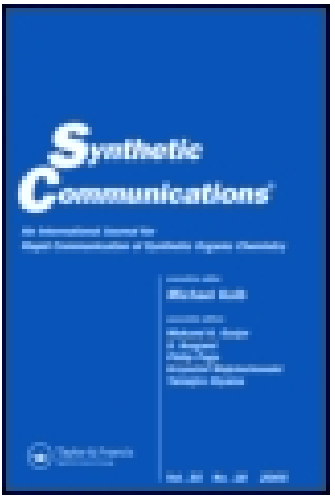

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Regioselective Cleavage of Tetrahydrofurans Bearing Proximate Functional Groups with Acid Iodides

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REGIOSELECTIVE CLEAVAGE OF TETRAHYDROFURANS BEARING PROXIMATE FUNCTIONAL GROUPS WITH ACID IODIDES

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ABSTRACT : Tetrahydrofurans functionalized at the C2 or C3 position (alcohols, esters, amine, ether, acetal) are cleaved with RCOCl/NaI (R = Me, tBu) in acetonitrile to give regioselectively trifunctionalized derivatives. In all cases the cleavage occurs mainly or exclusively at the C-O bond the most remote from the functional group.

INTRODUCTION

The cleavage of ethers is an important and versatile reaction in organic synthesis. The regiocontrolled ring-opening of substituted tetrahydrofurans is a potential route to small molecules with different functional groups.[1,2,3]

We have recently shown [4] that the regioselectivity of the ring-cleavage reaction of 2-methyltetrahydrofuran **1** with the RCOCl/$ZnCl_2$ or RCOCl/NaI depends on the nature of the acid halide and of the nucleophile (Cl^- or I^-). This

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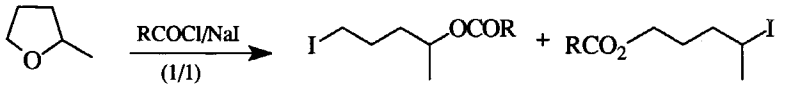
reaction gives specifically or predominantly the secondary chlorides with $RCOCl/ZnCl_2$. In the presence of sodium iodide, acetyl chloride (R = Me) gives a low regioselectivity (**a/b** ratio of primary vs. secondary iodides ≈ 38/62), while pivaloyl iodide (tBuCOCl/NaI) gives a very high regioselectivity (**a/b** ratio ≈ 98/2). In both cases, iodoesters **2** and **3** are formed in good yields (figure 1).

FIG. 1



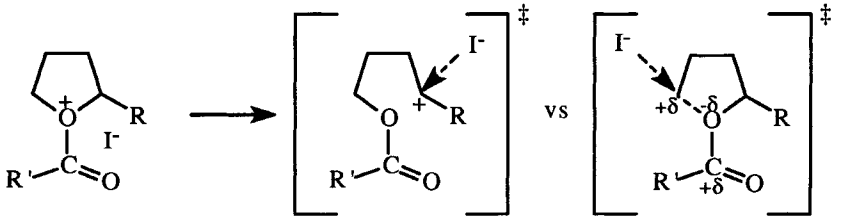
1

R = Me	**2a / 3a**	38 / 62 (85%)
R = tBu	**2b / 3b**	98 / 02 (95%)

Whereas functionalized oxiranes cleavage has been the object of extensive studies[5], there are relatively few references on the cleavage of functionalized tetrahydrofurans; they are generally limited to tetrahydrofurfurylic alcohol using various reagents (tBuCOCl/NaI [6], $Ac_2O/ZnCl_2$ [7], $MeCOBr/ZnCl_2$ [8], Me_3SiCl/NaI or $tBuMe_2SiCl/NaI$ [2,9], Me_2BBr[3], $AlCl_3/NaI$ [10]).

The ring opening reaction of tetrahydrofurans by means of an acid halide or others combinations of an electrophile and a nucleophile could arise *via* two different limiting mechanistic pathways.

FIG.2



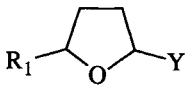
A **B** (S_N1 model) **C** (S_N2 model)

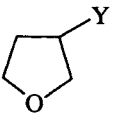
The two regiochemical modes of cleaving tetrahydrofurans can occur through either an electrophilic attack by the acid halide giving the more stable carbenium ion-like transition state **B** (figure 2) or nucleophilic attack by the halide ion on the presumed

intermediate **A**, giving the more stable transition state **C**. These mechanistic extremes closely resemble S_N1 and S_N2 models for aliphatic displacement. The possibility to form one or the other **B** or **C** transition states depends on the structure of the acid halide[4]. We think that the nature of the R group could also orient the reaction by stabilising or destabilising the carbenium ion in the transition state **B**.

In the present work, the regiocontrolled opening of unsymmetrical tetrahydrofuran derivatives bearing an electron-withdrawing functional group at C2 (and then at C3 position) has been investigated, using the substrates shown in figure 3. The reactions were performed in acetonitrile as solvent, with MeCOI or tBuCOI. These acid iodides are obtained *in situ* from the corresponding acid chlorides and sodium iodide.

FIG. 3





$R^1 = H$ Y = Me, CH_2OAc, CH_2OTHP, CH_2OMe, CH_2NH_2, $CH(OAc)_2$

Y = OH, OAc, Me, CH_2OH, CH_2OAc, $CH_2OCOtBu$

$R^1 = Me$ Y = CH_2OH, CH_2OAc

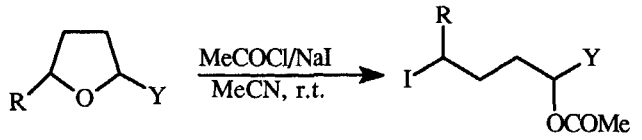
When free alcohols (or amine) are treated with RCOCl/NaI, an esterification (or amidification) takes place *in situ* preceding the ring opening reaction.

1. Cleavage of 2-substituted tetrahydrofurans

The 2-functionalized tetrahydrofurans represented in the figure 3 were treated by MeCOCl/NaI, in acetonitrile, at room temperature. The results are reported in table 1.

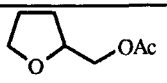
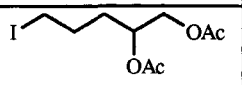
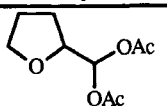
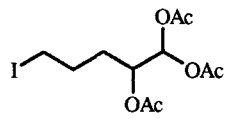
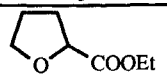
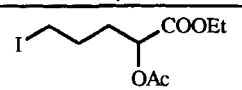
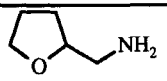
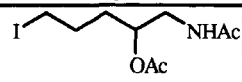
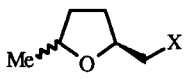
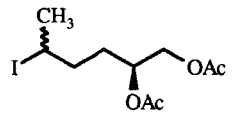
An excess of reagent is sometimes used to take into account the esterification or amidification reaction or to increase the rate of the ring opening

FIG. 4



R = H, Me

TABLE 1 : Regioselectivity in the cleavage of 2- and 2,5-substituted tetrahydrofurans

Run	Substrates	MeCOCl/NaI ratio [a]	Time (h.)	Products	Yields (%)
1	 **4**	1/1	24	 **5**	88
2	 **6**	3/3	24	 **7**	88
3	 **8**	2/2	24	 **9**	85
4	 **10**	2/2	24	 **11**	83
5	 X = OH **12**	2/2	72	 **13**	85
6	X = OAc **14**	1/1	72		82

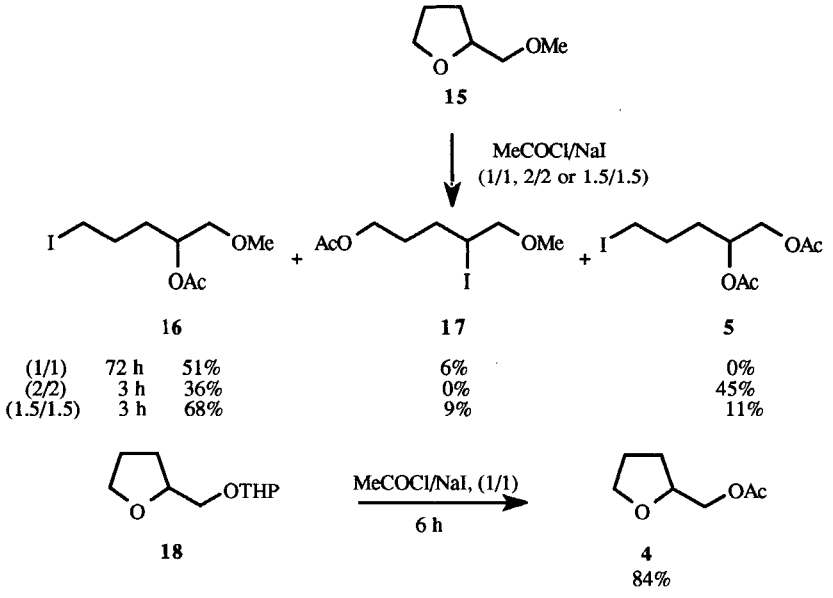
a) reagents molar ratio for one substrate equivalent

reaction with low reactive substrates (*i.e. gem*-diacetate **6** or ester **8**). As shown in the figure 4 and table 1, the ring opening is regioselective giving exclusively the primary iodide (runs 1-4, R=H). These results contrast with those of 2-methyltetrahydrofuran **1** which gave a poor regioselectivity with MeCOCl/NaI

(figure 1). These differences are probably due to an electronic effect. The donor group -CH_3 favours the cleavage of the adjacent C—O bond (transition state **B**, figure 2), while a withdrawing group, such as those containing oxygen or nitrogen atoms, tends to prevent the cleavage of this bond (transition state **C**, figure 2). This interpretation is confirmed by the result of the cleavage of the 2-hydroxymethyl-5-methyltetrahydrofuran **12** (mixture cis/trans) and its acetate **14** (runs 5 and 6, Table 1), leading to a mixture of two diastereoisomers of the 1,2-diacetoxy-5-iodohexane **13**. This compound comes from the cleavage of the C—O bond adjacent to the methyl group exclusively. In all cases, the different functionalities are preserved in these reaction conditions.

In order to demonstrate the chemoselectivity of the MeCOCl/NaI reagents, we studied the cleavage of tetrahydrofurfurylic alcohol protected as tetrahydropyranylether **18** and as methylether **15**. When **18** is treated with one equivalent of MeCOI, the expected ring opening product is not obtained; instead tetrahydrofurfurylic acetate **4** (figure 5) is obtained.

FIG . 5



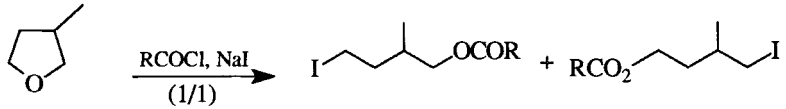
In the case of methoxytetrahydrofuran **15**, the most interesting results are obtained with 1.5 equivalent of reagents, giving mainly the primary iodide **16** with preservation of the methoxy group. With one equivalent, 34% of the starting material is present, while two equivalents give an important amount of iododiacetate **5** resulting from the cleavage of both the heterocycle and the methoxy group (figure 5).

In conclusion, it is possible to replace, in an one step reaction, an O-tetrapyranyl group by an acetoxy group without affecting the tetrahydrofuran ring. On the other hand, the methoxy group is more resistant to cleavage; the displacement of the methoxy group occurs only when an excess of reagent is employed.

2. Cleavage of 3-substituted tetrahydrofurans

Next, the cleavage reaction of several 3-substituted tetrahydrofurans with MeCOCl/NaI and tBuCOCl/NaI was investigated.

FIG. 6



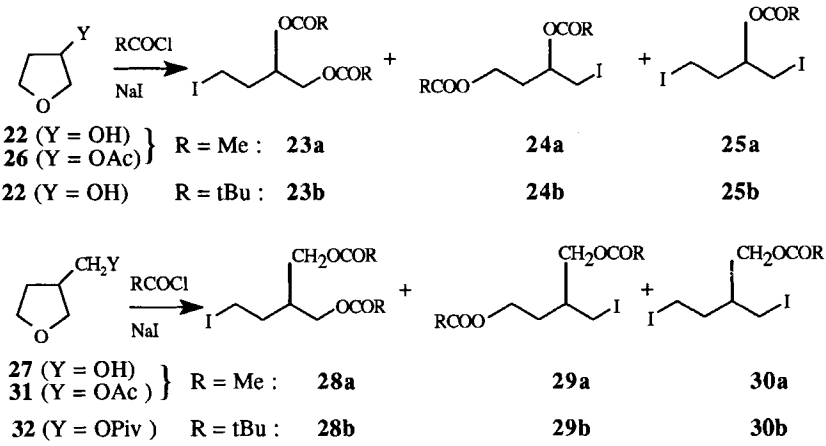
19

R = Me	**20a / 21a**	45 / 55 (81%)
R = tBu	**20b / 21b**	60 / 40 (90%)

A poor regioselectivity could be expected with this kind of substrate since the C2 and C5 carbons of the tetrahydrofuran are both unsubstituted. That was essentially what happened with 3-methyltetrahydrofuran **19** (figure 6). On the other hand, 3-hydroxytetrahydrofuran **22**, 3-hydroxymethyltetrahydrofuran **27** and their corresponding esters (**26, 31** and **32**) were opened with a good regioselectivity. With these substrates, two monoiododiester regioisomers are formed, along with a variable amount of diiodomonoester derivative (figure 7, table 2). When 3-

hydroxytetrahydrofuran **22** was treated with a stoechiometric amount of reagents for esterification and subsequent cleavage, the diiodo compounds **25a** and **25b** are obtained as major products (runs 7 and 9, table 2). If the diiodo compound **25a** is undesirable, the use of an excess of reagent is recommended (run 8). With the acetate **26** (runs 10 and 11) whatever the amount of reagent employed, almost no diiodo derivative is formed. In all cases, the cleavage occurs at the carbon the most remote from the functional group (C5 position). As for the 2-substituted tetrahydrofurans, the oxygen electron-withdrawing effect could be taken into account for this behaviour.

FIG 7



22 (Y = OH) } R = Me : **23a** **24a** **25a**
26 (Y = OAc) }

22 (Y = OH) R = tBu : **23b** **24b** **25b**

27 (Y = OH) } R = Me : **28a** **29a** **30a**
31 (Y = OAc) }

32 (Y = OPiv) R = tBu : **28b** **29b** **30b**

With regard to diiodide derivative formation, the nature (alcohol or ester) of the functional group seems a predominant factor. The difference of behaviour between the alcohol **22** and its acetate **26** could arise from the formation of iodhydric acid during the *in situ* esterification of the alcohol. The iodhydric acid can compete with the acid iodide and also seems to be more efficient than the latter for the C-O bond rupture of the iododiester intermediate **23**. Furthermore, this bond rupture can be favoured by an anchimeric assistance of a neighbouring

TABLE 2 : Regioselectivity of the cleavage of the 3-hydroxy- and 3-hydroxymethyl-tetrahydrofuran derivatives.

Run	Substrates	R (RCOCl/NaI)[a)]	Time h.	Products (yields %)[b)]		
7	**22**	Me (2/2)	24	**23a** (2)	**24a** (0)	**25a** (78)
8	**22**	Me (4/4)	24	**23a** (75)	**24a** (5)	**25a** (15)
9	**22**	tBu (2/2)	24	**23b** (9)	**24b** (< 5)	**25b** (68)
10	**26**	Me (1/1)	72	**23a** (61)	**24a** (7)	**25a** (6)
11	**26**	Me (2/2)	24	**23a** (78)	**24a** (5)	**25a** (6)
12	**27**	Me (2/2)	24	**28a** (72)	**29a** (15)	**30a** (13)
13	**31**	Me (1/1)	48	**28a** (74)	**29a** (20)	**30a** (0)
14	**32**	tBu (1/1)	48	**28b** (77)	**29b** (9)	**30b** (0)

a) molar reagent ratio for one substrate equivalent.

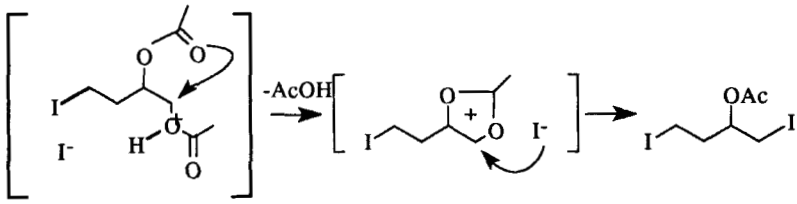
b) Yields are determined by GC and NMR.

acyloxy group as shown in figure 8. The subsequent attack of the resulting acyloxonium ion by an iodide ion gives the corresponding diiododerivative **25**.[9] The reason why the diiodide product **25a** is not observed when the alcohol **22** is treated with an excess of reagent (run 8) is probably due to the prevalence of acid iodide upon iodhydric acid in these reaction conditions.

A good regioselectivity is also observed with 3-hydroxymethyltetrahydrofuran **27**, and its derivatives **31** and **32.** As in the cases above, these three substrates are predominantly opened at the C5 position of the

heterocycle (runs 12, 13 and 14). Contrary to the alcohol **22**, the alcohol **27** gives, in the same conditions, a much lower amount of diiodide product (run 12). Probably, the anchimeric assistance is less effective when the two ester groups are in a 1,3 position.

FIG. 8



CONCLUSION

The regiocontrolled cleavage of 2- or 3-functionalized tetrahydrofurans with acid iodides provides a potential method for the synthesis of polyfunctional molecules. In all cases, a high regioselectivity is observed (cleavage at the C5 position of the tetrahydrofuran ring). Several functions are preserved in the used reaction conditions (*i.e.* CO_2Et, $CH(OAc)_2$, NHOAc and OMe). The use of these ring opening products towards the synthesis of natural products will be investigated.

EXPERIMENTAL

General

^1H NMR spectra were recorded at 200 MHz on Brucker AC 200 FT spectrophotometer. NMR samples were prepared in $CDCl_3$ containing 1% TMS as internal reference. ^{13}C NMR spectra were recorded at 50 MHz and assignments were made by polarisation transfer using a DEPT 135 sequence (NMR signals

reported in ppm). Mass spectra GC-MS (EI, 70 eV) are recorded as m/z (relative abundance).

Substrates **10**, **12**, **15**, **18**, **22** and **27** were purchased from Aldrich. The acetates **4**, **15**, **26**, **31** or pivalate **32** were prepared from alcohols and acid chlorides, by usual method. The *gem*-diacetate **6** and ethyl tetrahydrofuroate **8**[11] are obtained by hydrogenation of the corresponding furanic compounds.

Typical procedure :

To a solution of 2-hydroxymethyltetrahydrofuran **12** (1.16 g, 10 mmol), a mixture of diastereoisomers, with NaI (3 g, 20 mmol) in dry acetonitrile (10 mL) was added, dropwise, at 0°C, acetyl chloride (1.7 mL, 20 mmol). Then the reaction is stirred for 72 h at room temperature . The reaction mixture is hydrolysed with a saturated $NaHCO_3$ solution then extracted with Et_2O (3 x 20 mL). Organic layers are washed with brine, decolorized with an aqueous solution of $Na_2S_2O_3$ then dried over Na_2SO_4. The solvent was removed under vacuum. 1,2-diacetoxy-5-iodohexanes diastereoisomers **13** were obtained in 85% yield (2.79 g, 8.5 mmol)

The same procedure was applied to other substrates changing only the quantities of reagents and reaction times, as indicated in tables 1 and 2 and figure 5.

1,2-diacetoxy-5-iodopentane (5)

^{1}H NMR δ : 1.6-2.0 (m, 4H) ; 2.08 (s, 6H) ; 3.20 (t, 2H, J = 6.5) ; 4.05 (dd, 1H, J = 11.9 , J = 6.3) ; 4.23 (dd, 1H, J = 11.9, J = 3.5) ; 5.0-5.2 (m, 1H). ^{13}C NMR δ : 5.9 ; 20.7 ; 21.0 ; 28.9 ; 31.5 ; 64.7 ; 70.3 ; 170.4 ; 170.5. MS : m/z (%) : 314 (0.1, M^+) ; 241 (2) ; 187 (9) ; 145 (2) ; 117 (3) ; 99 (2) ; 71 (6) ; 55 (3) ; 44 (3) ; 43 (100) ; 41 (5) ; 29 (12).

5-iodo-1,1,2-triacetoxypentane (7)

^{1}H NMR : 1.6 - 1.9 (m, 4H); 2.01 (s, 6H); 2.09 (s, 3H); 3.19 (t, J = 6.0 , 2H);

5.0 - 5.1 (m, 1H); 6.88 (d, J = 3.9 , 1H). ^{13}C NMR : 5.5 ; 20.7 (2C) ; 20.8 ; 28.8 ; 29.4 ; 70.7 ; 87.7 ; 168.5 ; 168.6 ; 170.2.

*Ethyl 2-acetoxy-5-iodopentanoate (**9**)*

^{1}H NMR : 1.29 (t, J = 7.2 , 3H); 1.9 - 2.0 (m, 4H); 2.15 (s, 3H); 3.20 (t, J = 6.1 , 2H); 4.22 (q, J = 7.2 , 2H); 4.9 - 5.0 (m, 1H). ^{13}C NMR : 5.1 ; 14.2 ; 20.6 ; 29.0 ; 31.9 ; 61.5 ; 71.3 ; 169.7 ; 170.4. MS : m/z (%) : 314 (0.1, M^+) ; 187 (2) ; 127 (7) ; 85 (3) ; 67 (6) ; 44 (3) ; 43 (100) ; 41 (5) ; 39 (2) ; 29 (2).

*2-acetoxy-1-(N-acetoxy) amino-5-iodopentane (**11**)*

^{1}H NMR δ : 1.6 - 1.8 (m, 2H) ; 1.8 - 1.9 (m, 2H) ; 1.99 (s, 3H) ; 2.09 (s, 3H) ; 3.18 (t, 2H, J = 6.7) ; 3.3-3.5 (m, 2H) ; 4.94 (tdd, 1H, J = 6.4, J = 6.3 , J = 4.0) ; 5.96 (bs, 1H). ^{13}C NMR δ : 6.3 ; 21.2 ; 23.0 ; 29.0 ; 32.5 ; 42.2 ; 71.8 ; 170.9 ; 171.1. MS : m/z (%) : 313 (0.1, M^+) ; 253 (28) ; 212 (2) ; 127 (3) ; 126 (7) ; 115 (3) ; 84 (2) ; 74 (2) ; 73 (35) ; 72 (12) ; 67 (4) ; 60 (7) ; 57 (3) ; 56 (9) ; 55 (3) ; 45 (5) ; 44 (4) ; 43 (100) ; 42 (5) ; 41 (8) ; 39 (4) ; 31 (5) ; 30 (67) ; 29 (4).

*1,2-diacetoxy-5-iodohexane (**13**)* Diastereoisomeric mixture :

^{1}H NMR δ : 1.6 - 1.9 (m, 4H); 1.93 (d, J = 6.9 , 3H); 2.07 (s, 3H); 2.08 (s, 3H); 3.9 - 4.3 (m, 3H); 5.0 - 5.2 (m, 1H). ^{13}C NMR δ : 20.7 (2C) ; 20.9 ; 21.0 ; 28.8 (2C) ; 28.9 (2C) ; 31.0 ; 31.1 ; 38.0 ; 38.3 ; 64.7 ; 64.9 ; 70.4 ; 70.8 ; 170.4 ; 170.5 ; 170.6 (2C). MS : m/z (%) : 201 (4, M^+-127) ; 159 (3) ; 142 (2) ; 141 (17) ; 99 (3) ; 85 (2) ; 81 (18) ; 79 (2) ; 57 (3) ; 55 (5) ; 44 (3) ; 43 (100) ; 41 (6) ; 39 (2) ; 29 (5).

*2-acetoxy-5-iodo-1-methoxypentane (**16**)*

^{1}H NMR δ : 1.7 - 2.0 (m, 4H) ; 2.09 (s, 3H) ; 3.19 (t, 2H, J = 6.6) ; 3.37 (s, 3H) ; 3.44 (d, 1H, J = 4.4) ; 3.45 (d, 1H, J = 5.2) ; 5.03 (tdd, 1H, J = 6.3, J = 5.2, J = 4.4). ^{13}C NMR δ : 6.1 ; 21.1 ; 29.2 ; 31.7 ; 59.0 ; 71.3 ; 73.5 ; 170.4. MS : m/z

(%) : 286 (1, M^+) ; 241 (2) ; 226 (8) ; 159 (5) ; 127 (2) ; 117 (4) ; 99 (9) ; 85 (8) ; 71 (12) ; 67 (9) ; 58 (4) ; 45 (34) ; 44 (3) ; 43 (100) ; 41 (11) ; 39 (5) ; 29 (4).

*5-acetoxy-2-iodo-1-methoxypentane (**17**)*

^{1}H NMR δ : 1.7 - 2.0 (m, 4H) ; 2.09 (s, 3H) ; 3.37 (s, 3H); 3.6-4.2 (m, 5H). ^{13}C NMR δ : 20.9 ; 28.5 ; 32.6 ; 32.9; 58.5 ; 63.8; 77;9; 170.7. MS : m/z (%) : 281 (2) ; 159 (7, M^+ -127) ; 127 (11) ; 117 (11) ; 99 (12) ; 97 (2) ; 86 (4); 85 (65); 73 (3); 71 (26) ; 69 (5) ; 68 (5); 67 (38); 65 (2); 58 (4) ; 57 (4); 55 (9); 54 (2); 53 (4); 46 (2); 45 (69) ; 43 (100) ; 41 (30) ; 40 (2); 39 (9) ; 31 (2); 29 (12).

*1,2-diacetoxy-4-iodobutane (**23a**)*

^{1}H NMR δ : 2.08 (s, 3H) ; 2.09 (s, 3H) ; 2.1 - 2.3 (m, 2H) ; 3.16 (t, 2H, J = 7.6) ; 3.96 (dd, 1H, J = 12.0 , J = 5.5) ; 4.37 (dd, 1H, J = 12.0 , J = 3.8) ; 5.0 - 5.1 (m, 1H). ^{13}C NMR δ : -0.8 ; 20.7 ; 20.9; 34.9 ; 64.2 ; 71.6 ; 171.1 ; 171.4 . MS: m/z (%) : 300 (0.1, M^+) ; 173 (7) ; 113 (2) ; 71 (5) ; 44 (2) ; 43 (100) ; 41 (2) ; 39 (2) ; 29 (2).

*2,4-diacetoxy-1-iodobutane (**24a**)*

^{1}H NMR δ : 2.04 (s, 3H) ; 2.09 (s, 3H) ; 2.1-2.2 (m, 2H) ; 3.2- 3.4 (m, 2H) ; 4.10 (t, 2H, J = 6.2) ; 4.4-4.5 (m, 1H). ^{13}C NMR δ : 7.8 ; 20.9 ; 21.0 ; 34.9 ; 60.2 ; 69.3 ; 171.0 ; 171.7. MS : m/z : 300 (0.1, M^+) ; 180 (7) ; 173 (7) ; 113 (2) ; 71 (8) ; 61 (2) ; 54 (3) ; 53 (3) ; 44 (3) ; 43 (100) ; 42 (4) ; 41 (6) ; 39 (3) ; 29 (2).

*2-acetoxy-1,4-diiodobutane (**25a**)*

^{1}H NMR δ : 2.11 (s, 3H) ; 2.2 - 2.3 (m, 2H) ; 3.0-3.2 (m, 2H) ; 3.29 (dd, 1H, J = 10.8 , J = 4.5) ; 3.39 (dd, 1H, J = 10.8 , J = 5.4) ; 4.75 (tdd, 1H, J = 5.4 , J = 7.5 , J = 4.5). ^{13}C NMR δ : -0.8 ; 7.0 ; 21.1 ; 38.0 ; 72.2 ; 170.1.

*4-iodo-1,2-bis (trimethylacetoxy) butane (**23b**)*

^{1}H NMR δ : 1.20 (s, 9H) ; 1.21 (s, 9H) ; 2.0 - 2.4 (m, 2H) ; 3.15 (t, 2H , J = 7.0)

; 4.04 (dd, 1H, J = 10.9 , J = 5.5) ; 4.29 (dd, 1H, J = 10.9 , J = 3.6) ; 5.0 - 5.2 (m, 1H). ^{13}C NMR d : 27.0 (3C) ; 27.1 (3C) ; 35.1 ; 38.7 ; 38.8 ; 60.0 ; 64.1 ; 71.5 ; 177.9 ; 178.2.

*1,4-diiodo-2-trimethylacetoxybutane (**25b**)*

^1H NMR δ : 1.24 (s, 9H) ; 2.0 - 2.4 (m, 2H) ; 3.1 -3.2 (m, 2H) ; 3.27 (dd, 1H, J = 10.8, J = 4.2) ; 3.43 (dd, 1H, J = 10.8 , J = 5.0) ; 4.69 (tdd, 1H, J = 4.2 , J = 8.3 , J = 5.0). ^{13}C NMR δ : -0.8 ; 7.3 ; 27.2 (3C) ; 38.1 ; 38.94 ; 71.5 ; 177.4;

*1-acetoxy-2-acetoxymethyl-4-iodobutane (**28a**)*

^1H NMR δ : 1.95 (td, J = 7.2 et J = 7.1 , 2H); 2.06 (s, 6H); 2.1-2.3 (m, 1H); 3.24 (t, J = 7.2 , 2H); 4.07 (d, J = 5.5, 4H). ^{13}C NMR δ : 3.1 ; 20.8 (2C) ; 32.2 ; 38.1 ; 63.2 (2C) ; 170.7 (2C). MS : m/z (%) : 314 (0.1, M^+) ; 187 (11) ; 145 (11) ; 127 (8) ; 85 (9) ; 67 (9) ; 61 (2) ; 57 (2) ; 55 (10) ; 54 (2) ; 44 (3) ; 43 (100) ; 41 (5) ; 39 (3) ; 29 (4).

*4-acetoxy-2-acetoxymethyl-1-iodobutane (**29a**)*

^1H NMR δ : 1.7-1.8 (m, 3H) ; 2.07 (s, 6H) ; 3.32 (dd, J = 4.4, J = 5.5 , 2H) ; 3.9-4.2 (m, 4H). ^{13}C NMR δ : 10.0 ; 20.9 (2C) ; 30.4 ; 35.7 ; 61.4 ; 66.3 ; 170.5 (2C). MS : m/z (%) : 314 (0.1, M^+) ; 187 (12) ; 145 (10) ; 127 (5) ; 85 (13) ; 67 (10) ; 57 (2) ; 55 (7) ; 54 (2) ; 44 (2) ; 43 (100) ; 41 (5) ; 39 (4) ; 29 (4).

*1-acetoxy-4-iodo-2-iodomethylbutane (**30a**)*

^1H NMR δ : 1.7-1.9 (m, 3H) ; 2.08 (s, 3H) ; 3.2-3.4 (m, 4H) ; 3.9-4.1 (m, 2H). ^{13}C NMR δ : 2.8 ; 9 2 ; 20.8 ; 34.9 ; 38.9 ; 65.6 ; 170.3.

*4-iodo-1-trimethylacetoxy-2-trimethylacetoxymethylbutane (**28b**)*

^1H NMR δ : 1.21 (s, 18H) ; 1.94 (td, J = 7.0, J = 6.9 , 2H) ; 2.1 - 2.3 (m, 1H) ; 3.26 (t, J = 7.1 , 2H) ; 4.07 (d, J = 5.3 , 2H) ; 4.09 (d, J = 5.8 , 2H). ^{13}C NMR

δ : 2.9 ; 27.1 (6C) ; 32.4 ; 38.2 ; 38.8 (2C) ; 63.0 (2C) ; 178.1 (2C). MS : m/z (%) : 297 (2) ; 296 (2) ; 271 (13, M^+-127) ; 169 (7) ; 103 (2) ; 85 (16) ; 70 (2) ; 69 (6) ; 68 (2) ; 67 (7) ; 58 (5) ; 57 (100) ; 55 (6) ; 42 (3) ; 41 (24) ; 39 (4) ; 29 (18).

*2-iodomethyl-1,4-trimethylacetoxybutane (**29b**)*

^{1}H NMR δ : 1.24 (s, 18H) ; 1.7–1.8 (m, 2H) ; 1.9–2.1 (m, 1H) ; 3.32 (t, 2H, J = 6.8) ; 3.7-3.9 (m, 4H). ^{13}C NMR δ : 9.6 ; 27.0 (6C) ; 30.4 ; 36.0 ; 38.8 (2C) ; 61.5 ; 66.3 ; 178.0 (2C). MS : m/z (%) : 297 (2) ; 296 (2) ; 271 (29, M^+-127) ; 195 (2) ; 187 (2) ; 169 (5) ; 103 (2) ; 85 (12) ; 69 (4) ; 68 (3) ; 67 (13) ; 58 (4) ; 57 (100) ; 55 (5) ; 42 (2) ; 41 (16) ; 39 (3) ; 29 (11).

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