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Iodine as Acetylation Catalyst in the Preparation of 1,1-Diacetates from Aldehydes

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Aldehydes are known to react with simple anhydrides in the presence of acid catalysts to give 1,1-diacetates (acylals).[1] Because of their stability in neutral as well as basic media,[2] the acylals are gaining importance in synthetic organic chemistry as aldehyde protecting group alternatives to acetals.[3] The acylals of α,*β*-unsaturated aldehydes are important starting materials for the synthesis of acetoxy dienes and vinyl acetate.[4] Acylals have been applied as crosslinking reagents for cellulose in cotton.[5] One European patent claims the use of peroxygen compounds of the 1,1,5-triacetoxy-4-pentene type as activators in the composition of bleaching mixtures for wine-stained fabrics.[6]

Usually, the acylals **3** are prepared from aldehydes **1** and acetic anhydride **2** under the catalysis of strong acids such as sulfuric acid,[1] phosphoric acid, or methanesulfonic acid[7] (Scheme 1). Olah *et al.*[8] have reported the use of Nafion-H as a catalyst for this conversion where average yields of products are moderate and reaction times are 3−5 h, except in two cases. Lewis acids like $ZnCl_2$,[9] $FeCl_3$,[2] and PCl_3[10] and zeolites[11] of different types are also used as catalysts for this conversion. But in most cases, either a long reaction time (up to 120 h in the case of 2-furyl aldehyde with PCl_3[10]) or a low yield of product (4% in case of 4-nitro benzaldehyde[10]) is incurred. Therefore, the development of new reagents with more efficiency and better yield is of interest.

While the catalytic activity of iodine in the acetylation of alcohols with acetic anhydride was being studied,[12] the following conversion was observed (Scheme 2, eq 1) in more than 90% yield and after a short reaction time.

Table 1[a]

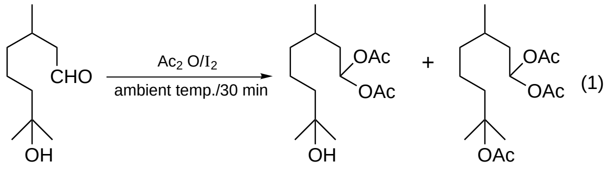
entry	substrate	(°C)/time (h)	yield mp (°C) (%)	found/reported
1	benzaldehyde	ambient/0.3	95	45−46/44−45[2]
2	4-$NO_2C_6H_4CHO$	ambient/2	99	125/125[11]
3	4-ClC_6H_4CHO	ambient/1	92	80/79−80[11]
4	4-$MeOC_6H_4CHO$	0−10/0.6	90	67/67−68[10]
5	cinnamaldehyde	0−10/1	86	86/84−86[2]
6	furfural	ambient/2.5	78	55/52−54[11]
7	butyraldehyde	ambient/0.5	90	
8	glutaraldehyde	0−10/1	98	63/64−65[5]
9	crotonaldehyde	0−10/0.2	80	
10	acrolein	0−10/0.5	70	

[a] All the compounds give satisfactory spectral analysis for IR, NMR (60 MHz), and MS. Yields are all of isolated pure products, and mp's are uncorrected.

Scheme 1

$$\underset{\mathbf{1}}{RCHO} + \underset{\mathbf{2}}{Ac_2O} \xrightarrow{H^+} \underset{\mathbf{3}}{RCH(OAc)_2}$$

Scheme 2



To generalize the feasibility of the reaction in other systems, we examined 10 different aldehydes (Table 1) including aromatic and aliphatic and α,*β*-unsaturated ones. In almost all cases, the reactions are quicker than those of the reported methods and the yields are quite high. The cases of 4-nitrobenzaldehyde and cinnamaldehyde are worth mentioning as they give quantitative yields by this method, in contrast to yields of 4% and 30%, respectively, with PCl_3.[10] The nature of the substituents on the aromatic ring seems to have no effect on the reaction system. In the case of aliphatic aldehydes, one also observes high yields in short reaction time. The 25% water solution of glutaraldehyde gives an almost quantitative yield of diacylal, thus indicating the versatility of this reagent system.

Experimental Section

Typical Procedure. A solution of benzaldehyde (2 mmol) in 2 mL of chloroform is stirred at room temperature under nitrogen atmosphere. Freshly distilled acetic anhydride (10 mmol) is added to it followed by the addition of iodine (0.2 mmol) as catalyst. The reaction is monitored in TLC and on completion worked up by adding water and chloroform to the reaction mixture followed by washing with a solution of sodium thiosulfate. The organic layer was then washed with water and dried over anhydrous sodium sulfate and evaporated under reduced pressure to get the desired product in pure form. The acylal of benzaldehyde showed identical spectral data and mp as reported earlier.[2] In an isolated example, 5.3 g (50 mmol) of benzaldehyde gives a satisfactory result (85% isolated yield) with 5% of the catalyst also.

Five of the compounds synthesized had spectra and mp's identical to those reported previously.[2,5] The reactions of anisole (Table 1, entry 4), cinnamaldehyde (Table 1, entry 5), glutaraldehyde, crotonaldehyde, and acrolein (Table 1, entries 8−10) are done at 0−10 °C.

The acylals of the following aldehydes show MS (EI), NMR (60 MHz, $CDCl_3$), and IR ($CHCl_3$) spectra as mentioned below.

4-Nitrobenzaldehyde: NMR δ 8.05 d ($J = 9$ Hz, 2H), 7.47 d ($J = 9$ Hz, 2H), 7.45 s (1H), 2.10 s (6H); IR 1760, 1540, 1460, 1235, 1095, 1060 cm^{-1}; MS *m/e* 253, 210, 194, 150, 134, 77.

4-Chlorobenzaldehyde: NMR δ 7.50 s (1H), 7.30 s (4H), 2.10 s (6H); IR 1755, 1605, 1495, 1375, 1215 cm^{-1}; MS *m/e* 244, 242, 201, 199, 185, 183, 156, 142, 141, 139, 111, 77.

4-Methoxybenzaldehyde: NMR δ 7.40 s (1H), 7.35 d ($J =$ 9Hz, 2H), 6.75 d ($J =$ 9Hz, 2H), 3.80 s (3H), 2.10 s (6H); IR 1763,

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1614, 1519, 1372, 1241, 1204 cm^{-1}; MS *m/e* 238, 195, 179, 152, 135, 107, 93, 92, 77, 65.

Butyraldehyde: NMR δ 6.50 m (1H), 2.40−2.00 brm (2H), 2.00 s (6H), 1.90−1.30 brm (2H), 1.00 t (J = 7 Hz, 3H); IR 2960, 1765, 1374, 1244, 1208, 1010 cm^{-1}; MS *m/e* 175 (M + 1), 161, 160, 132, 116, 101, 74.

Crotonaldehyde: NMR δ 6.70 d (J = 6 Hz, 1H), 6.00−5.10 m (2H), 2.10−1.90 (overlapping signals of 9H); IR 1760, 1390, 1250, 1215 cm^{-1}; MS, m/e 173 (M + 1), 159, 158, 145, 141, 131, 99, 71, 69, 55.

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Additions and Corrections

Vol. 61, 1996

Maurizio Pulici, Fumio Sugawara,* Hiroyuki Koshino, Jun Uzawa, Shigeo Yoshida, Emil Lobkovsky, and Jon Clardy*. Pestalotiopsins A and B: New Caryophyllenes from an Endophytic Fungus of *Taxus brevifolia*.

Page 2122, abstract, line 4. Ratio of 5:6, not 6:5.

Page 2123, column 2. All references to major conformer (component) should be for minor conformer (component), and vice versa.

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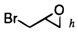
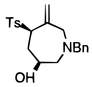
S0022-3263(96)04032-7

Diego A. Alonso, Larry R. Falvello, Balbino Mancheño, Carmen Nájera,* and Milagros Tomás. Lithiated γ-Tosyl-Substituted Benzylmethallylamine: New γ-Amino Methallyl Sulfone Anions in Organic Synthesis.

Page 5007, Table 2. Entry 9 (see below) was omitted from the table.

Table 2. Reaction of Intermediates 10 with Dielectrophiles

			product			
entry	intermediate	electrophile	no.	structure	yield,[a] (%)	mp,[b] (°C) or R_f[c]
9	**10b**	 [h]	**20f**		37[e]	100-101

JO964034U

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Hiroyuki Saimoto, Koji Yoshida, Tetsuya Murakami, Minoru Morimoto, Hitoshi Sashiwa, and Yoshihiro Shigemasa*. Effect of Calcium Reagents on Aldol Reactions of Phenolic Enolates with Aldehydes in Alcohol.

Page 6769, footnote *a* in Table 2 should read as follows: RCHO, 0.72 mmol; substrate, 0.60 mmol; solvent, 2 mL; 0 °C. Solvent: MeOH except run 1 (H_2O−MeOH 2:3) and run 6 (H_2O−MeOH 1:1).

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S0022-3263(96)04033-9

Melinda L. Greer and Silas C. Blackstock*. Complexes of Oxygenated *trans*-Azoalkanes and Tetracyanoethylene. The Interaction of π Oxygen Anions with an Electron Poor Alkene.

Pages 7897 (Table 1) and 7902 (Tables 3 and 4). Due to an error in calculation, the formation constants (K_f) reported in Tables 1, 3, and 4 are incorrect. The correct K_f values for Table 1 are (entries 1−5 sequentially) 2.8 ± 0.4, 0.8 ± 0.2, 0.4 ± 0.04, 0.8 ± 0.02, and 0.6 ± 0.04 M^{-1}. The corrected K_f values for Table 3 are 2.33 M^{-1} (λ 344 nm), 1.82 M^{-1} (λ 364 nm), 3.23 M^{-1} (λ 394 nm), and 4.55 M^{-1} (λ 410 nm) and for Table 4, 0.27 M^{-1} (λ 500 nm), 0.50 M^{-1} (λ 520 nm), 0.32 M^{-1} (λ 540 nm), and 0.36 M^{-1} (λ 550 nm).

Supporting Information Available: Corrected K_f values for Tables S1−S7 published with the original paper (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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