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The Chemistry of Acylals. Part I. The Reactivity of Acylals Towards Grignard and Organolithium Reagents

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Abstract: *Aldehyde acylals have been prepared and reacted with Grignard and alkyllithium reagents. Acylals from formaldehyde furnished complex reaction mixtures when reacted with both reagents. Acylals of other aldehydes gave reaction mixtures that consisted mainly of an ester, generated by replacing one of the carboxy groups with the organic part of the organometallic reagent, and regenerated aldehyde. The esters were formed in the highest yields. Yields above 90% were experienced when the acylals were reacted with Grignard reagents under Barbier conditions.*

INTRODUCTION

A number of methods have been developed for the synthesis of acylals (**1**),[1] also known as geminal dicarboxylates and diesters of 1,1-diols. The syntheses most widely applied are carried out under acidic conditions, giving **1** by treating aldehydes with carboxylic anhydrides in the presence of an acid as catalyst.[2-39] Strong protic acids such as sulfuric acid,[2-8] phosphoric acid,[3,8-10] perchloric acid,[7,11,12] and sulfonic acids [3,8,13] are most frequently used, although the yields may in cases be poor and the required reaction time quite long.[2] Good results are also achieved when protic acids are replaced by Lewis acids such as zinc(II) chloride, [3,14,15] zinc(II) sulfate,[3] tin(II) chloride,[3,16] copper(II) sulfate,[3] iron(II) sulfate,[3] iron(III) chloride,[3,17] cobalt(II) chloride,[18] boron trifluoride,[19,20] and phosphorus trichloride,[21] by an ion-exchange resin, [22] by iodine,[23] by phosphorus pentoxide,[24] and by various inorganic catalysts.[25] A few preparations have also been carried out by reacting 1,1-dihaloalkanes with carboxylates under various conditions,[26-30] by performing double addition of carboxylic acids to acetylene,[31] by treating 1,3-dithianes with mercury(II) acetate in acetic acid containing a small amount of boron trifluoride, [32] and by exposing ethanal derivatives to acetic anhydride in the presence of catalytic amounts of a protic or a Lewis acid.[33] Finally, several reports [34-39] have revealed that acylals can also be obtained from various starting materials in reactions involving noble-metal catalysis, but due to the reaction conditions required these processes are rather unattractive for syntheses on a laboratory scale.

From the preceding paragraph it is evident that acylals are readily available, even in large quantities, but in spite of this acylal chemistry has been little explored. An exception is the chemistry of Meldrum's acid and several of its derivatives which exhibit special chemical properties.[40, 41] Most studies have focused on acylal stability, which has been found to be fairly good under acidic conditions, but rather limited even under mildly basic conditititions due to attack of one of the carbonyl groups.[42-45] Under the latter conditions the

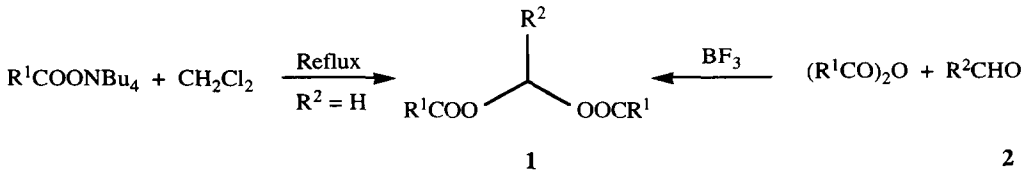
corresponding aldehydes are obtained in excellent yields when the right reagents are employed, viz. sodium or potassium hydroxide,[17] aniline,[46] the boron triiodide-*N,N*-diethylaniline complex,[47] and some phenoxides.[48] Aldehyde formation is also achieved by treating acylals with hydroxylamine and phenylhydrazine, but the aldehydes are not isolated because they react with the amines and afford the corresponding oximes [46] and hydrazones,[49] respectively. One report also reveals that ethanal is formed, albeit slowly, when 1,1-diacetoxyethane is allowed to react with 2-phenoxyethanol and 1-butanol in the presence of a catalytic amount of an acid.[50]

More significant transformations involving aldehyde acylals have been observed in a few cases only. When geminal diacetates are treated with carbanions, generated under phase-transfer conditions, substitution of one of the acetoxy groups by the carbanion takes place giving acetates of secondary alcohols in fair to good yields.[51, 52] Similar displacement of one acetoxy group also occurred when allylic geminal diacetates were treated with stabilized carbanions in the presence of a Pd(0) catalyst [53] or with butylmagnesium bromide in the presence of HMPA.[54] Finally, preparation of acyloxymethyl bromides was achieved by reacting aldehyde acylals with trimethylsilyl bromide under Lewis-acid catalysis.[55]

The limited knowledge about the chemical properties of acylals prompted us to study the reactivity of aldehyde acylals toward a number of reagents. In this paper we report the results of reactions with Grignard and alkyllithium reagents, the outcome of which proved to be influenced by the structure of the aldehyde and carboxylate moieties.

RESULTS AND DISCUSSION

The acylals used were synthesized by one of two methods. Dicarboxylates from formaldehyde (**1a-1f**) were obtained by reacting dichloromethane with selected tetrabutylammonium carboxylates following essentially the procedure of Holmberg and Hansen.[29] The yields varied from good to excellent, but no clear pattern in the variation was visible (Table 1). However, acylals from other aldehydes (**1g-1p**) were obtained by treating aldehydes with carboxylic anhydrides in the presence of boron trifluoride.[19] Again the yields varied from good to excellent, but no trend in the variation was obvious (Table 1). For instance, *para*-substituted benzaldehydes afforded good yields of acylals with both electron-donating (Me; 83%) and electron-withdrawing (NO_2; 70%) substituents, an observation which shows that the electronic influence is not decisive for the outcome of the reaction. Furthermore, steric interactions alone cannot be the overriding factor, because when hexanal and octanal are reacted separately with acetic anhydride, acylals **1l** and **1o** were isolated in 51 and 83% yield, respectively, despite the fact that the latter compound conceivably exhibits more steric crowding than the former.



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The acylals were reacted with alkyllithium reagents, which were added to the reaction flask, and Grignard reagents, which were either added to the reaction flask or generated *in situ*. Exploratory experiments, carried out with several 1,1-dicarboxylates, revealed that the most significant product from these reactions was

the ester resulting from replacement of one of the carboxy groups with an alkyl or a phenyl group (**3**). The same experiments also showed that the outcome depended on the reagent employed, the acylal used, and the mode of mixing. Generally speaking, the Grignard reagents afforded better yields of esters than the lithium reagents; for instance, the yield of 1-(4-methylphenyl)butyl acetate increased from 28% to 93% when **1h** was reacted with butylmagnesium bromide instead of butyllithium. Furthermore, the acylals from formaldehyde (**1a-1f**) afforded

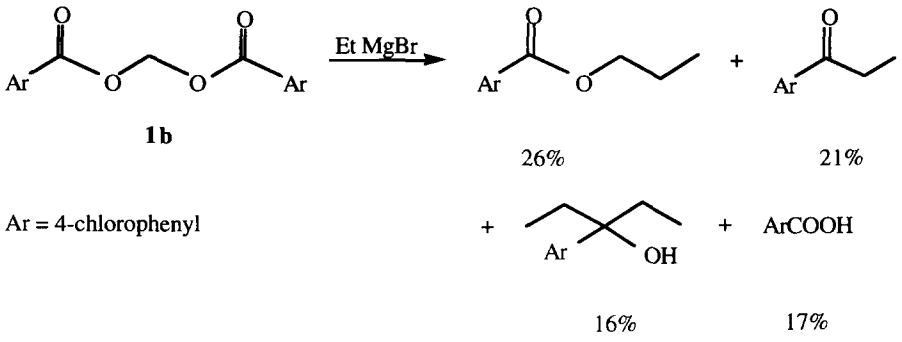
Table 1. Acylals **1** prepared and used in this study.

Product	Synthetic method [a]	R^1	R^2	Isolated yield/%
1a	A	Ph	H	83
1b	A	4-ClPh	H	88
1c	A	PhCH=CH	H	93
1d	A	*t*-Bu	H	73
1e	A	*n*-Pentyl	H	33
1f	A	$CH_3CH=CH$	H	63
1g	B	Me	Ph	78
1h	B	Me	4-MePh	83
1i	B	Me	4-ClPh	79
1j	B	Me	4-MeOPh	60
1k	B	Me	$4\text{-}NO_2Ph$	70
1l	B	Me	*n*-Pentyl	51
1m	B	Et	Ph	54
1n	B	*n*-Pentyl	Ph	75
1o	B	Me	*n*-Heptyl	83
1p	B	Me	*n*-Undecyl	75

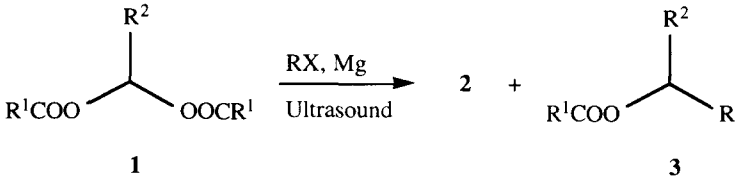
[a] Method A: Reaction of dichloromethane (R^2CHCl_2, R^2=H) with a tetrabutylammonium carboxylate ($R^1COOTBA$); method B: Reaction of an aldehyde (R^2CHO) with an anhydride ($(R^1COO)_2O$) in the presence of boron trifluoride etherate.

very complex reaction mixtures when reacted with lithium and magnesium reagents; for instance, treatment of **1b** with ethylmagnesium bromide gave a mixture consisting of 20% of unreacted starting material and four products isolated in yields better than 15%. Compounds **1a-1f** were therefore deemed inapplicable as substrates for synthetic purposes Finally, in all the cases investigated a much lower fraction of the starting material was converted to the corresponding aldehyde when the magnesium reagent was generated *in situ* under the influence of ultrasound as compared to external preparation followed by addition to the substrate. As a result the present study has been limited to reactions with selected Grignard reagents prepared *in situ* (Barbier conditions).

Acylals **1g-1p** were reacted under Barbier conditions by adding a 10% excess of the halides to a suspension of a 10% excess of magnesium in a THF solution of the acylals exposed to ultrasound radiation. In most cases the reaction mixture contained one major product, ester **3** generated by replacement of one of the carboxy groups with the organic part of the Grignard reagent, accompanied by varying amounts of the corresponding aldehyde (**2**) produced by attack at a carbonyl group (Table 2). However, some exceptions were



observed; thus, the reactions of **1m** with methylmagnesium iodide (entry 16), **1g**, **1l**, **1o** and **1p** with ethylmagnesium bromide (entries 2, 15, 19 and 20), and **1h** with butylmagnesium iodide (entry 7) furnished the corresponding esters **3** only. The esters were generally isolated in 60-90% yield, although exceptions were observed. Acylal **1k** was particularly unreactive and was recovered unchanged when reacted with EtMgBr under a variety of conditions. Several attempts to improve the outcome of this reaction by adding hexamethylphosphoramide (HMPA) were unsuccessful, although Alexakis *et al.* managed to facilitate a similar reaction by such a measure.[54]



The ester formation varied in a somewhat systematic way in several respects. When the lengths of both R^1 and R^2 in **1** increased the yield of **3** generally dropped. Thus, benzylidene diacetate gave 1-phenylpropyl acetate in 94% yield when reacted with ethylmagnesium bromide (Table 2, entry 2) whereas the corresponding distearate afforded the analogous ester in only 9% yield under identical conditions, and an elongation of R^2 from *n*-pentyl (**1l**) to *n*-undecyl (**1p**) lowered the yield from 70 to 50 %. Furthermore, when the *para* hydrogen in benzylidene diacetate was replaced by an electron-donating group the yield of aldehyde **2** increased at the expense of ester **3** (consult Table 2, entries 2, 5 and 11). This is probably caused by an increased electron density at the dicarboxylated carbon atom, which makes an attack by a nucleophile less likely. The reaction between the acylals and the Grignard reagents therefore resembles the cleavage of esters with powerful nucleophiles, e.g. iodide, cyanide or mercaptide, in dipolar, aprotic solvents.[56] Finally, it is obvious that the reaction is sensitive to the steric requirement of the Grignard reagent; this is, for instance, borne out by the fact that the yield of **3** is 2-3 times higher when **1g**, **1h** and **1j** are reacted with ethylmagnesium bromide (Table 2, entries 2, 5 and 11) as compared with isopropylmagnesium bromide (Table 2, entries 3, 6 and 12, respectively).

Table 2. Products from Ultrasound Irradiation of Mixtures of Acylal, Alkyl Halide (RX) and Magnesium Turnings.

Entry	Substrate	R	Isolated yield/%		Ratio
			2	**3**	**3 : 2**
1	**1g**	Me	8[a]	81[a]	90:10
2	**1g**	Et	0	94	100:0
3	**1g**[b]	*i*-Pr	11	44	80:20
4	**1h**	Me	9	82	90:10
5	**1h**	Et	9[a]	89[a]	90:10
6	**1h**[c,d]	*i*-Pr	13	36	73:27
7	**1h**	Bu	0	93	100:0
8	**1i**	Me	15[a]	71[a]	83:17
9	**1i**	Et	10[a]	78[a]	87:13
10	**1i**[c]	Ph	3[a]	67[a]	95:5
11	**1j**	Et	22	40	64:36
12	**1j**	*i*-Pr	59	15	20:80
13	**1j**[b]	Ph	15[a]	50[a]	77:23
14	**1k**	Et	*e*	*e*	-
15	**1l**	Et	0	70	100:0
16	**1m**	Me	0	87	100:0
17	**1m**	Et	4	71	95:5
18	**1n**	Et	18	71	80:20
19	**1o**[f]	Et	0	66	100:0
20	**1p**[b]	Et	0	50	100:0

[a] Isolated as a mixture; the yields calculated on the basis of ^{1}H NMR and GC analyses.

[b] 20% of acylal was recovered.

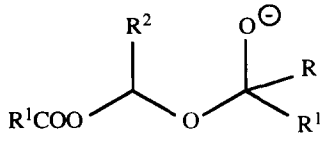
[c] 10% of acylal was recovered.

[d] In addition 10% of 4-methylbenzyl alcohol was isolated.

[e] No reaction took place.

[f] 10% of acylal was recovered.

The observation that **1g-1j** generally affords a mixture of only two compounds, an aldehyde (**2**) and an ester (**3**), when reacted with the Grignard reagents is somewhat surprising considering the fact that aldehydes and esters generally react easily with such reagents and afford secondary and tertiary alcohols, respectively. The composition of the reaction mixtures might, therefore, indicate that acylals **1** react more easily than **2** and **3** with Grignard reagents. It is also possible that the aldehydes are not formed during addition of the reagents, but by quenching of the conceivable intermediate **4** during the hydrolytic work-up. The first explanation is supported by the observation that only **1h** was consumed when 1:1 mixtures of **1h** with 4-methylbenzaldehyde and with 1-(4-methylphenyl)propyl acetate were allowed to react with 0.5 equivalent of ethylmagnesium bromide. The



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second explanation may be less likely, because attempts to trap **4** by adding trimethylsilyl chloride prior to hydrolysis were unsuccessful. However, this result is not quite unexpected considering the fact that the analogous intermediate in the reaction between **1g** and aniline decomposes spontaneously.[46]

EXPERIMENTAL SECTION

General: ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 200 spectrometer at 200 and 50 MHz, respectively, using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, q = quartet, and qn = quintet. IR spectra were recorded on a Perkin-Elmer model 1310 spectrometer. Flash chromatography was performed on Silica gel 60 (230-400 mesh) from Merck using either hexane : ethyl acetate 97.5 : 2.5 or hexane : ethyl acetate 95: 5 as eluent. Thin layer chromatography (TLC) was carried out on Silica 60 F_{254} from Merck. Preparative TLC was conducted using plates made from Silica 60 (70-230 mesh ASTM) and Silica 60 F_{254}. Analytical gas chromatography (GC) was performed on a Hewlett Packard 5720 A gas chromatograph equipped with a 4-m packed colomn (15% SP-2100 on Supelcoport); FID detection was applied and a HP 3380 A integrator was conected to the instrument. The sonication experiments were performed in a Bandelin Sonorex Super RK 255 H laboratory cleaner with a 320 W effect. THF was distilled from sodium/benzophenone.

*Syntheses of the acylals (**1**).* Acylals **1a-1f** were synthesized on a 50 - 140 mmol scale by method A, which is based on the work of Holmberg and Hansen.[29] Acylals **1g-1p** were prepared on a 58 - 400 mmol scale by method B, which is a modification of the procedure by Man *et al.*[19]

Method A: A typical synthesis was carried out as follows. Carboxylic acid (0.10 mol) and tetrabutylammonium hydrogensulfate (0.10 mol) were dissolved in 2 M aq NaOH (100 mL). The solution was extracted with CH_2Cl_2 (3 x 250 mL) and the combined extracts were dried ($MgSO_4$), filtered and refluxed for 4 days. After washing with 2.5 M aq H_2SO_4 (2 x 300 mL), H_2O (300 mL), saturated aq $NaHCO_3$ (2 x 300 mL), and H_2O (300 mL) the solution was dried ($MgSO_4$), filtered, and concentrated on a rotary evaporator. The crude product was subsequently purified by recrystallization from ethanol or ethyl acetate, or by distillation.

Method B: A representative synthesis was carried out as follows. Carboxylic anhydride (0.28 mol) and $BF_3{\cdot}OEt_2$ (10 drops) were introduced to a round-bottomed flask, equipped with a dropping funnel, a stirring magnet, and a thermometer, and immersed in a salt-ice slush. Aldehyde (0.14 mol) was added slowly with stirring, and the mixture was stirred at room temperature for 2-3 hours. The product mixture was poured into a 10% aq solution of NaOAc (200 mL) and stirred rapidly for 20 minutes. An oily layer was formed. The product was extracted with Et_2O (3 x 50 mL), the extracts were combined, and washed with aq $NaHCO_3$ followed by H_2O. After drying ($MgSO_4$) the crude product was concentrated under vacuum and isolated by recrystallization from ethanol or destillation.

The following acylals were prepared.

Methylidene dibenzoate (**1a**), a white, crystalline solid, m.p. 94-95 °C (lit.:[29] 96-97 °C). IR (CCl_4): ν_{max} 3040, 1725, 1590, 1440, 1240 cm^{-1}; ^1H NMR: δ 8.11-8.07 (4 H, m), 7.61-7.39 (6 H, m), 6.25 (2 H, s); ^{13}C NMR: δ 165.0, 133.5, 129.9, 128.8, 128.3, 79.8.

Methylidene di(4-chlorobenzoate) (**1b**), a white, crystalline solid, m.p. 94-95 °C (lit.:[29] 99-100 °C). IR (CCl_4): ν_{max} 1730, 1585, 1245, 1150, 1045 cm^{-1}; ^1H NMR: δ 8.05-7.99 (4 H, m), 7.45-7.40 (4 H, m), 6.22 (2 H, s); ^{13}C NMR: δ 164.4, 140.4, 131.5, 128.9, 127.3, 80.1.

Methylidene dicinnamate (**1c**), a white, crystalline solid, m.p. 84-85 °C. IR (CCl_4): ν_{max} 1735, 1625, 1440, 1120, 990 cm^{-1}; ^1H NMR: δ 7.79 (2 H, d, *J* 16 Hz), 7.54-7.48 (4 H, m), 7.41-7.36 (6 H, m), 6.47 (2 H, d, *J* 16 Hz), 6.03 (2 H, s); ^{13}C NMR: δ 165.6, 146.8, 134.0, 130.7, 128.9, 128.3, 166.7, 79.3.

Methylidene dipivalate (**1d**), a colourless liquid, B.p. 106-108 °C/15 mm Hg (lit.:[29] b.p. 34 °C/0.1 mm Hg). IR (neat): ν_{max} 2980, 1740, 1265, 1150, 1090 cm^{-1}; ^1H NMR: δ 5.76 (2 H, s), 1.21 (18 H, s); ^{13}C NMR: δ 177.1, 79.2, 38.7, 26.8.

Methylidene dihexanoate (**1e**), a pale yellow liquid. IR (film): ν_{max} 2940, 1750, 1130, 1090, 990 cm^{-1}; ^1H NMR: δ 5.75 (2 H, s), 2.35 (4 H, t, *J* 7.6 Hz), 1.64 (4 H, qn, *J* 7.1 Hz), 1.24-1.38 (8 H, m), 0.90 (6 H, t, *J* 6.6 Hz); ^{13}C NMR: δ 172.1, 78.7, 39.6, 30.9, 24.0, 22.0, 13.5.

Methylidene dicrotonoate (**1f**), a colourless liquid, b.p. 137-138 °C/10 mmHg. IR (film): ν_{max} 2980, 1720, 1645, 1440, 835 cm^{-1}; ^1H NMR: δ 7.17-6.99 (2 H, m), 5.91-5.81 (2 H, m), 5.87 (2H, s) 1.94-1.88 (6 H, m); ^{13}C NMR: δ 164.4, 146.6, 121.3, 78.7, 17.7.

Benzylidene diacetate (**1g**), white crystals, b.p. 120-122 °C/7 mmHg, m.p. 43-45 °C (lit.:[2] 45.8 °C). IR (CCl_4): ν_{max}1750, 1360, 1230, 1195, 1050 cm^{-1}; ^1H NMR: δ 7.69 (1 H, s), 7.53-7.50 (2 H, m), 7.42-7.38 (3 H, m), 2.11 (6 H, s); ^{13}C NMR: δ 168.8, 135.5, 129.8, 128.6, 126.7, 89.7, 20.8.

4-Methylbenzylidene diacetate (**1h**), a white, crystalline solid, m.p. 79-81 °C (lit.:[8] 81-82 °C). IR (CCl_4) : ν_{max} 1755, 1360, 1230, 1195, 1000 cm^{-1}; ^1H NMR: δ 7.65 (1 H, s), 7.43-7.39 (2 H, m), 7.22-7.18 (2 H, m), 2.35 (3 H, s), 2.09 (6 H, s); ^{13}C NMR: δ 168.6, 139.6, 132.4, 129.0, 126.4, 89.5, 21.1, 20.7.

4-Chlorbenzylidene diacetate (**1i**), a white, crystalline solid, m.p. 76-78 °C (lit.:[42] 80-81 °C). IR (CCl_4): ν_{max} 1750, 1485, 1360, 1230, 1190 cm^{-1}; ^1H NMR: δ 7.65 (1 H), 7.49-7.44 (2 H, m), 7.40-7.34 (2 H, m), 2.12 (6 H, s); ^{13}C NMR: δ 168.7, 135.7, 134.0, 128.8, 128.2, 89.0, 20.8.

4-Methoxybenzylidendiacetate (**1j**), a white, crystalline solid, m.p. 58-60 °C (lit.:[8] 64-65 °C). IR (CCl_4): ν_{max}1755, 1360, 1230, 1195, 1060 cm^{-1}; ^1H NMR: δ 7.63 (1 H, s), 7.47-7.43 (2 H, m), 6.93-6.88 (2 H, m), 3.79 (3 H, s), 2.09 (6 H, s); ^{13}C NMR: δ 168.5, 160.4, 127.9, 127.5, 113.7, 89.5, 55.0, 20.5.

4-Nitrobenzylidene diacetate (**1k**), a pale yellow, crystalline solid, m.p. 116-118 °C (lit.:[57] 125-126 °C). IR (CCl_4): ν_{max} 1730, 1500, 1320, 1205, 985 cm^{-1}; ^1H NMR: δ 8.28-8.23 (2 H, m), 7.75 (1 H, s), 7.75-7.70 (2 H, m), 2.17 (6 H, s); ^{13}C NMR: δ 168.3, 148.4, 141.7, 127.6, 123.5, 88.1, 20.4.

Hexylidene diacetate (**1l**), a pale yellow liquid. IR (film): ν_{max} 2950, 1750, 1370, 1240, 1200 cm^{-1}; ^1H NMR: δ 6.77 (1 H, t, *J* 5.6 Hz), 2.07 (6 H, s), 1.77-1.70 (2 H, m), 1.38-1.28 (6 H, m), 0.89 (3 H, t, *J* 6.5 Hz); ^{13}C NMR: δ 168.7, 90.3, 32.9, 31.1, 22.8, 22.2, 20.5, 13.6.

Benzylidene dipropanoate (**1m**), a white, crystalline solid, b.p. 162-164 °C/12 mmHg (lit.:[2] b.p. 158-159 °C/10 mmHg), m.p. 28-29 °C. IR (CCl_4): ν_{max} 2960, 1740, 1450, 1410, 1345 cm^{-1}; ^1H NMR: δ 7.72 (1 H, s), 7.55-7.50 (2 H, m), 7.42-7.38 (3 H, m), 2.40 (4 H, d q, *J* 5.7 and 2.1 Hz), 1.15 (6 H, t, *J* 7.6 Hz); ^{13}C NMR: δ 172.0, 135.5, 129.4, 128.3, 126.3, 89.3, 27.1, 8.4.

Benzylidene dihexanoate (**1n**), a pale yellow liquid, b.p. 153-156 °C/2 mmHg. IR (film): ν_{max} 2920, 1755, 1450, 1160, 700 cm^{-1}; ^1H NMR: δ 7.72 (1 H, s), 7.54-7.47 (2 H, m), 7.42-7.35 (3 H, m), 2.37 (4 H, t, *J* 7.7 Hz), 1.71-1.57 (4 H, m), 1.36-1.22 (8 H, m), 0.88 (6 H, t, *J* 6.4 Hz); ^{13}C NMR: δ 171.4, 135.6, 129.4, 128.3, 126.5, 89.3, 33.9, 30.9, 24.1, 22.1, 13.7.

Octylidene diacetate (**1o**), a colourless liquid, b.p. 95-96 °C/0.7 mmHg. IR (film): ν_{max} 2920, 1760, 1370, 1240, 970 cm^{-1} ; ^1H NMR: δ 6.77 (1 H, t, *J* 5.6 Hz), 2.07 (6 H, s), 1.80-1.70 (2 H, m), 1.50-1.15 (10 H, m), 0.88 (3H, t, *J* 6.8 Hz); ^{13}C NMR: δ 168.7, 90.3, 32.9, 31.4, 28.9, 28.8. 23.1, 22.3, 20.5, 13.8.

Dodecanylidene diacetate (**1p**), a white, crystalline solid b.p. 125-126 °C/0.5 mmHg, m.p. 32-34 °C. IR (CCl_4): ν_{max} 2920, 1755, 1365, 1240, 1200 cm^{-1}; ^{1}NMR: δ 6.77 (1 H, t, *J* 5.6 Hz), 2.07 (6 H, s), 1.80-1.65 (2 H, m), 1.45-1.10 (18 H, m), 0.88 (3 H, t, *J* 6.1 Hz); ^{13}C NMR: δ 168.8, 90.4, 33.0, 31.7, 29.4, 29.3, 29.25, 29.2, 29.0, 23.2, 22.5, 20.6, 13.9.

Benzylidene distearate was obtained as a white, fatty solid, m.p. 51-54 °C. IR (CCl_4): ν_{max} 2910, 2830, 1750, 1450, 710 cm^{-1}; ^1H NMR: δ 7.70 (1 H, s), 7.48-7.53 (2 H, m), 7.37-7.40 (3 H, m), 2.31-2.44 (4 H, m), 1.60-1.67 (4 H, m), 1.15-1.45 (56 H, m), 0.70-0.91 (6 H, m); ^{13}C NMR: δ 171.5, 135.7, 129.5, 128.4, 126.5, 89.4, 35.2, 34.0, 33.9, 31.8, 29.6, 29.5, 29.3, 29.25, 29.1, 29.0, 28.9, 24.6, 24.1, 22.6, 14.0.

Reactions of **1** *with alkyllithium reagents.* Acylals **1a**, **1h**, **1j** and **1m** were reacted on a 4.5-mmol scale with methyllithium and butyllithium using the following typical procedure. In a 50-mL flask filled with nitrogen was placed a stirring bar and acylal (4.50 mmol) dissolved in dry THF (5 mL). The flask was immersed in a dry-ice/acetone bath (- 78 °C) and the alkyllitium reagent (4.95 mmol) was added dropwise with stirring. Stirring was continued until room temperature was reached and subsequently for two hours at this temperature. The reaction mixture was acidified with 6 M aq HCl, and the products were extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with H_2O (2 x 40 mL) and dried ($MgSO_4$). Filtration followed by solvent removal on a rotary evaporator afforded a crude product which was purified by flash chromatography.

Reactions of **1** *with Grignard reagents.* The acylals were reacted on a 3.5 - 5.0 mmole scale by *in-situ* generated Grignard reagents (method A) and/or externally generated Grignard reagents (method B).

Method A: In a typical experiment a dry, nitrogen-filled, 50-mL, round-bottomed flask was charged with dry THF (5 mL), acylal (4.50 mmol) and Mg (0.120 g, 4.95 mmol). The flask was partially submerged in a sonicator in the position that produced the most vigorous agitation of the mixture. The alkyl halide (4.95 mmol) was then added in one portion, and after the reaction started the mixture was irradiated at room temperature for 3 hours. The resulting mixture was poured into 10 % aq HCl (50 mL) and the product was extracted with Et_2O (3 x 25 mL). The combined extracts were washed with H_2O (2 x 50 mL), dried ($MgSO_4$), and concetrated on a rotary evaporator. The product was isolated from the residue by flash chromatography.

Method B: In a typical experiment a dry, nitrogen-filled, 50-mL, round-bottomed flask was charged with acylal (4.5 mmol) in dry THF (5 mL). A solution of the Grignard reagent (4.95 mmol) was added dropwise at 0-5°C and the mixture was stirred for 3 h at room temperature. Subsequent work-up and product isolation were carried out as described for method A.

The outcome of the reactions with acylals **1g**-**1p** are summarized in Table 2.

The following esters were synthesized and isolated according to method A.

1-Phenylethyl acetate (entry 1), a clear liquid.[58] IR (neat): ν_{max} 1710, 1360, 1230, 900, 720 cm^{-1}; ^1H NMR: δ 7.35-7.24 (5 H, m), 5.87 (1 H, q, *J* 6.6 Hz), 2.03 (3 H, s), 1.51 (3 H, d, *J* 6.6 Hz); ^{13}C NMR: δ 170.0, 141.4, 128.1, 127.5, 125.8, 72.0, 21.9, 21.0.

1-Phenylpropyl acetate (entry 2), a pale yellow liquid.[59] IR (neat): ν_{max} 3005, 2940, 1720, 1355, 1225 cm^{-1}; ^1H NMR: δ 7.33-7.23 (5 H, m), 5.66 (1 H, t, *J* 6.7 Hz), 2.07 (3 H, s), 1.92-1.76 (2 H, m), 0.87 (3 H, t, *J* 7.4 Hz); ^{13}C NMR: δ 170.3, 140.3, 128.2, 127.6, 126.4, 77.2, 29.1, 21.1, 9.7.

2-Methyl-1-phenylpropyl acetate (entry 3), a colourless liquid.[60] IR (neat): ν_{max} 3010, 2950, 1725, 1360, 1225 cm^{-1}; ^1H NMR: δ 7.35-7.13 (5 H, m), 5.39 (1 H, d, *J* 7.6 Hz), 2.07-1.93 (4 H, s and m), 0.89 (3 H, d, *J* 6.8 Hz), 0.72 (3 H, d, *J* 6.8 Hz); ^{13}C NMR: δ 170.2, 129.2, 128.4, 127.5, 126.8, 80.8, 33.3, 21.0, 18.5, 18.4.

1-(4-Methylphenyl)ethyl acetate (entry 4), a colourless liquid.[58] IR (neat): ν_{max} 3000, 1730, 1595, 1230, 810 cm^{-1}; ^1H NMR: δ 7.33-7.27 (2 H, m), 7.16-7.12 (2 H, m), 5.85 (1 H, q, *J* 6.6 Hz), 2.33 (3 H, s), 2.04 (3 H, s), 1.50 (3 H, d, *J* 6.6 Hz); ^{13}C NMR: δ 169.9, 138.4, 137.2, 129.0, 125.9, 72.0, 21.9, 21.2, 20.9.

1-(4-Methylphenyl)propyl acetate (entry 5), a pale yellow liquid.[61] IR (neat): ν_{max} 2950, 1725, 1360, 1230, 805 cm^{-1}; ^1H NMR: δ 7.24-7.11 (4 H, m), 5.63 (1 H, t, *J* 6.9 Hz), 2.32 (3 H, s), 2.07 (3 H, s), 1.99-1.75 (2 H, m), 0.87 (3 H, t, *J* 7.3 Hz); ^{13}C NMR: δ 170.2, 137.3, 128.9, 126.4, 77.1, 29.0, 21.1, 20.9, 9.8.

2-Methyl-1-4-(methylphenyl) propyl acetate (entry 6), a pale yellow liquid. IR (neat): ν_{max} 2950, 1730, 1365, 1230, 1015 cm^{-1}; ^1H NMR: δ 7.25-7.11 (4 H, m), 5.42 (1 H, d, *J* 7.8 Hz), 2.33 (3 H, s), 2.13-2.03 (4 H, s and m), 0.97 (3 H, d, *J* 6.7 Hz), 0.78 (3 H, d, *J* 6.7 Hz); ^{13}C NMR: δ 170.3, 137.2, 136.6, 128.7, 126.9, 80.9, 33.3, 21.1, 21.0, 18.6, 18.5.

1-(4-Methylphenyl)pentyl acetate (entry 7), a pale yellow liquid. IR (neat): ν_{max} 3000, 2940, 1720, 1230, 1010; ^1H NMR: δ 7.24-7.11 (4 H, m), 5.69 (1 H, t, *J* 7.1 Hz), 2.32 (3 H, s), 2.04 (3 H, s), 1.93-1.68 (2 H, m), 1.34-1.17 (4 H, m), 0.87 (3 H, t, *J* 7.3); ^{13}C NMR: δ 170.2, 137.7, 137.3, 128.9, 126.4, 75.9, 35.7, 22.3, 21.1, 21.0, 13.8.

1-(4-Chlorophenyl)ethyl acetate (entry 8), a pale yellow liquid.[58] IR (neat): ν_{max} 2960, 1720, 1585, 1360, 1230 cm^{-1}; ^1H NMR: δ 7.35-7.27 (4 H, m), 5.84 (1 H, q, *J* 6.6 Hz), 2.07 (3 H, s), 1.51 (3 H, d, *J* 6.6 Hz); ^{13}C NMR: 170.0, 130.7, 129.3, 128.5, 127.4, 71.4, 22.0, 20.9.

1-(4-Chlorophenyl)propyl acetate (entry 9), a colouless liquid. IR (neat): ν_{max} 2950, 1735, 1480, 1360, 1230 cm^{-1}; ^1H NMR: δ 7.33-7.22 (4 H, m), 5.61 (1 H, t, *J* 7.0 Hz), 2.07 (3 H, s), 1.94-1.74 (2 H, m), 0.87 (3 H, t, *J* 7.4 Hz); ^{13}C NMR: δ 170.2, 130.7, 129.3, 128.4, 127.8, 76.5, 29.0, 21.0, 9.7.

(4-Chlorophenyl)(phenyl)methyl acetate (entry 10), a colourless oil.[62] IR (neat): ν_{max} 1730, 1585, 1480, 1360, 1220 cm^{-1}; ^1H NMR: δ 7.33-7.22 (9 H, m), 6.83 (1 H, s), 2.14 (3 H, s); ^{13}C NMR: δ 169.7, 139.6, 138.6, 133.6, 130.7, 128.5, 128.3, 127.9, 126.8, 76.0, 21.0.

1-(Methoxyphenyl)propyl acetate (entry 11), a pale yellow liquid.[63] IR (neat): ν_{max} 2995, 1710, 1350, 1230, 810 cm^{-1}; ^1H NMR: δ 7.28-7.24 (2 H, m), 6.90-6.84 (2 H, m), 5.61 (1 H, t, *J* 7.0 Hz), 3.78 (3 H, s), 2.04 (3 H, s), 1.96-1.77 (2 H, m), 0.86 (3 H, t, *J* 7.4 Hz); ^{13}C NMR: δ 170.3, 159.0, 132.4, 127.8, 113.5, 76.9, 55.0, 28.8, 21.1, 9.8.

1-(4-Methoxyphenyl)-2-methylpropyl acetate (entry 12), slightly yellow crystals, m.p. 28-29 °C. IR (CCl_4): ν_{max} 2920, 1715, 1490, 1350, 1220 cm^{-1}; ^1H NMR (200 MHz): δ 7.24-7.20 (2 H, m), 6.87-6.83 (2

H, m), 5.40 (1 H, d, *J* 8.0 Hz), 3.78 (3 H, s), 2.13-1.90 (4 H, s and m), 0.97 (3 H, d, *J* 6.7), 0.77 (3 H, d, *J* 6.7 Hz); ^{13}C NMR (50 MHz): δ 170.2, 158.9, 131.7, 128.1, 113.3, 80.6, 55.0, 33.2, 20.7, 18.5.

4-(Methoxyphenyl)(phenyl)methyl acetate (entry 13), a pale yellow liquid. IR (neat): ν_{max} 1710, 1565, 1210, 1000, 670 cm^{-1}; ^{1}H NMR: δ 7.39-7.20 (7 H, m), 6.86-6.82 (3 H, m), 3.73 (3 H, s), 2.11 (3 H, s); ^{13}C NMR: δ 169.8, 159.0, 140.2, 131.7, 128.4, 128.2, 127.5, 126.6, 113.6, 76.3, 54.9, 21.0.

1-Ethylhexyl acetate (entry 15), a pale yellow liquid.[64] IR (neat): ν_{max} 2940, 1715, 1440, 1355, 1225 cm^{-1}; ^{1}H NMR: δ 4.81 (1 H, qn, *J* 5.9 Hz), 2.03 (3 H, s), 1.49-1.66 (4 H, m), 1.28-1.47 (6 H, m), 0.81-0.91 (6 H, m); ^{13}C NMR: δ 170.7, 75.3, 33.4, 31.5, 26.7, 24.8, 22.3, 21.0, 13.8, 9.3.

1-Phenylethyl propanoate (entry 16), a pale yellow liquid.[65] IR (neat): ν_{max} 2920, 2960, 1725, 1180, 780 cm^{-1}; ^{1}H NMR: δ 7.28-7.18 (5 H, m), 5.81 (1 H, q, *J* 6.5 Hz), 2.35-2.20 (2 H, m), 1.52 (3 H, d, *J* 6.5 Hz), 1.14 (3 H, t, *J* 7.5 Hz); ^{13}C NMR: δ 171.5, 128.1, 127.6, 127.0, 125.8, 71.2, 27.3, 22.5, 8.9.

1-Phenylpropyl propanoate (entry 17), a colourless liquid. IR (film): ν_{max} 3020, 1725, 1450, 1175, 695 cm^{-1}; ^{1}H NMR: δ 7.30-7.13 (5 H, m), 5.60 (1 H, t, *J* 7.0 Hz), 2.33-2.21 (2 H, m), 1.85-1.73 (2 H, m), 1.10 (3 H, t, *J* 7.6 Hz), 0.87 (3 H, t, *J* 7.4 Hz); ^{13}C NMR: δ 173.8, 140.8, 128.4, 127.8, 126.5, 77.1, 29.4, 27.9, 9.9, 9.2.

1-Phenylpropyl hexanoate (entry 18), a colourless liquid. IR (neat): ν_{max} 3000, 2920, 1715, 1150, 685 cm^{-1}; ^{1}H NMR: δ 7.34-7.22 (5 H, m), 5.67 (1 H, t, *J* 6.6 Hz), 2.32 (2 H, t, *J* 7.9 Hz), 1.96-1.76 (2 H, m), 1.72-1.54 (2 H, m), 1.34-1.20 (4 H, m), 0.94-0.84 (6 H, m); ^{13}C NMR: δ 173.0, 140.6, 128.2, 127.6, 126.4, 76.9, 34.4, 31.1, 29.2, 24.5, 22.2, 13.7, 9.8.

1-Ethyloctyl acetate (entry 19), a colourless liquid. IR (neat): ν_{max} 2900, 1720, 1360, 1230, 720 cm^{-1}; ^{1}H NMR: δ 4.81 (1 H, qn, *J* 6.2 Hz), 2.04 (3 H, s), 1.59-1.43 (4 H, m), 1.30-1.20 (10 H, m), 0.91-0.84 (6 H, m); ^{13}C NMR: δ 170.8, 75.4, 33.5, 31.7, 29.2, 29.1, 27.2, 26.8, 22.5, 21.1, 13.9, 9.4.

1-Ethyldodecyl acetate (entry 20), a colourless liquid. IR (neat): ν_{max} 2880 , 1710, 1435, 1350, 1220 cm^{-1}; ^{1}H NMR: δ 4.81 (1 H, qu, *J* 6.2 Hz), 2.04 (3 H, s), 1.59-1.43 (4 H, m), 1.3-1.1 (18 H, m), 0.91-0.84 (6 H, m); ^{13}C NMR: δ 170.8, 75.4, 33.5, 31.8, 31.5, 30.2, 29.5, 29.4, 29.3, 29.2, 26.8, 25.2, 22.6, 21.1, 14.0, 9.4.

Competition experiments. Such experiments were performed between 4-methylbenzylidene diacetate and 4-methylbenzaldehyde (experiment 1) and between 4-methylbenzylidene diacetate and 1-(4-methylphenyl)propyl acetate (experiment 2). Both experiments were carried out as described for experiment 1.

Experiment 1. In a dry, 50-mL flask kept under nitrogen were placed 4-methylbenzylidene diacetate (1.00 g, 4.5 mmol) and 4-methylbenzaldehyde (0.54 g, 4.5 mmol) in dry THF (5 mL). After cooling the mixture to 0 °C ethylmagnesium bromide, prepared from Mg (0.11 g, 4.5 mmol) and ethyl bromide (0.49 g, 4.5 mmol) in dry THF (5 mL), was added dropwise with stirring. Stirring was continued for 3 hours at room temperature and the reaction mixture was worked up in the usual way and analyzed by ^{1}H NMR.

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