8-chloroformyloctanoate **6** (b.p. 131–137°/3 mm), from the corresponding acid monoesters commercially available, according to a conventional method. Methoxyacetyl chloride **18** (b.p. 47–50.5°/68 mm) was prepared readily from chloroacetic acid in 58% overall yield by the known procedures.[3] 2-Ethoxypropionyl chloride **19**[4] (b.p. 70–72°/42 mm) was obtained in 85% yield using $SOCl_2$ and commercially available 2-ethoxypropionic acid. 3-Methoxybutyryl chloride **20** (b.p. 30–31°/6–7 mm) was prepared via 4 steps from methyl cellosolve in 20% overall yield by a relay of the literature procedures.[5] For comparative purposes, authentic samples of following esters were prepared easily by alcoholysis from the corresponding ester acid chlorides obtained above, respectively: Dimethyl thiodiacetate **14a** (b.p. 120–123°/10 mm), methyl ethyl thiodiacetate **14b**, methyl *n*-propyl thiodiacetate **14c**, dimethyl diglycolate **15a** and methyl ethyl diglycolate **15b**.

Preparation of keto esters

General procedure. To a stirred soln of *o*-anisic acid (15.2 g; 0.1 mol) in dry THF (400 ml) containing triethylamine (10.1 g; 0.1 mol) at −10°, was added a soln of **1** (18.3 g, 0.1 mol) in dry THF (100 ml). The resultant mixture was kept at the same temp with stirring for 0.5 h and then cooled in a Dry Ice–acetone bath. To the well-stirred suspension at −70 to −75°, was then added dropwise an ethereal soln of a corresponding alkylmagnesium bromide (0.11 mol, previously prepared from a corresponding alkyl bromide and standardized). After stirring 0.5 h, the reaction mixture was quenched with 10% NH_4Cl and extracted with ether. The extracts were combined, washed successively with 2 N Na_2CO_3 and sat NaCl aq and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residual liquid was usually purified by silica gel chromatography, followed by distillation at reduced pressure. The yields and boiling points of these keto esters prepared are listed in Table 2.

Methyl 2-(3-alkylacetonylthio)acetates **7a–c**. These compounds were identified with their authentic samples,[1] alternatively prepared by the dialkylcadmium procedure, in comparison of IR and NMR spectra.

Methyl 2-(*o-methylbenzoylmethylthio*)*acetate* **7d'**. IR (neat) 1736 (C=O), 1677 (conj. C=O), 1600, 1570 cm^{-1} (arom.); NMR ($CDCl_3$) δ 2.51 (s, 3H, $CH_3C_6H_4$), 3.32 (s, 2H, SCH_2COO), 3.71 (s, 3H, $COOCH_3$), 3.95 (s, 2H, SCH_2CO), 7.0–8.0 (m, 4H, arom.). (Found: C, 60.23; H, 5.75; S, 13.11. $C_{12}H_{14}O_3S$ requires: C, 60.48; H, 5.92; S, 13.46%).

Methyl 2-(3-*benzylacetonylthio*)*acetate* **7e**. IR (neat) 1731, 1710 (sh.) (C=O), 1603, 1498 cm^{-1} (arom.); NMR ($CDCl_3$) δ 2.89 (s, 4H, $COCH_2CH_2$), 3.17 (s, 2H, SCH_2COO), 3.34 (s, 2H, SCH_2CO), 3.67 (s, 3H, $COOCH_3$), 7.19 (s, 5H, arom.). (Found: C, 61.75; H, 6.42; S, 12.77. $C_{13}H_{16}O_3S$ requires: C, 61.88; H, 6.39; S, 12.71%).

Methyl 2-(3-m-*methoxybenzylacetonylthio*)*acetate* **7f**. IR (neat) 1737, 1713 (sh.) (C=O), 1601, 1583, 1491 cm^{-1} (arom.); NMR ($CDCl_3$) δ 2.89 (s, 4H, $COCH_2CH_2$), 3.20, 3.36 (s, s, 4H, CH_2SCH_2), 3.70 (s, 3H, $COOCH_3$), 3.77 (s, 3H, OCH_3), 6.7–7.3 (m, 4H, arom.). (Found: C, 59.33; H, 6.50; S, 11.28. $C_{14}H_{18}O_4S$ requires: C, 59.55; H, 6.43; S, 11.36%).

Methyl 2-(3-β-*phenylethylacetonylthio*)*acetate* **7g**. IR (neat) 1739, 1711 (C=O), 1603, 1499 cm^{-1} (arom.); NMR ($CDCl_3$) δ 1.7–2.2 (m, 2H, CH_2), 2.4–2.8 (m, 4H, CH_2CH_2), 3.23, 3.36 (s, s, 4H, CH_2SCH_2), 3.68 (s, 3H, $COOCH_3$), 7.20 (bs, 5H, arom.). (Found: C, 62.98; H, 6.80; S, 11.81. $C_{14}H_{18}O_3S$ requires: C, 63.13; H, 6.81; S, 12.04%).

Methyl 2-(3-β-(m-*methoxy*)*phenylethylacetonylthio*)*acetate* **7h**. IR ($CHCl_3$) 1736, 1710 (sh.) (C=O), 1602, 1584, 1488 cm^{-1} (arom.); NMR ($CDCl_3$) δ 1.7–2.2 (m, 2H, CH_2), 2.4–2.8 (m, 4H, CH_2CH_2), 3.25, 3.38 (s, s, 4H, CH_2SCH_2), 3.71 (s, 3H, $COOCH_3$), 3.79 (s, 3H, OCH_3), 6.6–7.4 (m, 4H, arom.). (Found: C, 60.47; H, 6.68; S, 10.70. $C_{15}H_{20}O_4S$ requires: C, 60.78; H, 6.80; S, 10.82%).

Methyl 2-[3-β-(p-*methoxy*)*phenylethylacetonylthio*]*acetate* **7i**. IR (neat) 1738, 1710 (sh.) (C=O), 1612, 1583, 1515 cm^{-1} (arom.); NMR ($CDCl_3$) δ 1.7–2.2 (m, 2H, CH_2), 2.4–2.8 (m, 4H, CH_2CH_2), 3.25, 3.37 (s, s, 4H, CH_2SCH_2), 3.71 (s, 3H, $COOCH_3$), 3.77 (s, 3H, OCH_3), 6.7–7.3 (m, 4H, arom.). (Found: C, 60.60; H, 6.91; S, 10.70. $C_{15}H_{20}O_4S$ requires: C, 60.78; H, 6.80; S, 10.70. $C_{15}H_{20}O_4S$ requires: C, 60.78; H, 6.80; S, 10.82%).

Methyl levulinate **9a**. The spectral data (IR, NMR) were identical with those of the authentic sample commercially available.

Methyl 4-acetylbutylate **10a**. The physical constants, e.g. b.p. and n_D, were essentially identical with the literature data.[6] The structure was confirmed by virtue of its IR and NMR spectra.

Methyl 8-m-*methoxyphenyl-5-oxooctanoate* **10h**. IR (neat) 1737, 1731 (C=O), 1601, 1583, 1489 cm^{-1} (arom.); NMR ($CDCl_3$) δ 1.7–2.2 (m, 4H, CH_2CH_2), 2.2–2.8 (m, 8H, $(CH_2)_4$), 3.66 (bs, 3H, $COOCH_3$), 3.78 (s, 3H, OCH_3), 6.7–7.4 (m, 4H, arom.). (Found: C, 68.82; H, 8.10. $C_{16}H_{22}O_4$ requires: C, 69.04; H, 7.97%).

Methyl 8-p-*methoxyphenyl-5-oxooctanoate* **10i**. IR ($CHCl_3$) 1733, 1716 (C=O), 1612, 1583, 1514 cm^{-1} (arom.); NMR ($CDCl_3$) δ 1.7–2.2 (m, 4H, CH_2CH_2), 2.2–2.8 (m, 8H, $(CH_2)_4$), 3.65 (s, 3H, $COOCH_3$), 3.76 (s, 3H, OCH_3), 6.7–7.2 (m, 4H, arom.). (Found: C, 68.73; H, 7.91. $C_{16}H_{22}O_4$ requires: C, 69.04; H, 7.97%).

Methyl 6-oxooctanoate **11b**. IR (neat) 1740, 1715 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.04 (t, 3H, J = 7 Hz, CH_3), 1.5–1.8 (m, 4H, CH_2CH_2), 2.2–2.7 (m, 6H, $(CH_2)_3$), 3.66 (s, 3H, $COOCH_3$). The above data were consistent with the assigned structure.

Methyl 9-oxodecanoate **12a**. The IR and NMR spectra agreed nearly with that obtained by the organocadmium procedure. The other physical constants were also essentially identical with those given in the literature.[7]

Preparation of alkoxy ketones

Alkoxy ketones **22** and **23** were also prepared, essentially according to the general procedure described above using **19** and **20** (in place of **1**), respectively.

4-Ethoxy-2-butanone **22**, b.p. 74–76°/51 mm, n_D^{20} 1.4088 [lit.[8] b.p. 74°/50 mm], was obtained in 53.4% yield. IR (neat) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.17 (t, 3H, J = 7 Hz, CH_3), 2.18 (s, 3H, $COCH_3$), 2.68 (t, 2H, J = 6.5 Hz, $COCH_2$), 3.49 (q, 2H, J = 7 Hz, OCH_2CH_3), 3.69 (t, 2H, J = 6.5 Hz, $CH_2OC_2H_5$).

5-Methoxy-2-pentanone **23**, b.p. 82–83°/55 mm, n_D^{20} 1.4155 [lit.[9] b.p. 154°, n_D^{20} 1.4148], was obtained in 51.7% yield. IR (neat) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.89 (quint., 2H, J = 6.5 Hz, CCH_2C), 2.14 (s, 3H, $COCH_3$), 2.52 (t, 2H, J = 6.5 Hz, $COCH_2$), 3.30 (s, 3H, OCH_3), 3.38 (t, 2H, J = 6.5 Hz, OCH_2).

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