Reinvestigation of the Mechanism of *gem*-Diacylation: Chemoselective Conversion of Aldehydes to Various *gem*-Diacylates and Their Cleavage under Acidic and Basic Conditions

Veerababurao Kavala[a] and Bhisma K. Patel*[a]

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The mechanism of *gem*-diacylate formation has been studied extensively using tetrabutylammonium tribromide (TBATB) as the catalyst. The reaction proceeds by a nucleophilic attack of an anhydride on an aldehydic carbonyl group, nucleophilic attack of the hemiacylate intermediate on a second molecule of the anhydride, followed by an intermolecular attack of a second acetate group to regenerate the anhydride. *gem*-Diacylates of various aliphatic and aromatic aldehydes were obtained directly from the reaction of a variety of aliphatic and aromatic acid anhydrides in the presence of a catalytic quantity of tetrabutylammonium tribromide (TBATB) under solvent-free conditions. A significant electronic effect was observed during its formation as well as deprotection to the corresponding aldehyde. Chemoselective *gem*-diacylation of the aromatic aldehyde containing an electron-donating group has been achieved in the presence of an aldehyde containing an electron-withdrawing group. Deprotection of the *gem*-diacylate to the parent carbonyl compound can be accomplished in methanol in presence of the same catalyst. Here again, chemoselective deprotection of the *gem*-diacylate of a substrate containing an electron-donating group has been achieved in the presence of a substrate containing an electron-withdrawing group. Both the acid and base stability order of the various *gem*-diacylates examined follow a similar order. The stability order determined from the present study is: *gem*-dibenzoate > *gem*-dipivalate > *gem*-diisobutyrate > *gem*-diacetate > *gem*-dipropionate. All the *gem*-diacylals are more stable under basic conditions than acidic condition. No correlation was found between the stability order and the pK_a's of the corresponding acids; rather, the stability order is directly related to the steric crowding around the carbonyl carbon.

Introduction

The mechanism of the formation of *gem*-diacylate, the addition product of an acid anhydride with an aldehyde, is not yet well understood. *gem*-Diacylate functionalities have served as an interesting protecting group for aldehydes in addition to acetals, oxathioacetals and thioacetals. Unlike the acetal protecting group, which is removed only under acidic conditions, *gem*-diacylates can be removed under either acidic or basic conditions.[1] The *gem*-diacylates of aldehydes are useful precursors for nucleophilic-substitution reactions; they are used in the synthesis of acetoxydienes, vinyl acetates and dienes for Diels−Alder reactions, and are also used as several industrial intermediates.[2] Due to the remarkable stability of *gem*-diacetates towards a variety of reaction conditions, and their easy preparation, they are gaining importance in organic synthesis as an alternative to cyclic and acyclic acetals for the protection of aldehydes. They are superior to acetals because, during acetalization of acetals, the water formed in the reaction medium imust be removed either by physical or by chemical means using water scavengers such as orthoformates;[3] this procedure is not required during *gem*-diacylation of aldehydes.

Numerous methods are available in the literature for the conversion of an aldehydic carbonyl group to the corresponding *gem*-diacetates with acetic anhydride. Some of the reagents and catalysts that have been employed include H_2SO_4,[4] $HClO_4$,[5] H_3PO_4,[6] CH_3SO_3H,[7] PCl_3,[8] $FeSO_4 \cdot xH_2O$[9] I_2,[10] TMSCl-NaI,[11] NBS,[12] CAN,[13] $InCl_3$,[14] WCl_6,[15] $LiBF_4$,[16] $Zn(BF_4)_2$,[17] $ZrCl_4$,[18] $CoCl_2$,[19] NH_2SO_3H,[20] $Bi(OTf)_3 \cdot xH_2O$,[21] $Sc(OTf)_3$,[22] LiOTf,[23] $Cu(OTf)_2$,[24] $FeCl_3$,[1b,25] and sulfated zirconia.[26] Some solid acidic catalysts, for example NafionH,[27] zeolite,[28] montmorillonite clay,[29] graphite,[30] Fe^{3+} on montmorillonite,[31] PVC-$FeCl_3$ [32] Wells−Dawson acid,[33] zirconium sulfenyl phosphonate,[34] $AlPW_{12}O_{40}$ [35] and Amberlite15,[36] have also been used for this purpose. Recently, the diacylation of aldehydes has been achieved in ionic liquids.[37] However, none of the above-mentioned catalysts are capable of protecting as well as deprotecting *gem*-diacetates except CAN,[13] $ZrCl_4$,[17] expensive graphite[30] and HSZ360 (zeolite).[28b]

[a] Indian Institute of Technology, Guwahati,
Guwahati 781 039, Assam, India
Fax: (internat.) + 91-361-269-0762
E-mail: patel@iitg.ernet.in
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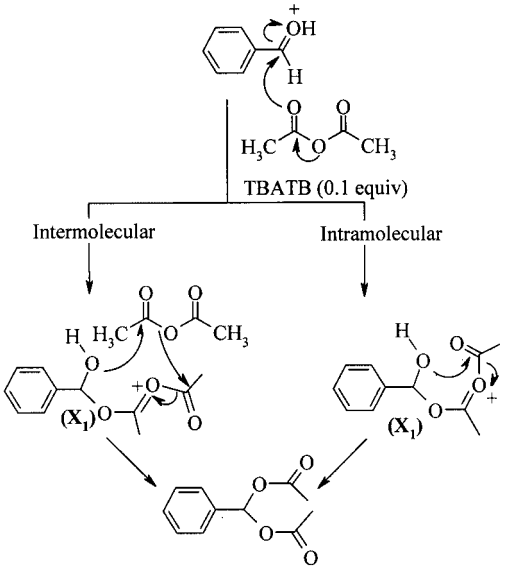
Although some of these methods are excellent in terms of yields but none of them have studied extensively their mechanism, *gem*-diacylation of aldehydes with a range of aliphatic and aromatic anhydrides, their chemoselectivities and relative stabilities of various *gem*-diacylates both under acidic and basic conditions. Except for acetic anhydride, only two other reports are available on reaction of aldehydes with other anhydrides, namely butyric, isobutryric and pivalic anhydride.[16a,18] Although there are several methods known for the chemoselective protection of aldehydes over ketones, there is only one method for the chemoselective *gem*-diacylation of different aromatic aldehydes.[34] Other problems associated with some of the existing methods are difficulties in workup and isolation, the use of organic solvents, the need for an inert atmosphere, harsh reaction conditions, expensive and stoichiometric amounts of reagents, incompatibility with other protecting groups and failure to protect deactivated substrates and substrates containing an amino functionality. Substrates containing hindered and acid-sensitive groups also fail in many instances. Hence, a practical and more efficient alternative using an inexpensive reagent under solvent-free conditions is of considerable interest. To achieve chemoselective *gem*-diacylation between aldehydes and ketones and between different aldehydes will be useful during a multi-step synthesis. Further, the stability order of various *gem*-diacylates of a substrate towards acidic and basic conditions is yet another interesting aspect in protection/deprotection chemistry. Finally, to have gain insight into the reaction mechanism of such a reaction is crucial to the scientific community.

Results and Discussion

Solvent-free reactions have gained considerable attention in chemical processes for environmental and economic reasons and their easy workup, high yields and usually faster reaction rates.[38] We have been interested in the development of several green chemical processes in aqueous media[39] and in exploring the catalytic properties of tetrabutylammonium tribromide (TBATB) for various organic transformations.[40] In this regard, we have found that TBATB is a useful reagent whose acidity can be tuned from highly acidic to near neutral pH in the appropriate organic solvent. This reagent has been proved to be a good catalyst for the chemoselective acetalization of carbonyl compounds,[40a] pyranylation/depyranylation of alcohols[40b] and thioacetalization and transthioacetalization of carbonyl compounds.[40f] Now we have utilized tetrabutylammonium tribromide (TBATB) to gain further understanding of the mechanism of formation of *gem*-diacylates and the chemoselective preparation of various *gem*-diacylates from structurally different aldehydes and different aliphatic and aromatic anhydrides with a catalytic quantity of this reagent at room temperature under solvent-free conditions. We have also studied the stability order of various *gem*-diacylates under acidic and basic conditions.

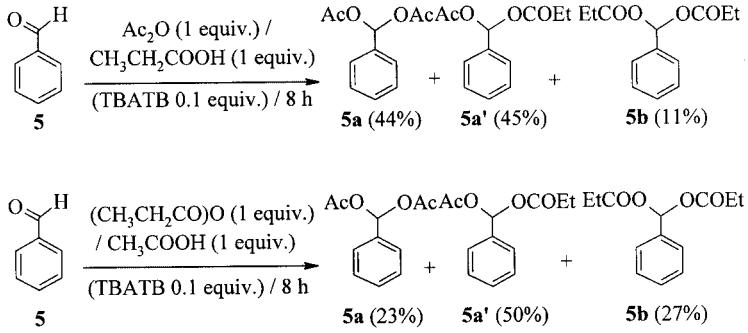
In a typical experimental procedure, a mixture of an aldehyde (5 mmol) and freshly distilled acetic anhydride (15 mmol) was stirred at room temperature in the presence of a catalytic amount of TBATB (0.5 mmol) for the time required for the completion of the reaction at room temperature. The exact role of the TBATB is not clear, but it is known to release anhydrous HBr in an alcoholic medium, and the medium becomes weakly acidic in a nonpolar aprotic solvent.[40a–40c] The pH of neat acetic anhydride is 0.1, and this drops to a value of −0.7 on addition of 0.1 equivalents of TBATB. Similarly, the pH of various neat aldehydes drop to a more acidic pH on addition of TBATB. The mechanism of this reaction has been the subject of some controversy.[19d,41] An intermolecular mechanism has been proposed involving an intermolecular transfer of a second acetate group after initial attack by acetic anhydride.[1b] To get further insight into the mechanism we have carried out a series of experiments. Two plausible mechanisms could be thought of for *gem*-diacylation, one involving an intramolecular and other an intermolecular transfer of a second acylate group after the initial nucleophilic attack by an anhydride on an aldehydic group, as shown in Scheme 1.



Scheme 1. Proposed mechanisms of *gem*-diacetylation

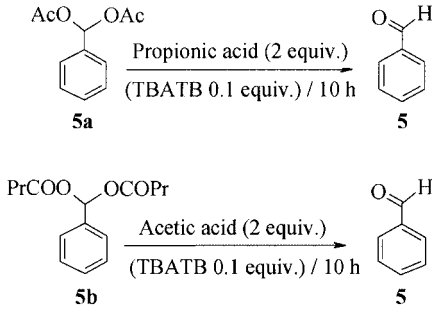
In order to test this, benzaldehyde (**5**; 1 equiv.) was treated with acetic anhydride (1 equiv.) in the presence of propionic acid (1 equiv.) and TBATB (0.1 equiv.). Analysis of the products by GC showed the formation of *gem*-diacetate **5a**, the mixed acetate-propionate **5a′** and the *gem*-dipropionate **5b**, in the ratio 44:45:11, respectively, after 8 h, as shown in Scheme 2. In another experiment, benzaldehyde (**5**; 1 equiv.) was treated with propionic anhydride (1 equiv.) in the presence of acetic acid (1 equiv.) under identical conditions. The ratio of *gem*-dipropionate **5b**, mixed acetate-propionate **5a′** and *gem*-diacetate **5a** obtained was 23:50:27, respectively, after 8 h, as shown in Scheme 2.

The failure to form the *gem*-diacetate as the sole product in the above reactions clearly rules out the possibility of an



Scheme 2. Formation of mixed *gem*-diacylate

intramolecular mechanism (Scheme 1). The formation of the mixed *gem*-diacylate **5a′** may be due to the attack of a second acylate group by an intermolecular path or by a transacylation of the symmetrical *gem*-diacylate (**5a**/**5b**) with an acylate (acetate or propionate). In order to ascertain the latter possibility, the *gem*-diacetate of benzaldehyde (**5a**; 1 equiv.) was treated with propionic acid (2 equiv.) in the presence of TBATB (0.1 equiv.) and the *gem*-dipropionate of benzaldehyde (**5b**; 1 equiv.) was treated with acetic acid (2 equiv.) in the presence of TBATB (0.1 equiv.). No mixed *gem*-diacylal **5a′** could be detected by GC at any stage of the reaction; rather, the *gem*-diacylates **5a** and **5b** were quantitatively deprotected to benzaldehyde after 10 h (Scheme 3), thus ruling out the possibility of a transacylation process for the formation of mixed diacylates.



Scheme 3. Deprotection of *gem*-diacylates with TBATB

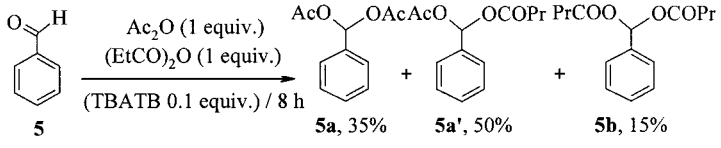
The *gem*-diacylate formation may be occurring by an intermolecular mechanism, however. To support this, benzaldehyde (**5**; 1 equiv.) was treated with an equimolar mixture of acetic anhydride (1 equiv.) and propionic anhydride (1 equiv.) in the presence of TBATB (0.1 equiv.). Analysis of the products by GC showed the formation of *gem*-diacetate **5a** (35%), mixed acetate-propionate **5a′** (50%) and *gem*-dipropionate **5b** (14%) after 8 h (Scheme 4).

In another experiment, benzaldehyde (**5;** 1 equiv.) was treated with a mixed anhydride, acetic-propionic anhydride (1 equiv.). Here again, *gem*-diacetate **5a**, mixed acetate-propionate **5a′** and *gem*-dipropionate **5b** were obtained in the ratio 16:34:50, respectively (Scheme 5), instead of the mixed diacylate, which would have been formed as the sole product if the mechanism followed an intramolecular path. This observation is consistent with the observation made by other groups, except for the distribution of the products.[1b]

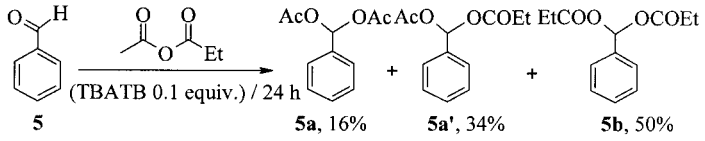
The formation of mixed diacylates **5a′** in Scheme 2 can only be explained if there is formation of the mixed anhydride in the reaction medium itself. This was confirmed from the following experiments: Acetic anhydride (1 equiv.) was treated with propionic acid (1 equiv.) in the presence of a catalytic quantity of TBATB (0.1 equiv.), the percentage of acetic anhydride remaining and mixed anhydride formed after 0.5 h, as determined by GC, was 60% and 40%, respectively. Similarly, when propionic anhydride (1 equiv.) was treated with acetic acid (1 equiv.) under identical conditions the ratio of acetic anhydride, mixed anhydride and propionic anhydride formed after 0.5 h were 40%, 55% and 5%, respectively (Scheme 6).

The formation of more than 90% of the *gem*-diacetate by the reaction of benzaldehyde with just one equivalent of acetic anhydride supports the regeneration of acetic anhydride and hence the intermolecular nature of the mechanism (Scheme 1).

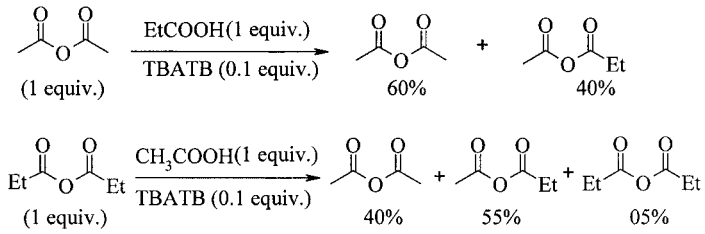
Aliphatic aldehydes **1**−**4** were converted into their corresponding *gem*-diacylates in excellent yields at room temperature by employing this reagent. A wide range of aldehydes containing activated, deactivated and hindered groups could all be diacylated in good to excellent yields, as shown in Table 1. Moreover, the protocol also worked equally well with α,β-unsaturated aldehydes **4** and **16** and with an aldehyde containing an allylic functionality (**17**). Importantly, no other side-product, for example from bromination, was observed, although this reagent is an excel-



Scheme 4. Formation of mixed *gem*-diacylates from two different anhydrides



Scheme 5. Formation of a mixed *gem*-diacylate from a mixed anhydride



Scheme 6. Formation of mixed anhydride

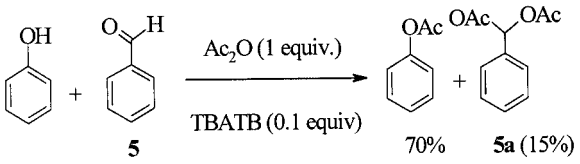
Table 1. Diacylation of aldehydes by acetic anhydride and TBATB[a]

Substrate	Product[b]	Time (h)	Yield[c] (%)
$CH_3(CH_2)_4CH_2CHO$ (**1**)	$CH_3(CH_2)_4CH_2CH(OAc)_2$ (**1a**)	6	78
$CH_3(CH_2)_7CH_2CHO$ (**2**)	$CH_3(CH_2)_7CH_2CH(OAc)_2$ (**2a**)	6.2	82
$CH_3(CH_2)_{13}CH_2CHO$ (**3**)	$CH_3(CH_2)_{13}CH_2CH(OAc)_2$ (**3a**)	7	83
$CH_3CH{=}CHCHO$ (**4**)	$CH_3CH{=}CHCH(OAc)_2$ (**4a**)	5	84
PhCHO (**5**)	$PhCH(OAc)_2$ (**5a**)	4	90
2-(OH)C_6H_4CHO (**6**)	2-(OAc)$C_6H_4CH(OAc)_2$ (**6a**)	5.3	93
3-(NO_2)C_6H_4CHO (**7**)	3-(NO_2)$C_6H_4CH(OAc)_2$ (**7a**)	22	82
4-(Me)C_6H_4CHO (**8**)	4-(Me)$C_6H_4CH(OAc)_2$ (**8a**)	2.5	94
4-(Cl)C_6H_4CHO (**9**)	4-(Cl)$C_6H_4CH(OAc)_2$ (**9a**)	5	88
4-(OH)C_6H_4CHO (**10**)	4-(OAc)$C_6H_4CH(OAc)_2$ (**10a**)	6	93
4-(OMe)C_6H_4CHO (**11**)	4-(OMe)$C_6H_4CH(OAc)_2$ (**11a**)	5.5	92
4-(NO_2)C_6H_4CHO (**12**)	4-(NO_2)$C_6H_4CH(OAc)_2$ (**12a**)	22	78
4-(OH)-3-(OMe)C_6H_3CHO (**13**)	4-(OAc)-3-(OMe)$C_6H_3CH(OAc)_2$ (**13a**)	9	80
2-(Cl)-6-(NO_2)C_6H_3CHO (**14**)	2-(Cl)-6-(NO_2)$C_6H_3CH(OAc)_2$ (**14a**)	22	78
3,4,5-$(OMe)_3C_6H_2CHO$ (**15**)	3,4,5-$(OMe)_3C_6H_2CH(OAc)_2$ (**15a**)	4	94
PhCH=CHCHO (**16**)	$PhCH{=}CHCH(OAc)_2$ (**16a**)	5.2	87
4-(Oallyl)C_6H_4CHO (**17**)	4-(Oallyl)$C_6H_4CH(OAc)_2$ (**17a**)	5.5	86
4-(OBz)C_6H_4CHO (**18**)	4-(OBz)$C_6H_4CH(OAc)_2$ (**18a**)	6.5	87
4-(OTBS)C_6H_4CHO (**19**)	4-(OTBS)$C_6H_4CH(OAc)_2$ (**19a**)	7	90
2-FurylCHO (**20**)	2-Furyl$CH(OAc)_2$ (**20a**)	7	80[d]
4-(*N*,*N*-diMe)C_6H_4CHO (**21**)	4-(*N*,*N*-diMe)$C_6H_4CH(OAc)_2$ (**21a**)	24	00
4-(*N*,*N*-diMeHCl)C_6H_4CHO (**21′**)	4-(*N*,*N*-diMe)$C_6H_4CH(OAc)_2$ (**21a**)	7	90
2-NapthylCHO (**22**)	2-Napthyl$CH(OAc)_2$ (**22a**)	8	91
9-AnthranylCHO (**23**)	9-Anthranyl$CH(OAc)_2$ (**23a**)	16	92
9-FluorenylCHO (**24**)	9-Fluorenyl$CH(OAc)_2$ (**24a**)	24	61
4-(CHO)C_6H_4CHO (**25**)	$(OAc)_2CHC_6H_4CH(OAc)_2$ (**25a**)	12	80
C_6H_4COCHO (**26**)	$C_6H_4COCH(OAc)_2$ (**26a**)	25	89

[a] Reactions were monitored by TLC/GC. [b] Products were characterised by IR, ^1H and ^{13}C NMR spectroscopy. [c] Yield of isolated product. [d] Performed at 0 °C.

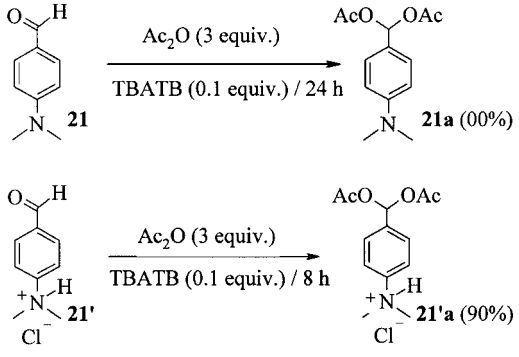
lent brominating agent for ethylenic substrates.[40d,40e] However, hindered aldehydes **14**, **23** and **24** required much longer reaction times, as did aromatic aldehydes containing an electron-withdrawing group, like a nitro group (**7**, **12** and **14**). This observation is not consistent with the observations by other groups that the presence of electron-donating and electron-withdrawing groups does not cause any difference in reactivity.[1b,11,17,18,23,33] Moreover, acid-sensitive groups such as a methoxy group (**11**, **13** and **15**), a TBS ether (**19**) and a furyl ring (**20**) are stable under the described reaction conditions. Hydroxy aldehydes (**6**, **10** and **13**) gave the corresponding triacetates. In fact, phenol could be chemoselectively acetylated over aldehyde **5**, thus demonstrating the higher reactivity of the phenolic functionality towards acetylation over an aldehydic group for diacylation (Scheme 7).

2-Furaldehyde (**20**) gave a dark-coloured polymeric compound when catalyzed by a heterogeneous inorganic acid[35] but gave an excellent yield of the product at 0 °C in the presence of TBATB as the catalyst. It has been reported



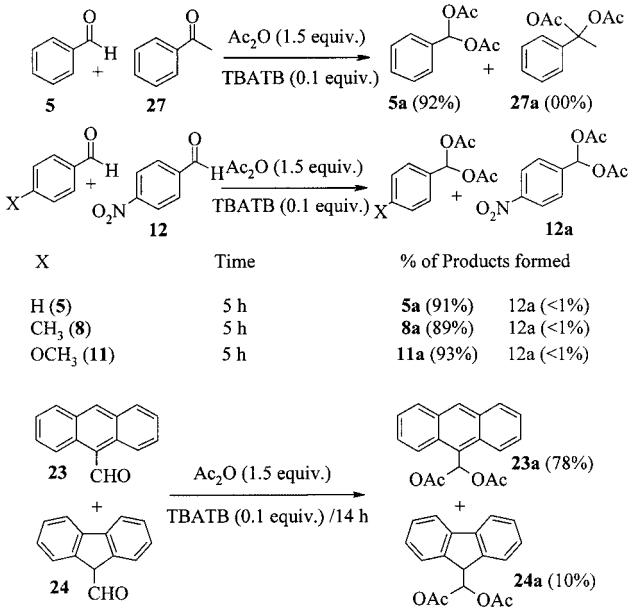
Scheme 7. Chemoselective acetylation of phenol

that many catalysts are not suitable for the preparation of *gem*-diacylates from aldehydes carrying an amino functionality group, such as 4-(dimethylamino)benzaldehyde (**21**),[20,33,35,37] possibly due to the existence of the quinoid structure with an aldehyde which decreases the reactivity of the aldehyde group, as explained previously.[20,35,37] However, it is worth noting that in the case of its protonated species, i.e. *N*,*N*′-dimethylammonium benzaldehyde (**21′**), the reaction progressed smoothly at room temperature to afford excellent yields of the corresponding *gem*-diacylate **21′a**, which was isolated as its free amine **21a** after hydrogencarbonate work up (Scheme 8). In spite of the strongly electron-withdrawing nature of the *N*,*N*′-dimethylammonium ion the reaction works well because the hydrochloride, being strongly acidic, activates the carbonyl towards nucleophilic attack by an anhydride. This was further confirmed by performing the diacylation of a substrate containing an electron-withdrawing group, such as a nitro group, in the presence of triethylamine hydrochloride. When 4-nitrobenzaldehyde (**12**; 1 equiv.) was treated with acetic anhydride (3 equiv.) in the presence of TBATB (0.1 equiv.) and triethylamine hydrochloride (1 equiv.) the reaction went to completion, with an 85% yield of isolated product, within 7 h, which is much faster than the formation in the absence of any hydrochloride (Table 1).



Scheme 8. Diacylation of 4-(*N*,*N*-dimethylammonium)benzaldehyde (**21′**)

Terephthaldehyde (**25**), a substrate containing two aldehydic groups, could be tetraacylated with six equivalents of acetic anhydride under the present conditions. Ketones such as cyclohexanone and acetophenone did not yield any diacylates in the presence of TBATB. Aldehydes having higher ground state and lower activation energy compared to ketones having lower ground state and higher activation energy are more reactive than ketones. Therefore it is not surprising to observe the chemoselective diacylation of aldehydes over ketones (Scheme 9).[40a,40f] Furthermore, the chemoselective diacylation of a aldehyde over a ketone was demonstrated in an intramolecular fashion with ketoaldehyde **26**. The nature of the substituents on the aromatic ring has a substantial effect on the reaction, as demonstrated in Scheme 9. Selective *gem*-diacylation of benzaldehyde (**5**), 4-methylbenzaldehyde (**8**) and 4-methoxybenzaldehyde (**11**) could be achieved in the presence of 4-nitrobenzaldehyde (**12**) with TBATB as the catalyst at room temperature; this shows the influence of electronic effects on these reactions. Similar results have been obtained with $AlPW_{12}O_{40}$.[35]



Scheme 9. Chemoselective *gem*-diacylation of aldehydes

We have also studied the competitive *gem*-diacylation reaction between 9-anthraldehyde (**23**) and 9-fluorenecarboxaldehyde (**24**). The former was chemoselectively diacylated over the latter, which further shows the significance of steric effects on these reactions in the presence of this reagent.

There are few reports of a geminal diester possessing a carboxyl moiety (butyryloxy, isobutyryloxy and pivaloxy) other than the acetoxy group,[16a,18] and not a single report could be found of the reaction of aldehydes with benzoic anhydride. Employing propionic anhydride in the same manner as acetic anhydride furnished the corresponding *gem*-dipropionates (Table 2 compounds **5b**, **11b**, **16b** and **23b**). Similarly, isobutyric, pivalic and benzoic anhydride gave the corresponding *gem*-diisobutyrates (Table 2 compounds **5c**, **11c**, **16c** and **23c**), *gem*-dipivalates (Table 2 compounds **5d**, **8d**, **11d** and **16d**) and *gem*-dibenzoates (Table 2 compounds **16e** and **23e**), respectively. Two equivalents of anhydrides were used for each equivalent of the aldehyde for propionic, isobutyric and pivalic anhydride, whereas the ratio was 1:1 in the case of benzoic anhydride.

Only a few methods have been reported in the literature for the deprotection of diacylates to their corresponding aldehydes. The reagents used are H_2SO_4,[6c] HCl,[42] boron triiodide−*N*,*N*-dimethylaniline complex,[2g] CAN on silica

Table 2. Diacylation of aldehydes using propionic, isobutyric, pivalic and benzoic anhydride with TBATB[a]

Substrate	Product[b]	Time (h)	Yield[c] (%)
PhCHO (**5**)	PhCH(OCOEt)$_2$ (**5b**)	4	90
4-(OMe)C$_6$H$_4$CHO (**11**)	4-(OMe)C$_6$H$_4$CH(OCOEt)$_2$ (**11b**)	5.5	92
PhCH=CHCHO (**16**)	PhCH=CHCH(OCOEt)$_2$ (**16b**)	5.2	87
9-AnthranylCHCHO (**23**)	9-AnthranylCH(OCOEt)$_2$ (**23b**)	16	92
PhCHO (**5**)	PhCH(OCO*i*Pr)$_2$ (**5c**)	4	90
4-(OMe)C$_6$H$_4$CHO (**11**)	4-(OMe)C$_6$H$_4$CH(OCO*i*Pr)$_2$ (**11c**)	5.5	92
PhCH=CHCHO (**16**)	PhCH=CHCH(OCO*i*Pr)$_2$ (**16c**)	5.2	87
9-AnthranylCHO (**23**)	9-AnthranylCH(OCO*i*Pr)$_2$ (**23c**)	18	90
PhCHO (**5**)	PhCH(OCO*t*Bu)$_2$ (**5d**)	19	85
4-(Me)C$_6$H$_4$CHO (**8**)	4-(Me)C$_6$H$_4$CH(OCO*t*Bu)$_2$ (**8d**)	17	80
4-(OMe)C$_6$H$_4$CHO (**11**)	4-(OMe)C$_6$H$_4$CH(OCO*t*Bu)$_2$ (**11d**)	10	92
PhCH=CHCHO (**16**)	PhCH=CHCH(OCO*t*Bu)$_2$ (**16d**)	22	87
PhCH=CHCHO (**16**)	PhCH=CHCH(OCOPh)$_2$ (**16e**)	10	90
9-AnthranylCHO (**23**)	9-AnthranylCH(OCOPh)$_2$ (**23e**)	24	89

[a] Reactions were monitored by TLC/GC. [b] Products were characterised by IR, ^{1}H and ^{13}C NMR spectroscopy. [c] Yield of isolated product.

gel,[43] $BiCl_3$,[44] CBr_4,[45] $CeCl_3 \cdot 7H_2O$/NaI,[46] KSF,[47] montmorillonite K-10,[48] neutral alumina under microwave irradiation,[49] phenoxide,[50] sodium hydroxide or aqueous K_2CO_3,[1b] or envirocat EPZG.[51] Some of the reagents that are capable of promoting acylation can also cause cleavage to the parent aldehyde upon changing the reaction conditions. These reagents are zeolite,[28b] graphite,[30] zirconium sulfenyl phosphonate[34] and $ZrCl_4$.[18] We investigated the use of a catalytic quantity of TBATB (0.1 equiv.) for the deprotection of *gem*-diacetates to their corresponding aldehydes. When the *gem*-diacetate of benzaldehyde (**5a**; 1 mmol) was treated with a catalytic quantity of TBATB (0.1 equiv.) in methanol (1 mL) at room temperature the diacetate was cleanly deprotected to benzaldehyde. This protocol was applied to the diacetates of several aliphatic and aromatic aldehydes (Table 3) to give excellent yields of the corresponding aldehydes. Zirconium sulfenyl phosphonate,[34] although capable of deprotecting the *gem*-diacetates of several aromatic aldehydes, was found to be unsuitable for the cleavage of aliphatic diacetates. However, we observed complete deprotection of aliphatic diacetates to their corresponding aldehydes at room temperature (**1a**, **2a**) with our system. It is surprising to note that no additional water is necessary for the deprotection. The deprotection reaction is expected to proceed by an intramolecular path, as proposed previously.[51] It is noteworthy that the phenolic acetate **10a** is untouched during the reaction. Therefore, the present procedure is selective for deprotection of an aldehydic *gem*-diacetate to aldehyde in the presence of phenolic acetate (Scheme 7), which suggests a faster rate of formation of phenolic acetate but slower rate of deprotection (Table 3). Similar to their formation, substrates containing electron-withdrawing groups, such as nitro, react slowly and require longer reaction times for their deprotection, as shown in the case of **12a**. This observation is consistent with the observation using zirconium sulfenyl phosphonate.[34] However, it is surprising to note that the catalyst $ZrCl_4$[18] can deprotect *gem*-diacylates of substrates containing electron-withdrawing groups within five minutes at room temperature with only 5 mol % of the catalyst. Acid-sensitive substrates such as the phenolic OTBS ether **19a** remained unaffected. Several *gem*-dipropionates (**5b**, **11b**, **16b** and **23b**) and *gem*-diisobutyrates (**5c**, **11c** and **16c**) could also be smoothly deprotected under identical reaction conditions (Table 3). It is pertinent to note that *gem*-dipivalates (**5d**, **8d**, **11d** and **16d**) and the *gem*-dibenzoate **16e** remained unchanged up to 4 h under these reaction conditions. However, they can be deprotected at reflux temperature (Table 3).

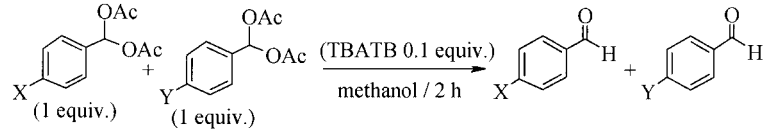
The slower rate of deprotection of 4-nitrobenzaldehyde diacetate (**12a**) prompted us to test the chemoselective deprotection with other *gem*-diacetates. Thus, when an equimolar mixture of 4-methylbenzaldehyde diacetate (**8a**) and 4-nitrobenzaldehyde diacetate (**12a**) was treated with TBATB (0.1 equiv.) in methanol, the former was completely deprotected and the latter unaffected after 1.5 h. Similarly, 4-methoxybenzaldehyde diacetate (**11a**) could also be chemoselectively deprotected in the presence of 4-nitrobenzaldehyde diacetate (**12a**), thereby showing the influence of electronic effects on these reactions in the presence of this reagent (Scheme 10).

As can be seen from Table 3, *gem*-diisobutyrates, *gem*-dipivalates and *gem*-dibenzoates are relatively stable compared to *gem*-diacetates and *gem*-dipropionates. Therefore, we investigated the possible chemoselective cleavage of different *gem*-diacylates in the presence of each other, as shown in Scheme 11. We focused our attention on diacylates of α,β-unsaturated aldehydes since they serve as an important building blocks for the synthesis of dienes to be used for Diels−Alder reactions. In a competitive intermolecular deprotection[52] between cinnamaldehyde diacetate (**16a**) and cinnamaldehyde dipropionate (**16b**) in methanol at room temperature, we observed that both were deprotected with nearly equal ease. A better intermolecular chemoselectivity (80%) was obtained for **16a** by performing the reaction in methanol/water (5:1), although a longer reaction time (2 h) was required for the process (Scheme 11). A relatively poor chemoselectivity was observed for cinnamaldehyde diisobutyrate (**16c**) over **16b** (40%) and

Table 3. Deprotection of *gem*-diacylates using TBATB in MeOH[a]

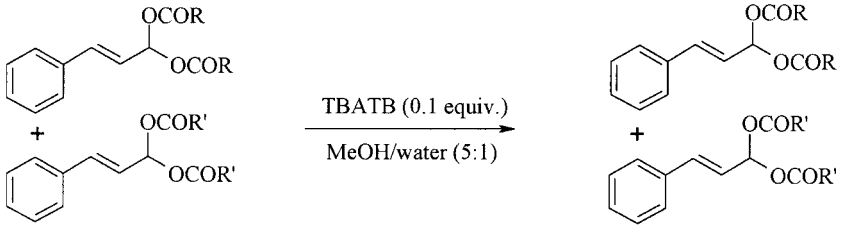
Substrate	Product[b]	Time (h)	Yield[c] (%)
$CH_3(CH_2)_2CH_2CH(OAc)_2$ (**1a**)	$CH_3(CH_2)_2CH_2CHO$ (**1**)	0.25	95
$CH_3(CH_2)_4CH_2CH(OAc)_2$ (**2a**)	$CH_3(CH_2)_4CH_2CHO$ (**2**)	0.25	97
$PhCH(OAc)_2$ (**5a**)	PhCHO (**5**)	1.25	90
4-(Me)$C_6H_4CH(OAc)_2$ (**8a**)	4-(Me)C_6H_4CHO (**8**)	1.5	94
4-(Cl)$C_6H_4CH(OAc)_2$ (**9a**)	4-(Cl)C_6H_4CHO (**9**)	3	93
4-(OAc)$C_6H_4CH(OAc)_2$ (**10a**)	4-(OAc)C_6H_4CHO (**10′**)	5.0	93
4-(OMe)$C_6H_4CH(OAc)_2$ (**11a**)	4-(OMe)C_6H_4CHO (**11**)	0.80	92
4-(NO_2)$C_6H_4CH(OAc)_2$ (**12a**)	4-(NO_2)C_6H_4CHO (**12**)	15	78
PhCH=CHCH$(OAc)_2$ (**16a**)	PhCH=CHCHO (**16**)	0.75	98
4-(OBz)$C_6H_4CH(OAc)_2$ (**18a**)	4-(OBz)C_6H_4CHO (**18**)	8.00	87
4-(OTBS)$C_6H_4CH(OAc)_2$ (**19a**)	4-(OTBS)C_6H_4CHO (**19**)	4.00	90
9-AnthranylCH$(OAc)_2$ (**23a**)	9-AnthranylCHO (**23**)	12	85
$PhCH(OCOEt)_2$ (**5b**)	PhCHO (**5**)	0.25	97
4-(OMe)$C_6H_4CH(OCOEt)_2$ (**11b**)	4-(OMe)C_6H_4CHO (**11**)	0.25	96
PhCH=CHCH$(OCOEt)_2$ (**16b**)	PhCH=CHCHO (**16**)	0.40	95
9-AnthranylCH$(OCOEt)_2$ (**23b**)	9-AnthranylCHO (**23**)	9	91
$PhCH(OCOiPr)_2$ (**5c**)	PhCHO (**5**)	0.75	97
4-(OMe)$C_6H_4CH(OCOiPr)_2$ (**11c**)	4-(OMe)C_6H_4CHO (**11**)	1.15	95
PhCH=CHCH$(OCOiPr)_2$ (**16c**)	PhCH=CHCHO (**16**)	1.00	95
$PhCH(OCOtBu)_2$ (**5d**)	PhCHO (**5**)	1.10[d]	90
4-(Me)$C_6H_4CH(OCOtBu)_2$ (**8d**)	4-(Me)C_6H_4CHO (**8**)	1.30[d]	92
4-(OMe)$C_6H_4CH(OCOtBu)_2$ (**11d**)	4-(OMe)C_6H_4CHO (**11**)	1.30[d]	96
PhCH=CHCH$(OCOtBu)_2$ (**16d**)	PhCH=CHCHO (**16**)	2.20[d]	85
PhCH=CHCH$(OBz)_2$ (**16e**)	PhCH=CHCHO (**16**)	5.30[d]	80

Reactions performed at reflux temperature.



	Time	% of Products formed
X = CH_3 (**8a**) + Y = NO_2 (**12a**)	2 h	**8** (90%) + **12** (00 %)
X = OCH_3 (**11a**) + Y = NO_2 (**12a**)	2 h	**11** (90%) + **12** (00 %)

Scheme 10. Chemoselective deprotection of *gem*-diacylates



R	R'	Time	% Remaining	Selectivity
CH_3 (**16a**)	Et (**16b**)	2 h	**16a** (90%) / **16b** (10%)	80
Et (**16b**)	*i*Pr (**16c**)	2 h	**16b** (30%) / **16c** (70%)	40
CH_3 (**16a**)	*i*Pr (**16c**)	2 h	**16a** (20%) / **16c** (80%)	60
*i*Pr (**16c**)	*t*Bu (**16d**)	8 h	**16c** (00%) / **16d** (100%)	100
*t*Bu (**16d**)	Ph (**16e**)	12 h	**16d** (10%) / **16e** (100%)	90

Scheme 11. Intermolecular chemoselectity of different *gem*-diacylates of cinnamaldehyde

over **16a** (60%). Excellent intermolecular chemoselectivity was observed for cinnamaldehyde dipivalate (**16d**) in the presence of **16c** (100%), and for cinnamaldehyde dibenzoate (**16e**) over **16d** (90%). Thus, the relative stability order found from the present experimental study is *gem*-dibenzoate > *gem*-dipivalate > *gem*-diisobutyrate > *gem*-diacetate >

gem-dipropionate; the relative stability of different acylates will be of interest in the field of protection and deprotection chemistry.

We further investigated the stability of various acylates under basic conditions (10% aq. sodium hydroxide) because acylates differ from acetals in this respect. Cinnamaldehyde *gem*-diacetate (**16a**), *gem*-dipropionate (**16b**), *gem*-diisobutyrate (**16c**), *gem*-dipivalate (**16d**) and *gem*-dibenzoate (**16e**) were each stirred with 10% aq. NaOH in dioxane and deprotection was monitored by GC. Complete deprotection of cinnamaldehyde *gem*-dipropionate, *gem*-diacetate and *gem*-diisobutyrate was observed after 9 h, 13 h and 17 h, respectively. The *gem*-dipivalate and *gem*-dibenzoate could be deprotected after 25 h and 56 h, respectively. Interestingly, we obtained a similar stability order as obtained in an acidic medium, although the compounds are more stable under basic conditions. The pK_a's of acetic acid (4.75), propionic acid (4.87), isobutyric acid (4.84), pivalic acid (4.76) and benzoic acid (4.19), are very similar; they differ by less than one pK_a unit. The stability orders of the different *gem*-diacylates determined above do not correlate with the pK_a's of the corresponding acid; rather, they are directly related to the steric crowding around the carbonyl carbon.

Conclusion

In conclusion, we have demonstrated that *gem*-diacylation of aldehyde is an acid-catalyzed process. The first step of the reaction is initiated by protonation of an aldehydic carbonyl group, followed by nucleophilic attack of an anhydride on an activated aldehydic carbonyl group, nucleophilic attack of the hemiacylate intermediate on a second molecule of anhydride and an intermolecular attack of the second acetate group. We have also demonstrated that *gem*-diacylates of various aliphatic and aromatic aldehydes can be prepared from a variety of aliphatic and aromatic anhydrides under solvent-free conditions in the presence of a catalytic quantity of tetrabutylammonium tribromide (TBATB). The faster rate of *gem*-diacylate formation for substrates containing electron-donating substituents as compared to substrates containing electron-withdrawing substituents, and chemoselective protection of the latter in the presence of the former, shows the significance of electronic effects during the formation. Deprotection of *gem*-diacylates to the corresponding parent carbonyl compounds has been accomplished by performing the reaction in methanol with the same catalyst. Chemoselective deprotection of the *gem*-diacylate of a substrate containing an electron-donating group has been achieved in the presence of a substrate containing an electron-withdrawing group, further showing the electronic effects during the deprotection. *gem*-Diacylates are more stable under basic conditions than acidic conditions. Interestingly, both the acid and base stability of various *gem*-diacylates follow the same order. The stability order obtained from a series of competitive experiments is: *gem*-dibenzoate > *gem*-dipivalate > *gem*-diisobutyrate > *gem*-diacetate > *gem*-dipropionate, and is directly related to the steric crowding around the carbonyl carbon rather than to the pK_a of the corresponding acid.

Experimental Section

All the reagents were of commercial grade and were purified according to established procedures. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed on a rotary evaporator under reduced pressure. Silica gel (60−120 mesh size) was used for column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254}(0.25 mm). Gas-liquid chromatography was performed using a cross-linked methyl silicon gum capillary column (30 m × 0.32 mm × 0.25 μm) fitted with a FID. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H (300 and 400 MHz) or $CDCl_3$ solvent as the internal standard ^{13}C (75 and 100 MHz). FAB mass spectra were recorded using a JEOLSX-102/DA-6000 instrument with argon (6 kV, 10 mA) as the flow gas. Elemental analysis was performed with a Perkin−Elmer 2400 elemental analyzer. Melting points were recorded with a Buchi B-540 melting point apparatus. The pH of the solution was measured with a pH Scan 2 from Eutech Instruments. The follwing *gem*-diacylates derived from the parent aldehydes have been reported in the literature: *gem*-diacetates **1a**,[16b] **2a**,[35] **4a** and **5a**,[10] **6a**, **9a**−**13a**,[19a] **7a**, **8a**, **16a**, **20a**,[1b] **15a** and **17a**,[14] **18a**,[23] **19a** and **22a**,[23] **23a**,[19d] **25a**,[24] **26a**;[16b] *gem*-dipropionate **5b**;[16a] *gem*-diisobutyrate **5c**;[16a] *gem*-dipivalates **5d**,[16a] **8d**, **16d**.[18]

Change of pH of Organic Liquid with TBATB: Acetic anhydride (2.5 mL, 27 mmol) was placed in a 10 mL beaker. The pH of the solution was measured by dipping the pH meter into it after calibrating with a pH 4 buffer. The pH of the solution was found to be 0.1. TBATB (1.3 g, 2.7 mmol) was added and the mixture stirred. The final pH was −0.7 after complete dissolution of TBATB, and it remained unchanged thereafter.

Formation of Mixed Acylates from an Acid Anhydride and Carboxylic Acid: Benzaldehyde (1 mmol) was added to a mixture of acetic anhydride (or propionic anhydride; 1 mmol), and propionic acid (or acetic acid; 1 mmol), and then TBATB (0.1 mmol) was also added. The homogeneous reaction was left at room temperature. The percentage of products formed at different times was determined by gas-liquid chromatography.

Formation of Mixed Acylates from a Mixture of Anhydrides: Benzaldehyde (1 mmol) was added to a mixture of acetic anhydride (1 mmol) and propionic anhydride (1 mmol), and then TBATB (0.1 mmol) was also added. The homogeneous reaction was left at room temperature. The percentage of products formed at different times was determined by gas-liquid chromatography.

Formation of Mixed Acylates from a Mixed Anhydride: Benzaldehyde (1 mmol) was added to acetic-propionic anhydride (1 mmol), prepared by the reaction of acetyl chloride and propionic acid with pyridine, and then TBATB (0.1 mmol) was also added. The homogeneous reaction was left at room temperature. The percentage of products formed at different times was determined by gas-liquid chromatography.

Formation of the Mixed Anhydride: TBATB (0.1 mmol) was added to a mixture of acetic anhydride (or propionic anhydride; 1 mmol) and propionic acid (or acetic acid; 1 mmol). The homogeneous reaction was left at room temperature. The percentage of different anhydrides formed at different times was determined by gas-liquid chromatography.

General Procedure for the Preparation of *gem*-Diacetates: TBATB (0.5 mmol) was added to a mixture of aldehyde (5 mmol) and acetic anhydride (15 mmol). The homogeneous reaction was left stirring at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was poured into saturated $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (3 × 25 mL). The organic layer was separated, dried over anhydrous sodium sulfate and concentrated. Further purification was achieved by passing through a short column of silica gel, and the products were identified by comparison of their NMR and IR spectra, GC profile, and GC coinjection, with authentic samples prepared by known methods.

General Procedure for the Preparation of *gem*-Dipropionate, *gem*-Diisobutyrate and *gem*-Dipivalate: Similar to the preparation of *gem*-diacetate, except 10 mmol of anhydride (propionic, isobutyric and pivalic) was used per 5 mmol of the aldehyde.

General Procedure for Preparation of *gem*-Dibenzoate: Similar to the preparation of *gem*-diacetate, except 5 mmol of benzoic anhydride was used per 5 mmol of the aldehyde in acetonitrile (0.5 mL).

Chemoselective Diacylation of Benzaldehyde in the Presence of Acetophenone: Acetic anhydride (1.5 mmol) and TBATB (0.1 mmol) were added to an equimolar mixture of acetophenone (1 mmol) and benzaldehyde (**5**; 1 mmol) in acetonitrile (1 mL). The homogeneous reaction was left at room temperature. The percentage of products formed at different times was determined by gas-liquid chromatography.

Chemoselective *gem*-Diacylation of 4-Methylbenzaldehyde (8) or 4-Methoxybenzaldehyde (11) in the Presence of 4-Nitrobenzaldehyde (12): Acetic anhydride (1.5 mmol) and TBATB (0.1 mmol) were added to an equimolar mixture of 4-methylbenzaldehyde (**8**) or 4-methoxybenzaldehyde (**11**; 1 mmol), and 4-nitrobenzaldehyde (**12**; 1 mmol) in acetonitrile (1 mL). The homogeneous reaction was left stirring at room temperature and the percentage of products formed at different times was determined by gas-liquid chromatography.

Chemoselective Diacylation of 9-Anthraldehyde (23) in the Presence of 9-Fluorenecarboxaldehyde (24): Acetic anhydride (1.5 mmol) and TBATB (0.1 mmol) were added to an equimolar mixture of 9-anthraldehyde (**23**; 1 mmol) and 9-fluorenecarboxaldehyde (**24**; 1 mmol) in acetonitrile (1 mL). The homogeneous reaction was left stirring at room temperature and the percentage of products formed at different times was determined by gas-liquid chromatography.

General Procedure for the Deprotection of *gem*-Diacylates: TBATB (0.1 mmol) was added to a mixture of diacylate (2 mmol) and methanol (2 mL). The homogeneous reaction was left stirring at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the methanol was evaporated on a rotary evaporator and ethyl acetate (20 mL) was added to the residue. The organic layer was washed with 10% sodium hydrogencarbonate (10 mL). The organic layer was separated, dried over anhydrous sodium sulfate and concentrated. Further purification was achieved by passing through a short column of silica gel, and the products were identified by comparison of their NMR and IR spectra and GC profile, and GC coinjection, with authentic samples.

General Procedure for the Chemoselective Deprotection of Different *gem*-Diacylates of Cinnamaldehyde: TBATB (0.1 mmol) was added to an equimolar mixture of two different cinnamyl diacylate (say *X* and *Y*) in methanol/water (5:1; 1 mL). The homogeneous reaction was left stirring at room temperature and the progress of the reaction was monitored by gas-liquid chromatography. The percentage of products formed at different times was determined by gas-liquid chromatography using benzophenone as an internal standard. The percentage selectivity was calculated as follows: Selectivity = percentage of *Y* deprotected − percentage of *X* deprotected at time *t*.

1-(2-Chloro-5-nitrophenyl)-1,1-diacetoxymethane (14a): M.p. 66.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 6 H), 5.27 (s, 1 H), 7.58 (d, J = 8.7 Hz, 1 H), 8.14 (dd, J = 2.7 Hz and 8.7 Hz, 1 H), 8.31 (d, J = 2.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 62.4, 123.8, 130.4, 135.7, 139.7, 146.6, 170.2 ppm. IR (KBr): $\tilde{\nu}$ = 3100, 3073, 1742, 1537, 1352, 1261, 1244, 1071, 1040 cm^{-1}. $C_{11}H_{10}ClNO_6$ (287.66): calcd. C 45.93, H 3.50, N 4.87; found C 46.01, H, 3.41, N 4.78.

1,1-Diacetoxy-1-[4-(dimethylamino)phenyl]methane (21a): M.p. 66−68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 6 H), 2.96 (s, 6 H), 6.70 (d, J = 9.2 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.59 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 40.7, 90.6, 112.0, 123.0, 127.9, 151.5, 168.9 ppm. IR (KBr): $\tilde{\nu}$ = 2998, 2909, 2838, 1762, 1624, 1520, 1378, 1250, 1214, 1076 cm^{-1}. MS (FAB): [M$^+$] calcd. for $C_{13}H_{17}NO_4$ 251.28; found 251.0. $C_{13}H_{17}NO_4$ (251.28): calcd. C 62.14, H 6.82, N 5.57; found C 62.38, H, 6.70, N, 5.50.

9-(Diacetoxymethyl)-9*H*-fluorene (24a): M.p. 95−97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 6 H), 7.23−7.51 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 99.6, 119.3, 119.4, 119.6, 124.9, 125.5, 125.6, 125.9, 126.2, 126.5, 127.7, 128.2, 128.5, 140.8, 141.0, 114.3, 141.5, 141.8, 143.1, 143.4, 169.2 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2856, 1755, 1447, 1369, 1222, 1002, 743 cm^{-1}. MS (FAB): [M$^+$] calcd. for $C_{18}H_{16}O_4$ 296.33; found 296.0. $C_{18}H_{16}O_4$ (296.33): calcd. C 72.96, H 5.44; found C 73.18, H, 5.54.

1,1-Dipropionyloxy-1-(4-methoxyphenyl)methane (11b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, J = 7.6 Hz, 6 H), 2.38 (m, 4 H), 3.81 (s, 3 H), 6.91 (d, J = 8.8 Hz, 2 H), 7.45 (d, J = 8.8 Hz, 2 H), 7.65 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.2, 27.8, 55.6, 89.8, 114.1, 128.1, 128.2, 160.6, 172.3 ppm. IR (KBr): $\tilde{\nu}$ = 2986, 2950, 2843, 1762, 1614, 1516, 1470,1363, 1260, 1220, 1168, 840 cm^{-1}. $C_{14}H_{18}O_6$ (266.30): calcd. C 63.15, H 6.81; found C 63.21, H, 6.93.

1,1-Dipropionyloxy-3-phenylprop-2-ene (16b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, 6 H), 2.41 (q, 4 H), 6.23 (dd, J = 15.9, 6.6 Hz, 1 H), 6.87 (d, J = 16.2 Hz, 1 H), 7.30 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.7, 27.3, 89.6, 121.8, 126.9, 128.6, 128.7, 135.4, 172.1 ppm. IR (KBr): $\tilde{\nu}$ = 2991, 2940, 1762, 1460, 1363, 1281, 1194, 1143, 958, 753, 697 cm^{-1}. $C_{15}H_{18}O_4$ (262.31): calcd. C 68.69, H 6.92; found C 68.54, H, 7.04.

9-(Dipropionyloxymethyl)anthracene (23b): M.p. 141−142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (t, J = 7.2 Hz, 6 H), 2.38 (m, 4 H), 7.45 (t, J = 7.2 Hz, 2 H), 7.58 (t, J = 6.9 Hz, 2 H), 7.96 (d, J = 8.4 Hz, 2 H), 8.47 (s, 1 H), 8.72 (d, J = 9.3 Hz, 2 H), 9.27 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.6, 27.3, 87.4, 124.7, 125.0, 125.5, 126.6, 128.9, 129.8, 130.4, 131.3, 172.4 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2983, 2943, 1755, 1625, 1449, 1189, 1144, 978, 903, 738 cm^{-1}. MS (FAB): [M$^+$] calcd. for $C_{21}H_{20}O_4$, 336.39, found 336. $C_{21}H_{20}O_4$ (336.39): calcd. C 74.98, H 5.99; found C 74.76, H, 6.13.

1,1-Diisobutyryloxy-1-(4-methoxyphenyl)methane (11c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (m, 12 H), 2.58 (m, 2 H), 3.80 (s, 3

H), 6.91 (d, J = 8.7 Hz, 2 H), 7.45 (d, J = 8.4, 2 H), 7.64 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4, 18.6, 33.8, 55.1, 89.5, 113.8, 127.9, 131.9, 160.4, 174.8 ppm. IR (KBr): $\tilde{\nu}$ = 2981, 2940, 2884, 1762, 1624, 1516, 1470, 1255, 1158, 1035, 963, 834 cm^{-1}. $C_{16}H_{22}O_5$ (294.35): calcd. C 65.29, H 7.53; found C 65.39, H, 7.69.

1,1-Diisobutyryloxy-3-phenylprop-2-ene (16c): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (m, 12 H), 2.56 (m, 2 H), 6.22 (dd, J = 6.3, 15.9 Hz, 1 H), 6.83 (d, J = 15.9 Hz, 1 H), 7.29 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2, 18.5, 18.6, 18.7, 33.7, 33.8, 35.0, 50.4, 89.5, 121.9, 127.0, 128.6, 128.7, 129.1, 135.2, 174.8 ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2976, 2935, 2879, 1757, 1470, 1245, 1205, 1158, 1096, 958 cm^{-1}. $C_{17}H_{22}O_4$ (290.36): calcd. C 70.32, H 7.64; found C 69.99, H, 7.79.

9-(Diisobutyryloxymethyl)anthracene (23c): M.p. 132−134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.9 Hz, 6 H), 1.21 (d, J = 6.9, 6 H), 2.61(m, 2 H), 7.47 (t, J = 7.2 Hz, 2 H), 7.58 (t, J = 8.4 Hz, 2 H), 8.0 (d, J = 8.4 Hz, 2 H), 8.51 (s, 1 H), 8.72 (d, J = 9 Hz, 2 H), 9.20 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = ?18.4, 18.7, 33.9, 49.9, 87.6, 124.7, 125.0, 125.6, 126.5, 128.9, 129.9, 130.4, 131.4, 175.0 ppm. IR (KBr):2976, 2930, 2879, 1757, 1470, 1388, 1250, 1194, 1158, 1050, 974, 738 cm^{-1}. MS (FAB): [M$^+$] calcd. for $C_{23}H_{24}O_4$ 364.45; found 364. $C_{23}H_{24}O_4$ (364.45): calcd. C 75.80, H 6.64; found C 76.01, H, 6.71.

1,1-Dipivaloyloxy-1-(4-methoxyphenyl)methane (11d): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (s, 18 H), 3.81 (s, 3 H), 6.90 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H), 7.60 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.0, 38.9, 55.3, 89.5, 113.7, 127.7, 128.0, 160.1, 176.0 ppm. IR (KBr): $\tilde{\nu}$ = 2981, 2935, 2873,1757, 1481, 1281, 1168, 1112, 968 cm^{-1}. MS (FAB): [M$^+$] calcd. for $C_{18}H_{26}O_5$ 322.40; found 322. $C_{18}H_{26}O_5$ (322.40): calcd. C 67.06, H 8.13; found C 66.88, H, 8.28.

1,1-Dibenzoyloxy-3-phenylprop-2-ene (16e): M.p. 145−147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.49 (dd, J = 6.3, 16.2 Hz, 1 H), 7.05 (d, J = 16.2, 1 H), 7.32−7.55 (m, 11 H), 7.85 (d, J = 6.3 Hz, 1 H), 8.11 (d, J = 7.5 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 90.7, 121.9, 127.1, 128.4, 128.7, 128.8, 129.2, 130.0, 133.5, 135.8, 164.4 ppm. IR (KBr): $\tilde{\nu}$ = 3073, 3027, 2981, 1737, 1603, 1455, 1281, 1250, 1148, 1061, 958, 702 cm^{-1}. MS (FAB) [M$^+$] calcd. for $C_{23}H_{18}O_4$ 358.40, found 358.0. $C_{23}H_{18}O_4$ (358.40): calcd. C 77.08, H 5.06; found C 76.88, H, 5.28.

9-(Dibenzoyloxymethyl)anthracene (23e): M.p. 171.5−173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 4 H), 7.46 (m, 4 H), 7.67 (t, J = 8.4 Hz, 2 H), 7.98 (d, J = 8.7 Hz, 2 H), 8.06 (d, J = 7.8 Hz, 3 H), 8.48 (s, 1 H), 9.02 (d, 2 H), 9.82 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 88.3, 124.6, 125.1, 125.4, 126.9, 128.4, 129.1, 130.0, 130.6, 131.4, 133.5, 164.5 ppm. IR (KBr): $\tilde{\nu}$ = 3063, 3007, 1747, 1726, 1286, 1250, 1081, 1061, 963 cm^{-1}. MS (FAB) [M$^+$] calcd. for $C_{29}H_{20}O_4$ 432.48; found 432.0. $C_{29}H_{20}O_4$ (432.48): calcd. C 80.54, H 4.66; found C 80.42, H, 4.78.

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