Scientific paper

Chemistry of Organo Halogenic Molecules. Part 229. The Role of Iodine in Acetyl Group Transfer to Oxygen-containing Molecules under Solvent-free Reaction Conditions

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Received: 09-12-2008

Dedicated to Professor Branko Stanovnik on the occasion of his 70th birthday

Abstract

Iodine was shown to be an efficient catalyst for the conversion of phenyl-substituted aldehydes to the corresponding 1,1-diacetate derivatives under solvent-free reaction conditions (SFRC), which are superior to the classical solution conditions. It was demonstrated that the order of the addition of reactants was of fundamental importance; the ability of substituents on the phenyl ring modified reactivity irrespectively to electronic properties, the pentafluorophenyl group significantly reduced reactivity of the aldehyde. Alcohols yielded acetates; acetic anhydride was found to be the most efficient reagent; isopropenyl acetate and vinyl acetate were less reactive; however the pentafluorophenyl group enhanced reactivity with the latter two reagents. Beside the esterification of benzyl alcohol and its pentafluorophenyl analogue, the formation of acetals was also observed.

Keywords: Iodine, catalyst, solvent-free, acetylation.

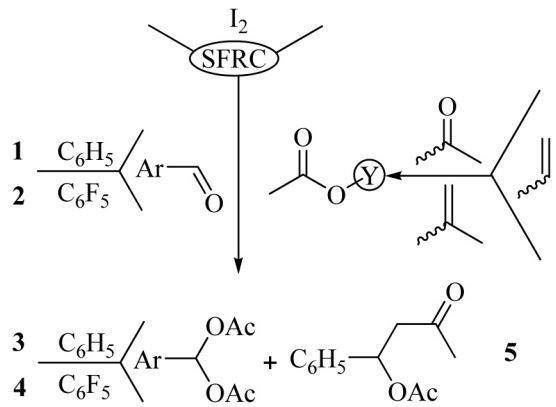
1. Introduction

Rapidly changing climatic and environmental circumstances have a significantly growing impact on the life on Earth. Consequently, the field of chemistry has been turning to 'green chemistry'; endeavoring to reduce the waste, to minimize the costs, to simplify and optimize reaction protocols.[1] One of the important contributions in this respect is functionalization without the use of solvent.[2] Considerable attention should be paid to exothermic and reactions with extensive gas evolution, since there is no medium to relieve the heat or pressure shock; furthermore, scale-up might be a challenging task.[3] Another critical aspect could be associated with the heterogeneity of the reaction mixture and insufficient stirring; particularly when only solid reactants are involved. Acetylation has been extensively investigated;[4] its products are important intermediates in the synthesis, the acetyl group frequently serves as a protecting group of hydroxy, amino and thiol functionality in biologically-important molecules; at the same time, acetylated products have found broad application in industry. The transformation of aldehydes to 1,1-diacetate analogues has been widely studied: without catalyst,[5] H_2NSO_3H,[6] $Fe_2(SO_4)_3 \cdot xH_2O$,[7] $KHSO_4$,[8] heteropolyacids,[9] P_2O_5/Al_2O_3,[10] $HBF_4–SiO_2$,[11] silica sulfuric acid,[12] $HClO_4–SiO_2$,[13] $FeCl_3/SiO_2$,[14] solid silica sulfuric acid,[15] $[Yb(OPf)_3]$,[16] LiOTf,[17] $Zr(SO_4)_2 \cdot 4H_2O/SiO_2$,[18] zeolites,[19] $Bi(OTf)_3 \cdot xH_2O$,[20] $RuCl_3$,[21] $InBr_3$,[22] tetrabutylammonium tribromide,[23] and others. However, many procedures employed heavy-metallic, hazardous, strongly-acidic and moisture-sensitive catalysts. Iodine has several advantages over the existing catalysts: it is mild and remarkably versatile catalyst in organic chemistry,[24] and one of its major advantages is neutrality. It has high affinity to the molecular oxygen and oxygen-functional groups; it is able to discriminate between H_2O_2, MeOH and H_2O, and hydroxy, hydroperoxy and methoxy groups.[25] The iodine-catalyzed transformation of aldehydes to 1,1-diacetate derivatives has already been publis-

hed, however in a $CHCl_3$ solution and with a huge excess of Ac_2O.[26] The acetylation of alcohols catalyzed by I_2 was accomplished using Ac_2O,[27] isopropenyl acetate (IPA)[28] and vinyl acetate (VA).[29] Here, we report on iodine-catalyzed acetyl group transfer to aldehydes and alcohols, comparing the reactivity of acetic anhydride, isopropenyl acetate and vinyl acetate under SFRC.

2. Results and Discussion

The pentafluorophenyl ring often exhibits uncommon and intriguing behavior; it is frequently employed as molecular marker in crystal engineering, biological recognition and supramolecular assemblies.[30] The pentafluorophenyl group can also significantly modify the reactivity of substrates; little information is available on its effect on the reactivity on transformations under SFRC. We have examined the role of the structure of the acetylation reagent on I_2-catalyzed transformation of benzaldehyde **1a** and pentafluorobenzaldehyde **2** under SFRC (Scheme 1).



Ar	Y	Reaction conditions[a]		Conv.[b] (%)
		T (°C)	t (min)	
C_6H_5	COMe	25	25	95
	$CMeCH_2$	85	480	91[c]
	$CHCH_2$	85	960	0
C_6F_5	COMe	25	1440	25
	$CMeCH_2$	85	480	0
	$CHCH_2$	85	960	0

[a] 1 mmol of ArCHO, 1.1 mmol of Ac_2O or 2 mmol of IPA or 2 mmol of VA and 0.03 mmol I_2. [b] Determined by ^1H NMR. [c] A mixture of **3** and **5** in a ratio of 23:77.

Sheme 1

It was established that **1a** and **2** could be converted to their 1,1-diacetate derivatives **3a** and **4** using Ac_2O, where **1a** was remarkably more reactive than **2**. Transformation of **1a** with isopropenyl acetate gave an unexpected result; beside **3a**, **5** was obtained as well, whereas **2** did not react under these conditions. In an independent experiment, a 17% conversion of **3a** to **1a** in the presence of 3 mol % I_2 (7 h at 85 °C, SFRC) was noted; after 27 h, conversion rose to 39%. Transformation of **3a** with IPA in the presence of 3 mol % of I_2 (7 h at 85 °C, SFRC) furnished **5** (31%) and **1a** (6%). Vinyl acetate was not sufficiently reactive to convert **1a** and **2** to **3a** and **4**.

In order to understand the effect of reaction conditions on the functionalization of organic molecules under SFRC, it is reasonable to compare reactivity in various solvents. We further examined the role of solvent on the transformation of **1a** to **3a** in the presence of 3 mol % of I_2; the results are given in Table 1.

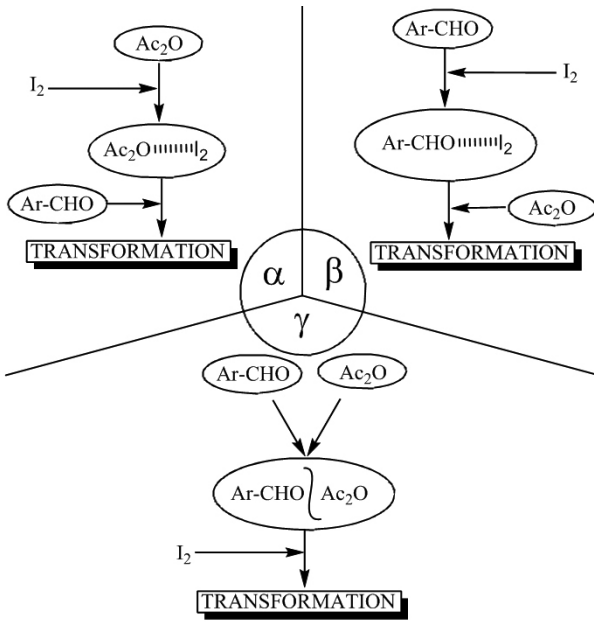
Table 1: The effect of iodine and solvent on transformation of benzaldehyde **1a** to 1,1-diacetoxy-1-phenylmethane **3a** with acetic anhydride.[a]

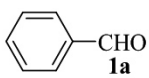
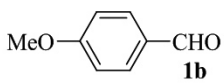
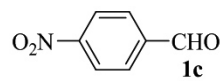
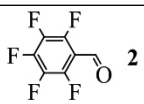
Solvent	I_2 (mol %)	Conversion[b] (%)
CH_2Cl_2	0	0
	3	42
$CHCl_3$	0	0
	3	5
CH_3CN	0	0
	3	75
H_2O	0	0
	3	0
SFRC	0	0
	3	95

[a] 1 mmol of **1a**, 1.1 mmol of Ac_2O, 0.03 mmol I_2 , 2 mL of solvent; r.t. = 25 min; T = 25 °C. [b] Determined by ^1H NMR.

It is evident that reactions under SFRC gave superior results; conversions in solution were lower, while water was not suitable at all, and the presence of iodine was found to be indispensable for the functionalization. Iodine is capable of coordinating organic molecules in a different fashion; one of the decisive moments could be sequence of the addition of reactants. Therefore, we have examined the role of reaction protocol on the I_2-catalyzed transformation of **1** and **2** (Scheme 2).

In general, the best results were obtained following the protocol α where I_2 was added to Ac_2O; the mixture was heated to dissolution, cooled to room temperature, and aldehyde was added last. Transformation of **1a** was found to be independent of the reaction protocol; substituted aldehydes **1b** and **1c** exhibited higher differences in reactivity. Substituents containing oxygen atom(s) on the aromatic ring are capable of additional complexation of iodine; the transformation may not be straightforward and reactivity opposite from expected. The protocol β (aldehyde and I_2 heated to dissolution and cooled to room temperature) gave similar results to what α did; except for **1c** which is solid, in contrast to other tested substrates.



Aldehyde	Reaction protocol[a]	Conv.[c] (%)
 **1a**	α	95
	β	98
	γ	97
 **1b**	α	54
	β	49
	γ	32
 **1c**	α	94
	β	0
	γ	0
 **2**	α[b]	67
	β[b]	66
	γ[b]	54

[a] Reaction conditions: 1 mmol of ArCHO, 1.1 mmol of Ac_2O, 0.05 mmol I_2; r.t. = 25 min; T = 25 °C. [b] R.t. = 24 h. [c] Determined by ^{1}H NMR.

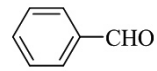
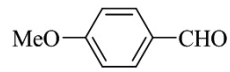
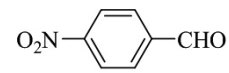
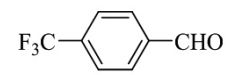
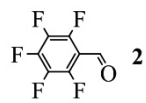
Scheme 2: The role of reaction protocol on the I_2-catalyzed transformation

The protocol γ, where I_2 was added last, was found to be the least favorable; it worked well only in the case of **1a**. Iodine was separately dissolved in Ac_2O, in **1a**, and in **1b** and IR spectra of the mixtures were recorded; however, no perceivable differences were noted when compared with spectra of the pure reactants.

Additionally, we studied the role of the amount of I_2 on the transformation of aldehydes with Ac_2O, Table 2.

The reactivity pattern was not uniform; substituents exhibited a strong, but atypical influence. No general threshold of I_2 amount was observed; as low as 1 mol % of I_2 was a sufficient amount for almost complete transformation of **1a** to **3a** within 25 min at room temperature. **1b** exhibited a controversial reactivity; increasing conversion

Table 2: The effect of aldehyde structure and quantity of iodine on transformations to geminal diacetates[a]

Aldehyde	I_2 (mol %)	Conv.[b] (%)
 **1a**	5	95
	3	95
	1	97
	0	0
 **1b**	10	37
	5	54
	3	71
	1	69
	0	0
 **1c**	5	94
	3	54
	1	0
	0	0
 **1d**	5	100
	3	100
	1	77
	0	0
 **2**	10	94[c]
	5	67[c]
	3	25[c]
	0	0[c]

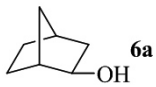
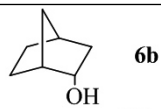
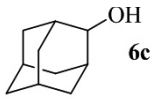
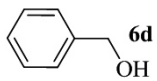
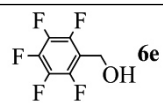
[a] Reac. cond.: 1 mmol of ArCHO, 1.1 mmol of Ac_2O and I_2, r.t. = 25 min; T = 25 °C. [b] Determined by ^{1}H NMR. [c] R.t. = 24 h.

with decreasing amount of I_2. The methoxy group obviously plays a unique role in complexation with I_2. 4-Nitrobenzaldehyde **1c** required 5 mol % of I_2 to achieve high conversion; in the case of **1d**, only 3 mol % was needed, but no appreciable difference in reactivity against **1a** was noted. Pentafluoro analogue **2** was the least reactive substrate, requiring 10 mol % of I_2 and 24 h at room temperature to reach high conversion.

I_2-catalyzed acetylation of alcohols using Ac_2O, isopropenyl acetate and vinyl acetate has been already published;[27–29] here we present a comparison of their reactivity on selected alcohols under SFRC, Table 3.

It is not clear which reactant is activated by iodine; alcohol or acetyl group donating reagent or both. For this reason, we studied the esterification of alcohols whose activation could involve carbocations upon activation with iodine; consequently, rearranged products would be formed. *Exo*-norborneol (**6a**) and *endo*-norborneol (**6b**) were suitable targets in this respect, but no rearranged products were formed. The *exo*-isomer **6a** gave the *exo*-acetate **7a** and the *endo*-alcohol **6b** furnished the *endo*-acetate **7b**. 2-Adamantanol **6c** could also yield rearranged products, but only 2-adamantyl acetate **7c** was obtained. Benzyl alcohol **6d** and its pentafluoro congener **6e** yielded the corresponding acetate derivatives **7d** and **7e**, both exhibiting surprisingly similar reactivity with Ac_2O. Moreover, the fluorinated analogue displayed higher reactivity in reaction with IPA and VA. Interestingly, ethanal formed from VA

Table 3: The effect of reagent on iodine induced acetyl transfer to alcohols

Alcohol	Reaction conditions[a]	Conv. (%)
 **6a**	Ac_2O/25 °C/5 min	100
	IPA/85 °C/8 h	96
	VA/85 °C/16 h	79
 **6b**	Ac_2O/25 °C/5 min	100
	IPA/85 °C/8 h	87
	VA/85 °C/16 h	67
 **6c**	Ac_2O/25 °C/5 min	100
	IPA/85 °C/8 h	82
	VA/85 °C/16 h	75
 **6d**	Ac_2O/25 °C/5 min	99
	IPA/25 °C/10 min	27
	VA/85 °C/1 h	53[b]
 **6e**	Ac_2O/25 °C/5 min	100
	IPA/25 °C/10 min	85
	VA/85 °C/30 min	85[c]

[a] 1 mmol of **6**, 0.03 mmol I_2 and 1.1 mmol of Ac_2O, IPA or VA stirred at given conditions. [b] A mixture of **7d** and **8d** in a ratio of 1:1. [c] A mixture of **7e** and **8e** in a ratio of 47:53.

during acetylation underwent acetalation to **8d** and **8e** with both benzyl alcohols **6d** and **6e**, the ratio acetate/acetal being approximately 1/1. Observation of acetal and ketal formation was reported during acetylation of saccharides using VA and IPA.[28a]

3. Conclusion

We have established that the reactivity of acetyl transfer agents (acetic anhydride, isopropenyl acetate and vinyl acetate) towards aldehydes and alcohols differs considerably; the best conversions were obtained under solvent-free reaction conditions. It was found that the sequence of the addition of reactants importantly influences the reaction outcome in the case of aldehydes; however no general reactivity pattern was observed, pentafluorobenzaldehyde was significantly less reactive than benzaldehyde. Alcohols as stereochemical probes, underwent acetylation without rearrangements, pentafluorobenzyl alcohol exhibited surprisingly high reactivity in comparison with benzyl alcohol.

4. Experimental

Reactions were performed under an air atmosphere in conical reactors using a small stirring bar. Chemicals were obtained from commercial sources and were used as received. Crude reaction mixtures were directly subjected to column chromatography. Flash-column chromatography was carried out using Fluka 60 silica gel (63–200 μm, 70–230 mesh ASTM) and monitored by thin-layer chromatography on Merck 60 F_{254} TLC plates, utilising mixtures of light petrol ether (b.p. 40–60 °C) and *t*-butyl methyl ether. NMR spectra were recorded on a Bruker Avance 300 DPX instrument. The following procedures are the same regardless of the aggregate state of aldehyde or alcohol.

A typical general procedure for I_2-catalyzed transformation of aldehydes with acetic anhydride, isopropenyl acetate, or vinyl acetate.

Iodine (0.03 mmol, 7.6 mg) was dissolved in acetic anhydride (1.1 mmol, 112 mg) or in isopropenyl acetate (2 mmol, 200 mg) or in vinyl acetate (2 mmol, 172 mg), benzaldehyde (**1a**, 1 mmol, 106 mg) was added, and the reaction mixture stirred until the TLC showed complete conversion. The crude reaction mixture was diluted with *t*-butyl methyl ether, washed with aqueous $Na_2S_2O_3$, Na_2CO_3 (only in the case of Ac_2O) and water and dried over anhydrous Na_2SO_4. The solution was filtered and solvent removed under reduced pressure. The crude products were purified by column chromatography and pure products were obtained.

1,1-Diacetoxy-1-phenylmethane (3a).[26b] Column chromatography (157 mg, 75%), mp 43.9–44.3 °C (lit. 45–46 °C). IR (neat) ν 1751, 1377, 1246, 1210, 1013, 991, 948, 762, 701 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 6H), 7.40–7.53 (m, 5H), 7.68 (s, 1H).

1,1-Diacetoxy-1-(4-methoxyphenyl)methane (3b).[26b] Column chromatography (138 mg, 58%), mp 65.0–67.2 °C (lit. 67 °C). IR (neat) ν 1749, 1619, 1522, 1378, 1244, 1206, 1169, 1062, 1018, 935, 832, cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 6H), 3.82 (s, 3H), 6.92 (d, J = 9 Hz, 2H), 7.45 (d, J = 9 Hz, 2H), 7.62 (s, 1H).

1,1-Diacetoxy-1-(4-nitrophenyl)methane (3c).[26b] Column chromatography (226 mg, 89%), mp 126.0–126.4 °C (lit. 125 °C). IR (neat) ν 1762, 1611, 1528, 1376, 1351, 1230, 1204, 1063, 976, 944, 857, 831, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 6H), 7.70 (d, J = 8.7 Hz, 2H), 7.73 (s, 1H), 8.27 (d, J = 8.7 Hz, 2H).

1,1-Diacetoxy-1-(4-trifluoromethylphenyl)methane (3d).[31] Column chromatography (215 mg, 78%), mp 27.0–28.0 °C (lit. 31–33 °C). IR (neat) ν 1763, 1326, 1238, 1201, 1126, 1068, 1010 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 6H), 7.62–7.69 (m, 4H), 7.71 (s, 1H).

1,1-Diacetoxy-1-(2,3,4,5,6-pentafluorophenyl)methane (4).[32] Column chromatography (236 mg, 79%), mp 63.8–64.4 °C (lit. 64–65 °C). IR (neat) ν 1769, 1508, 1376, 1233, 1196, 1155, 1014, 947 cm^{-1}. ^1H NMR (300

MHz, $CDCl_3$) δ 2.14 (s, 6H), 7.90 (s, 1H). Anal. Calcd. for $C_{11}H_7F_5O_4$ (298.16): C, 44.31; H, 2.37; Found: C, 44.49; H, 2.43.

4-Acetoxy-4-phenyl-2-butanone (5).[33] Column chromatography, oily product (107 mg, 52%). IR (neat) ν 1739, 1720, 1371, 1240, 1163, 1045, 757, 701 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.15 (s, 3H), 2.83 (dd, *J* = 16.6 Hz, *J* = 5.0 Hz, 1H), 3.11 (dd, *J* = 16.6 Hz, *J* = 8.6 Hz, 1H), 6.19 (dd, *J* = 8.6 Hz, *J* = 5.0 Hz, 1H), 7.28–7.37 (m, 5H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 204.5, 169.7, 139.6, 128.6, 128.2, 126.4, 71.6, 49.8, 30.3, 21.0.

A typical general procedure for I_2-catalyzed transformation of alcohols with acetic anhydride, isopropenyl acetate, or vinyl acetate.

Benzyl alcohol (**6d**, 1mmol, 108 mg) was dissolved in acetic anhydride (1.1 mmol, 112 mg) or in isopropenyl acetate (1.1 mmol, 110 mg) or in vinyl acetate (1.1 mmol, 95 mg) and iodine (0.03 mmol, 7.6 mg) was added and the reaction mixture stirred until the TLC showed complete conversion. Isolation and purification procedure were the same as described above.

***Exo*-2-Norbornyl acetate (7a).**[34] Column chromatography, oily product (106 mg, 69%). IR (neat) ν 1736, 1449, 1369, 1246, 1072, 1018, 988 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.03–1.21 (m, 3H), 1.33–1.60 (m, 4H), 1.64–1.78 (m, 1H), 1.98 (s, 3H), 2.15–2.32 (m, 2H), 4.51–4.60 (m, 1H). MS *m/z* (%): 139 (M^+–Me, 1), 111 (31), 94 (47), 79 (34), 71 (19), 66 (100).

***Endo*-2-Norbornyl acetate (7b).**[34] Column chromatography, oily product (111 mg, 72%). IR (neat) ν 1733, 1449, 1361, 1246 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.92–1.02 (m, 1H), 1.21–1.45 (m, 4H), 1.49–1.66 (m, 1H), 1.67–1.81 (m, 1H), 1.91–2.06 (m, 4H), 2.17–2.26 (m, 1H), 2.43–2.50 (m, 1H), 4.84–4.95 (m, 1H). MS *m/z* (%): 154 (M^+, <1), 111 (36), 94 (57), 79 (55), 71 (21), 66 (100).

2-Adamantyl acetate (7c).[35] Column chromatography, oily product (146 mg, 75%). IR (neat) ν 1735, 1449, 1368, 1243, 1025, 985 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.50–1.61 (m, 2H), 1.70–1.90 (m, 8H), 1.94–2.06 (m, 4H), 2.07 (s, 3H), 4.86–4.94 (m, 1H). MS *m/z* (%): 194 (M^+, <1), 151 (<1), 134 (100), 105 (15), 92 (98), 79 (32).

Benzyl acetate (7d).[36] Column chromatography, oily product (119 mg, 79%). IR (neat) ν 1742, 1497, 1454, 1379, 1229, 1027, 746, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 3H), 5.09 (s, 2H), 7.26–7.37 (m, 5H). MS *m/z* (%): 150 (M^+, 35), 108 (100), 91 (59), 77 (15).

2,3,4,5,6-Pentafluorobenzyl acetate (7e).[37] Column chromatography, oily product (197 mg, 82%). IR (neat) ν 1753, 1657, 1509, 1225, 1134, 1058, 1033, 939 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 3H), 5.16 (s, 2H). MS *m/z* (%): 240 (M^+, 33), 197 (17), 181 (100). HRMS Calcd. for: $C_9H_5F_5O_2$ 240.0210; Found 240.0213.

Acetaldehyde bis(pentafluorobenzyl) acetal (8e). Compound **8e** was formed in the reaction of pentafluorobenzyl alcohol (**6e**, 198 mg, 1 mmol) with vinyl acetate (95 mg, 1.1 mmol) in the presence of 3 mol % I_2 in 30 minutes at 85 °C, following the procedure described above. Separation on column chromatography (SiO_2, petrol ether/*t*-butyl methyl ether) yielded pure oily product **8e** (91 mg, 43%). IR (neat) ν 1655, 1509, 1129, 1056, 939 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.43 (d, *J* = 5.4 Hz, 3H), 4.62 (td, *J* = 11 Hz, *J* = 1.7 Hz, 2xC*H*H, 2H), 4.73 (td, *J* = 11 Hz, *J* = 1.7 Hz, 2xCH*H*, 2H), 4.96 (q, *J* = 5.4 Hz, CH, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.6 (m), 141.4 (m), 137.5 (m), 111.1 (m), 99.9, 53.9, 19.0. HRMS Calcd. for: $C_{15}H_5F_{10}O_2$ 407.0142 (M^+–Me); Found 407.0130. Anal. Calcd. for $C_{16}H_8F_{10}O_2$ (422.22): C, 45.51; H, 1.91; Found: C, 45.57; H, 2.00.

5. Acknowledgement

We are grateful to Dr. B. Kralj and Dr. D. Žigon at the Mass Spectroscopy Centre at the 'Jožef Stefan' Institute in Ljubljana, to Prof. A. Petrič for using nmr instrument and to T. Stipanovič and Prof. B. Stanovnik for elemental combustion analysis.

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Povzetek

Pokazali smo, da je jod učinkovit katalizator za pretvorbo fenil-substituranih aldehidov v ustrezne 1,1-diacetate pod reakcijskimi pogoji brez topil (RPBT), ki so ustreznejši od klasičnih pogojev v raztopini. Ugotovili smo, da vrstni red dodajanja reaktantov igra ključno vlogo; substituenti, ne glede na elektronske lastnosti, na aromatskem obroču vplivajo na reaktivnost; pentafluorofenilna skupina močno zmanjša reaktivnost aldehida. Alkohole smo pretvorili v acetate; acetanhidrid je bil najučinkovitejši reagent, izopropenil acetat in vinil acetat sta bila manj reaktivna, vendar pentafluorofenilna skupina poveča reaktivnost s slednjima reagentoma. Poleg esterifikacije benzil in pentafluorobenzil alkohola smo opazili tudi nastanek acetalov.