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Preparation of Geminal Diacylates (Acylals) of Aldehydes – Scope and Reactivity of Aldehydes with Acid Anhydrides

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The geminal diacylates of a variety of aldehydes were prepared in good yields without any catalysts or solvent by simply refluxing the aldehydes with aliphatic acid anhydrides. The scope of the reactions and relative reactivities of aldehydes and acid anhydrides were examined.

Introduction

The merits of geminal diacylates (acylals) as useful protecting groups for aldehydes stem from not only their stability in neutral and basic media[1] as well as towards aqueous acids[2] but also the ease with which they can be deprotected.[3] The geminal diacylates have an additional advantage over acetals in that water, generated during the formation of acetals, must be removed either by physical or chemical methods with a water scavenger, which is not necessary during the diacylation of aldehydes.

Additionally, geminal diacylates are stable towards a variety of reactions. Thus, geminal diacylates have been used as important protecting groups for aldehydes and played important roles in organic synthesis.[4] Geminal diacylates derived from α,β-unsaturated aldehydes are not only important starting materials for the synthesis of acetoxy dienes and vinyl acetates[4a] but are also good substrates for the S_N2' coupling reaction with organocuprates to afford β-substituted aldehydes after hydrolysis.[4c]

Recently, Kavala and Patel extensively studied the reaction mechanism for the formation of geminal diacylates with tetrabutylammonium tribromide (TBATB).[5] The suggested mechanism included reaction initiation with acid and proceeded by a nucleophilic attack of an anhydride on an aldehyde carbonyl group, followed by nucleophilic attack of the hemiacylate intermediate on a second molecule of the anhydride, which was followed by an intermolecular attack of a second acylate to generate the anhydride.

The reaction of aldehydes with simple acid anhydrides was originally pursued in the presence of acidic catalysts and afforded geminal diacylates.[6] A variety of strong protic acids[7] were employed as catalysts, but reactions suffered from poor yields and long reaction times. Lewis acids and various metal salts[8] replaced protic acids in order to improve yields and reduce reaction times substantially. Additionally, P_2O_5,[9] I_2,[10] and NBS[11] as well as solid acidic materials such as Nafion-H,[12] tungstosilicic acid and HZSM-5,[13] Y-zeolite,[14] β-zeolite,[15] graphite,[16] Amberlyst-15,[17] montmorillonites,[18] PVC-$FeCl_3$ complex,[19] and $ZrCl_4$[20] were recently introduced as catalysts, most of which employed solvent-free reaction conditions. Nevertheless, up to this point the development of procedures for the preparation of geminal diacylates has relied on the use of rather strong acids or toxic and/or expensive reagents, which has led to a continuing interest in the development of a more efficient procedure. A practical and more efficient alternative with an inexpensive reagent under solvent-free condition is of considerable interest. We herein describe a simple and efficient procedure for the preparation of geminal diacylates of aldehydes and examine the scope of such a reaction.[21]

Results and Discussion

The present method describes the preparation of geminal acylals by simply refluxing aldehydes and acid anhydrides without any additional catalyst or solvent. Although it was recently claimed that no considerable amount of the corresponding diacetate was formed upon the reactions of aldehydes with Ac_2O in the absence of catalyst,[8m,8r] we found that the reactions proceeded smoothly. Although the reaction of benzaldehyde (**1a**) with Ac_2O in refluxing acetonitrile failed to provide the corresponding geminal diacetate,[8t] we successfully isolated benzylidene diacetate in 85% yield. Although a low yield (4%) was reported for 4-nitrobenzaldehyde in the presence of a catalyst,[8e] all three isomers (compounds **1e**, **i**, and **m**) yielded the corresponding

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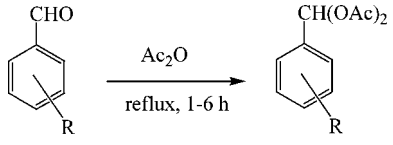
geminal diacetates in 82–93% yield. Methyl ether (**2o**) and methylthio ether (**2p**) moieties were not disturbed under the reaction condition.

Although a variety of aldehydes were converted into the corresponding geminal diacetates in good yields (Table 1), we failed to convert 2-chlorobenzaldehyde (**1c**) and 4-(dimethylamino)benzaldehyde (**1q**) to their geminal diacetates. The lack of reactivity of the latter could be explained by the electron-donating effect of the *N*,*N*–dimethylamino moiety, which reduces the electron deficiency of the carbonyl carbon and induces the quinonoid resonance structure, as had been studied.[7c,8r] The lack of reactivity of 2-chlorobenzaldehyde was somewhat surprising and remained to be explored since the reactions in the presence of a catalyst[6,8r] were reported to produce the corresponding diacetate in good yields.

Table 1. Preparation of geminal diacetates from aromatic aldehdyes.

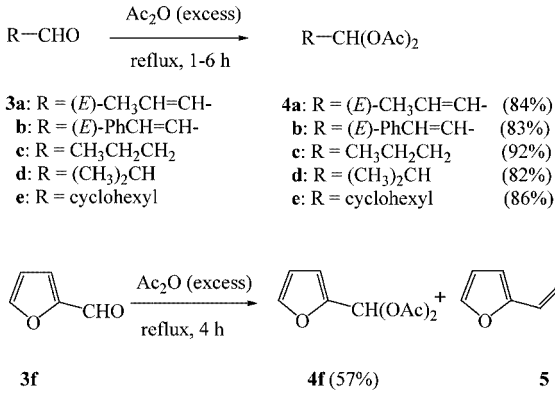


1 **2**

	R	Time [h][a]	Yield [%][a,b]	M.p. [°C]
2a	H	1.5	85	43–44 (45.8[6])
2b	2-F	3.5	82	27
2c	2-Cl	24	no reaction	–
2d	2-Br	4	73	80
2e	2-NO_2	6	85	92 (91–92[8e])
2f	3-F	2	78	30–31
2g	3-Cl	3	75	65 (65–66[8e])
2h	3-Br	4	79	thick liquid
2i	3-NO_2	5.5	93	63 (64–66[2])
2j	4-F	2	74	39
2k	4-Cl	3	65	84–85 (80–81[22])
2l	4-Br	4	82	85
2m	4-NO_2	5.5	82	121 (125–126[4e])
2n	4-SCH_3	1	70	50
2o	4-OCH_3	1.5	71	65 (64–65[4e])
2p	3,5-$(OMe)_2$, 4-OAc	3	83	125–127
2q	4-(dimethylamino)	24	no reaction	–

[a] Reaction times and yields are not optimized. In most cases, the value given is from a single experiment. [b] All yields refer to pure isolated products.

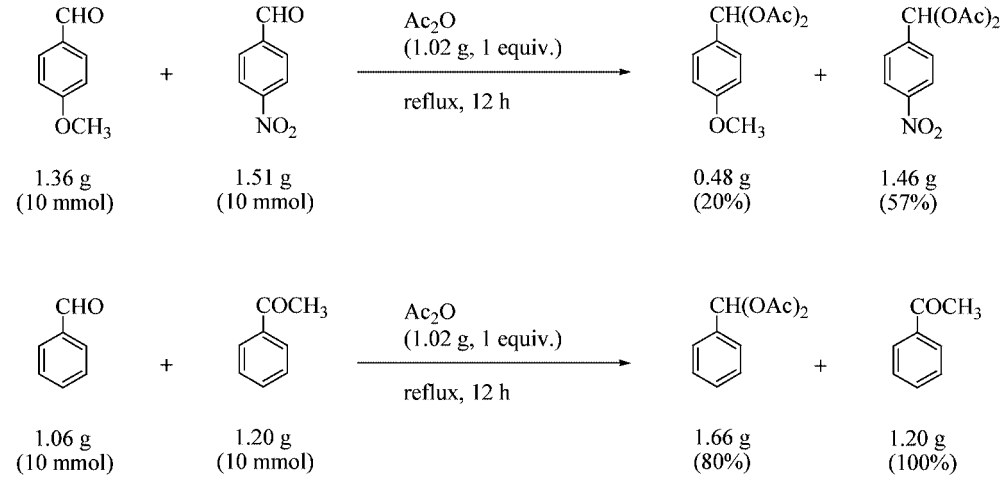
The scope of the reaction was examined with selected α,β-unsaturated aldehydes and aliphatic aldehydes. The reactions of (*E*)-crotonaldehyde (**3a**) and (*E*)-cinnamaldehyde (**3b**) provided the corresponding geminal diacetates **4a** and **4b** in 84% and 83% yield, respectively. Similarly, the reactions of selected aliphatic aldehydes such as butyraldehyde (**3c**), isobutyraldehyde (**3d**), and cyclohexanecarbaldehyde (**3e**) also proceeded smoothly to afford the corresponding diacetates (**4c**, **d**, and **e**) in 82–92% yields. The reactivity of furan-2-carbaldehyde (**3f**), one of the most fragile aldehydes, was additionally examined and found to give the corresponding diacetate (**4f**) in 57% yield along with 3-(fur-2-yl)crotonic acid (**5**) in 10% yield.

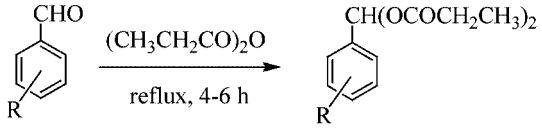


The chemoselectivity of this reaction was studied with a variety of aromatic substituents of varying electron-withdrawing ability. The reaction of a mixture of equimolar 4-methoxybenzaldehyde or 4-nitrobenzaldehyde with 1 equiv. of Ac_2O gave the corresponding diacetates in 20% or 57% isolated yield, respectively. Such a result may reflect the electrophilicity of the carbonyl carbon. This result is inconsistent with a previous report, in which 4-methoxybenzaldehyde showed more reactivity than 4-nitrobenzaldehyde by a factor of 93.[5] Although one can claim that the reaction temperature and presence of a catalyst (TBATB) may affect the reaction, it is clear that the more electron-deficient carbonyl carbon on 4-nitrobenzaldehyde is more reactive towards nucleophilic attack than is the less electron-deficient carbonyl of 4-methoxybenzaldehyde.

Additionally, the chemoselectivity of aldehyde versus ketone was examined by reacting a mixture of benzaldehyde and acetophenone with 1 equiv. of Ac_2O to afford only benzylidene diacetate in 80% yield. The reaction of acetophenone alone with Ac_2O was also pursued, but failed to give any evidence of the corresponding diacetate.

Only a very limited number of acid anhydrides (propionic, butyric, isobutyric, pivalic, and benzoic anhydride)[5,17,20] were previously employed in the pursuit of geminal diacylates. To examine the generality of the reaction, the present reaction conditions were applied to propionic anhydride, benzoic anhydride, and phthalic anhydride with benzaldehyde or substituted benzaldehydes. Although all the reactions with propionic anhydride proceeded smoothly to afford the corresponding geminal dipropionates (**6a**–**d**) in 72–82% yield, the reactions with benzoic anhydride and phthalic anhydride were too sluggish to afford the corresponding acylates. A reaction with benzoic anhydride in the presence of H_2SO_4, however, provided the corresponding dibenzoate in 77% yield (not described herein in detail). On the other hand, a reaction with phthalic anhydride did not proceed, even in the presence of H_2SO_4. Such results may imply that the nucleophilicity of the acid anhydride is important for the reaction.





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6a: R = H (78%)
b: R = 3-Br (82%)
c: R = 4-OCH_3 (72%)
d: R = 4-NO_2 (82%)

Conclusions

In summary, a simple and efficient procedure for the preparation of geminal diacylates of a variety of aldehydes such as aliphatic, aromatic, and α,β-unsaturated aldehydes was established by simply refluxing aldehydes with acid anhydrides. Although the application of the present method seems to be limited to aliphatic acid anhydrides, the method has advantages over previously described methods in yield, simplicity of operation, and economy as well as the environmental aspect of running the reaction without any halogenated solvents, additional additives, and/or catalyst.

Experimental Section

Melting points were determined with a Fisher–Jones melting point apparatus and are uncorrected. Infrared spectra were recorded with KBr pellets for solids and neat liquids with a Perkin–Elmer 1330 grating spectrometer. NMR spectra were obtained with a Bruker-250 spectrometer (250 MHz for ^{1}H NMR and 62.5 MHz for ^{13}C NMR) and reported as parts per million (ppm) from the internal standard, tetramethylsilane (TMS). Column chromatography was carried out with 60–120 mesh silica gel. Chemicals and solvents were commercial reagent grade and used without further purification. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed with a LCQ advantage-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA).

Preparation of Diacetates of Aldehydes (General Method): A mixture of aldehyde (1.00 mmol) and Ac_2O (10 mL) was refluxed for 1–6 h. The reaction was monitored by TLC. After the given reaction time, the reaction mixture was poured into 5% aqueous NaOH. The resulting mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water successively and dried with anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to provide crude product, which was chromatographed on silica gel with CH_2Cl_2/*n*-hexane (1:1). The early fractions afforded the desired geminal diacetates pure enough for the analysis. Spectral data of unreported compounds and selected diacylates follows.

Crotonylidene Diacetate (4a): Colorless liquid (84% yield), b.p. 45–48 °C (14 Torr), ref.[10] b.p. 44–46 °C (14 Torr). IR (thin film) $\tilde{\nu}$ = 1760, 1390, 1250, 1215 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.08 (d, J = 6.6 Hz, 1 H, 1-H), 6.03 (dq, J = 15.5, 6.6 Hz, 1 H, 3-H), 5.57 (ddt, J = 15.5, 6.6, 1.2 Hz, 1 H, 2-H), 2.08 (s, 6 H), 1.76 (dd, J = 6.6, 1.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 168.5, 133.0, 124.4, 89.5, 20.7, 17.4 ppm.

Cinnamylidene Diacetate (4b): White solid (83% yield), m.p. 84–85 °C (ref.[8d] m.p. 84–87 °C), R_f = 0.3 (CH_2Cl_2). IR (thin film) $\tilde{\nu}$ = 1760, 1390, 1250, 1215 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.42–7.28 (m, 6 H), 6.85 (d, J = 15.6 Hz, 1 H, 1-H), 6.19 (dd, J = 15.5, 6.6 Hz, 1 H, 3-H), 2.10 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 168.7, 135.6, 135.1, 128.8, 128.6, 127.0, 121.6, 89.7, 20.9 ppm.

Butylidene Diacetate (4c): Colorless liquid (92% yield). IR (thin film) $\tilde{\nu}$ = 2960, 1760, 1375, 1250, 1220 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.74 (t, J = 5.6 Hz, 1 H, 1-H), 2.05 (s, 6 H), 1.75–1.68 (m, 2 H, H-2), 1.44–1.34 (m, 2 H, H-3), 0.93 (t, J = 6.1 Hz, 3 H, H-4) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 168.6, 90.7, 27.12, 31.12, 20.70, 14.02 ppm. MS (ESI): calcd. for $C_8H_{14}O_4$ 175 $[M + H]^+$; found 175.

Isobutylidene Diacetate (4d): Pale yellow liquid (82% yield). IR (thin film) $\tilde{\nu}$ = 2965, 1765, 1370, 1248, 1210 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.58 (d, J = 5.3 Hz, 1 H, 1-H), 2.08–2.03 (m, 1 H, H-2), 2.05 (s, 6 H), 1.15 (d, J = 6.8 Hz, 6 H) ppm. MS (ESI): calcd. for $C_8H_{14}O_4$ 175 $[M + H]^+$; found 175.

Cyclohexylmethylene Diacetate (4e): Pale yellow liquid (86% yield). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.54 (d, J = 5.3 Hz, 1 H, 1-H), 2.00 (s, 6 H), 1.67–1.44 (m, 6 H), 1.19–0.98 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 169.0, 98.2, 70.7, 26.6, 26.0, 25.3, 20.6 ppm. MS (ESI): calcd. for $C_{11}H_{18}O_4$ 215 $[M + H]^+$; found 215.

(Furan-2-yl)methylene Diacetate (4f): A mixture of furan-2-carbaldehyde (0.96 g, 10.0 mmol) and Ac_2O (10 mL) was refluxed for 4 h. The reaction mixture was poured into 5% aqueous NaOH and was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers

were washed with water successively and dried with anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to provide the crude product, which was chromatographed on silica gel with CH_2Cl_2. The early fractions afforded the desired geminal diacetate as colorless liquid [57% yield, R_f = 0.6 (CH_2Cl_2)], which could be crystallized in the refrigerator. M.p. 54–55 °C (ref.[23] m.p. 52–53 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.70 (s, 1 H), 7.44 (d, J = 0.8 Hz, 1 H), 6.52 (d, J = 2.2 Hz, 1 H), 6.37 (dd, J = 3.2, 1.8 Hz, 1 H), 2.12 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 186.4, 147.8, 143.6, 110.3, 109.7, 83.4, 20.7 ppm. The latter fractions afforded 3-(fur-2-yl)crotonic acid (**5**) as colorless liquid [10% yield, R_f = 0.35 (CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.52 (d, J = 16.5 Hz, 1 H, 3-H), 7.50 (d, J = 0.7 Hz, 1 H, 5′-H), 6.67 (d, J = 3.3 Hz, 1 H, 3′-H), 6.50 (dd, J = 3.3, 1.7 Hz, 1 H, 4′-H), 6.33 (d, J = 15.6 Hz, 1 H, 2-H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 172.3, 150.6, 145.3, 133.0, 115.8, 114.8, 112.5 ppm. MS (ESI): calcd. for $C_7H_6O_3$ 139 $[M + H]^+$; found 139.

Benzylidene Dipropionate (6a): Colorless liquid [78% yield, R_f = 0.2 (CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.71 (s, 1 H), 7.52–7.49 (m, 2 H), 7.40–7.37 (m, 3 H), 2.40 (overlapped q, J = 6.7 Hz, 4 H), 1.14 (t, J = 7.5 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 172.2, 135.6, 129.6, 128.5, 126.5, 89.5, 27.3, 8.6 ppm. MS (ESI): calcd. for $C_{13}H_{16}O_4$ 237 $[M + H]^+$; found 237.

3-Bromobenzylidene Dipropionate (6b): Colorless liquid [82% yield, R_f = 0.27 (CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.64 (s, 1 H), 7.63 (s, 1 H), 7.50 (dt, J = 8.1, 1.3 Hz, 1 H), 7.40 (dt, J = 7.8, 1.5 Hz, 1 H), 7.24 (t, J = 8.0 Hz, 1 H), 2.40 (q, J = 7.7 Hz, 2 H), 2.39 (q, J = 7.7 Hz, 2 H), 2.13 (t, J = 7.7 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 172.1, 137.8, 132.7, 130.1, 129.7, 125.4, 122.5, 88.6, 27.3, 8.7 ppm. MS (ESI): calcd. for $C_{13}H_{15}BrO_4$ 316 $[M + H]^+$; found 316.

4-Methoxybenzylidene Dipropionate (6c): Colorless liquid [72% yield, R_f = 0.4 (CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.65 (s, 1 H), 7.42 (dm, J = 8.5 Hz, 2 H), 6.87 (dm, J = 8.5 Hz, 2 H), 3.81 (s, 3 H), 2.37 (q, J = 7.7 Hz, 2 H), 2.35 (q, J = 7.7 Hz, 2 H), 2.13 (t, J = 7.7 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 172.2, 160.6, 128.2, 128.1, 114.2, 89.8, 55.6, 27.8, 9.2 ppm. MS (ESI): calcd. for $C_{14}H_{18}O_4$ 267 $[M + H]^+$; found 267.

4-Nitrobenzylidene Dipropionate (6d): Colorless liquid [82% yield, R_f = 0.4 (CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.24 (dm, J = 8.5 Hz, 2 H), 7.74 (s, 1 H), 7.67 (dm, J = 8.5 Hz, 2 H), 2.43 (q, J = 7.5 Hz, 2 H), 2.42 (q, J = 7.6 Hz, 2 H), 1.15 (t, J = 7.7 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 172.1, 142.2, 127.8, 123.8, 123.7, 88.2, 27.3, 8.6 ppm. MS (ESI): calcd. for $C_{13}H_{15}NO_6$ 282 $[M + H]^+$; found 282.

Study of Relative Reactivity: An equimolar mixture of 4-nitrobenzaldehyde (1.51 g, 10 mmol) and 4-methoxybenzaldehyde (1.36 g, 10 mmol) was refluxed with 1 equiv. of Ac_2O (1.02 g, 10 mmol) for 12 h. Work up as described above in the general method afforded a mixture of 4-nitrobenzylidene diacetate and 4-methoxybenzylidene diacetate in 77% yield. Each compound was separated by column chromatography with CH_2Cl_2/*n*-hexane (1:1) to give 1.46 g (57% yield) of 4-nitrobenzylidene diacetate and 0.48 g (20% yield) of 4-methoxybenzylidene diacetate.

Study of Chemoselectivity: An equimolar mixture of benzaldehyde (1.06 g, 10 mmol) and acetophenone (1.20 g, 10 mmol) was refluxed with 1 equiv. of Ac_2O (1.02 g, 10 mmol) for 12 h. Work up as described above in the general method afforded benzylidene diacetate (1.66 g, 80% yield), while acetophenone was quantitatively recovered.

Acknowledgments

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