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A convenient and practical method for the selective benzoylation of primary hydroxyl groups using microwave heating

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Abstract—A convenient method for the selective protection of primary hydroxyl groups in 1,*n* diols is described. The use of microwave heating is shown to be advantageous. © 2001 Elsevier Science Ltd. All rights reserved.

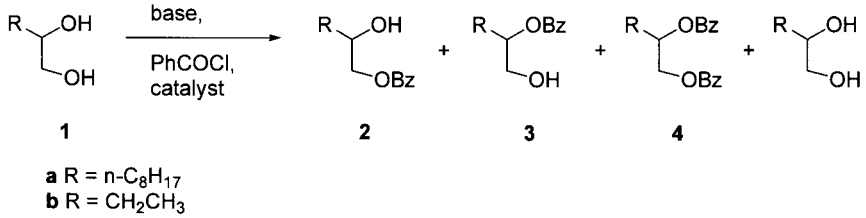
1. Introduction

The selective protection of hydroxyl groups is a valuable technique in organic synthesis.[1,2] The benzoyl moiety (Bz) is frequently employed as a protecting group owing to its stability to hydrolysis, and selective benzoylation of polyols has been described by many groups. Reagents such as *N*-benzyl-2-(6-methyl)pyridinecarbamoyl chloride,[3] 3-benzoylthiazolidine-2-thione,[4] and 1-(benzoyloxy)benzotriazole[5] have been designed specifically for this purpose, however these can be expensive or awkward to prepare, and selectivity is not always excellent. An alternative approach has seen tin oxides and ethers used to preform stannylene complexes from 1,2 or 1,3-diols.[6] The nucleophilicity of one of the oxygen atoms is enhanced, leading to regioselective protection. The method has been widely used, especially in carbohydrate chemistry,[7] but there are still several drawbacks: tin compounds are extremely toxic, the stannylene intermediate has to be preformed, and again selectivity is not always exceptional. In an interesting development, it was reported that by using microwave conditions benzoylation could be effected using substoichiometric quantities of the dibutyltin oxide.[8] Notably, it appeared that a rare example of a 'microwave-specific reaction' had been uncovered.[9] Although the amount of tin was reduced, it was not completely eliminated, and the reactions were not always completely regioselective.

We wish to report that primary hydroxyl groups can be protected with complete selectivity in the presence of secondary hydroxyl groups using inexpensive reagents in a one-pot reaction. The use of microwave irradiation enables precise heating time and thus better control, facilitating the interception of a reaction at an intermediate point.

2. Results and discussion

The starting point for our investigations was the aforementioned literature report of benzoylation under microwave conditions.[8] We were intrigued by the possibility that the regioselective stannane-mediated monoprotection of diols could be selectively accelerated in the microwave oven, and set about investigating the reaction further using 1,2-decanediol (Scheme 1). The microwave oven employed was a commercially available machine that had been



Scheme 1.

Keywords: acylation; diols; microwave heating; protecting groups.

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Table 1. Protection of 1,2-decanediol **1a** with 1 equiv. of PhCOCl

Entry	Catalyst	Base	Reaction time (min)[a]	Solvent	Yields[b]			
					2a	**3a**	**4a**	S.M.
1	Bu_2SnO	Et_3N	9×1	Toluene	77	16	0	7
2	None	Et_3N	9×1	Toluene	29	0	0	71
3	None	Et_3N	5×5	Toluene	24	0	0	76
4	None	Et_3N	1×40	Toluene	32	1	0	67
5	Bu_2SnO	Collidine	9×1	Toluene	77[c]	0	0	23
6	Bu_2SnO	K_2CO_3	9×1	Toluene	14	4	0	82
7	Bu_2SnO	Et_3N	1×9	Toluene	69	15	0	16

[a] 9×1 min denotes that the reaction mixture was irradiated 9 times for 1 min each time, punctuated by 30 s intervals.
[b] Yields refer to NMR yields.
[c] Yield increased to 92% by use of a 10% excess of collidine and benzoyl chloride.

adapted to allow a reflux condenser to be fitted, which enabled prolonged irradiation periods. Crude yields and ratios were determined by ^{1}H NMR spectroscopic analysis, by comparison of integration of the peaks due to the H_nCO protons occurring between 3.5 and 5.8 ppm.

The results obtained in the presence or absence of dibutyltin oxide as a catalyst were generally in accord with the literature, although we only observed mono-benzoylated product in the absence of a tin catalyst (entry 2). Prolonged microwave heating gave only marginal advantage in terms of product yields. We examined the use of 2,4,6-collidine as base (entry 5), which has been used for the selective acetylation of diols,[10] which led to high selectivity in the tin-catalysed procedure, but use of potassium carbonate as a heterogeneous base (entry 6)[11] gave poor results. It was also established that the discontinuous sequences of radiation were not necessary (entry 7, cf. entry 1).

We were intrigued by the apparent selectivity of the microwave-mediated reactions using 1 equiv. of triethylamine and benzoyl chloride (Table 1, entry 2), and undertook to utilise this in a synthetically useful transformation. The results of these further studies are presented in Table 2. Increasing the conversion was a priority but as previously noted, extended microwave irradiation did not lead to improved yield. However improved conversion could be achieved simply by increasing the concentration of the triethylamine and benzoyl chloride by a factor of five (entry 3) and surprisingly, there was little bis-benzoylation, leading to **4a**. Thus the procedure could be optimised by using a reaction time of 7 min leading to quantitative yield of desired product (entry 5).

The heating conditions provided by microwave ovens differ greatly from those provided by conventional heating sources. One consequence is that heating is almost instantaneous in the microwave oven, allowing a more accurate measure of heating time. This phenomenon was simulated using conventional conditions by immersing the reaction mixture in an oil bath preheated to 140°C, and timing from the moment the internal temperature reached 109°C (method B). The technique led to almost identical results (entry 6) as those obtained using microwave irradiation. The slight discrepancy occurs because of the inertia present in heat transfer from the oil bath to the reaction mixture; heating is not instant, and heating time is therefore slightly longer than indicated. Once the reactions were removed from the heat source they were allowed to cool slowly to room temperature after both microwave and oil bath heating. It is worth noting that it was not necessary to perform the reaction under nitrogen to obtain the excellent yields shown.

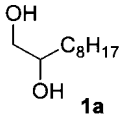
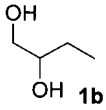
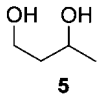
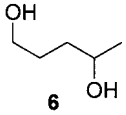
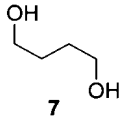
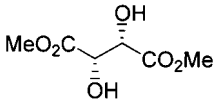
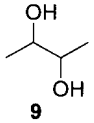
In control experiments, using only 1 equiv. of reagents under conventional conditions, selectivity was shown to be poor, and extended reaction times were required (entry 7). Extended exposure to microwave conditions using an

Table 2. Optimising the benzoylation of 1,2-decanediol

Entry	Method[a]	Solvent	Time (min)	NEt_3, PhCOCl (equiv.)	Yields[b]			
					2a	**3a**	**4a**	S.M.
1	A	Toluene	9	1	29	0	0	71
2	A	Toluene	9	3	76	<1	0	23
3	A	Toluene	9	5	95	0	5	0
4	A	Toluene	5	5	80	0	0	20
5	A	Toluene	7	5	>99 (90)	0	0	0
6	B	Toluene	7	5	94 (87)	0	6	0
7	B	Toluene	8220	1.1	61	17	13	9
8	A	Toluene	240	5	65	0	35	0
9	C	Toluene	60	5	95	0	5	0
10	A	MeCN[c]	0.5	5	>99	0	0	0
11	B	MeCN	0.5	5	>99	0	0	0

[a] Conditions A: microwaved continuously at full power for time indicated. B: mixture lowered into oilbath at 140°C (110°C with acetonitrile as solvent). Timing started from moment reaction temperature reached 109°C. C: mixture heated from rt.
[b] Yields refer to NMR yields. Figures in parentheses refer to isolated yields.
[c] Acetonitrile (MeCN) was lost rapidly on microwave irradiation.

Table 3. Protection and isolation of diols

Entry	Diol	Method	Time (min)	NEt_3, PhCOCl (equiv.)	Yields[a]			
					Primary benzoate	Secondary benzoate	Bisbenzoate	S.M.
1	 **1a**	A	7	5	>99 (90)	0	0	0
2		B	7	5	94 (87)	0	6	0
3	 **1b**	A	7	5	>99 (90)	0	0	0
4		B	7	5	94 (82)	0	6	0
5	 **5**	A	7	5	>99 (84)	0	0	0
6		B	7	5	91(90)	0	9	0
7	 **6**	A	7	5	>99 (88)	0	0	0
8		B	7	5	95 (82)	0	5	0
9	 **7**	A	9	5	0	–	>99 (96)	0
10	 **8**	A	9	5	–	0	100	0
11	 **9**	A	9	5	–	<20		

Conditions A: microwaved continuously at full power for time indicated. B: mixture lowered into oil bath at ~140°C. Timing started from the moment reaction temperature reached 109°C.

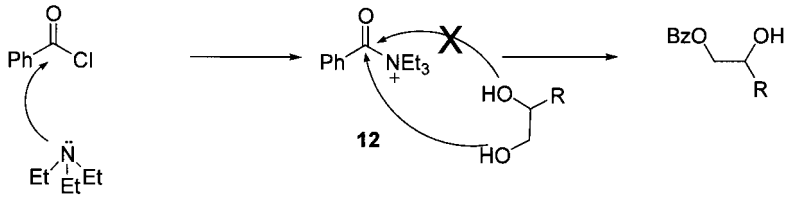
[a] Yields refer to NMR yields. Figures in parentheses refer to isolated yields.

excess of reagents led to significant formation of 1,2-bis(benzoyloxy)decane **4a** (entry 8), indicating that microwave irradiation does not inhibit this reaction. Stuerga and co-workers have demonstrated that improved selectivity in the sulfonation of naphthalene can be induced under microwave conditions owing to the heating rate in the microwave oven.[12] In the present study however, we were able to show that the observed selectivity is not a result of the rate of heating. When we allowed the reaction mixture to warm slowly from room temperature to reflux under conventional heating conditions we obtained similar results (cf. entries 3, 6 and 9).

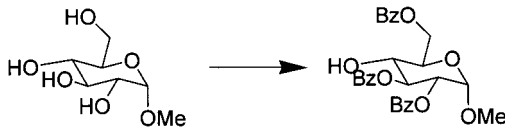
The reaction was also performed in acetonitrile (entries 10 and 11). Even with the adapted apparatus, cooling was not efficient enough to prevent immediate rapid solvent loss, a serious disadvantage. However, good crude yields were observed after only 30 s of irradiation. A second disadvantage was noted using this solvent; unlike in toluene, the triethylamine hydrochloride by-product is soluble and cannot simply be removed by filtration.

Our investigations were extended to determine the scope of this reaction. The results, summarised in Table 3 indicate that very good selectivity can be achieved in simple diols containing a primary and a secondary hydroxyl group (entries 1–8). Crude yields were again determined from NMR spectroscopic integration[13–17] and isolated yields of over 85% were obtained in most cases. The reactions performed using the microwave oven (entries 1, 3, 5 and 7) gave generally higher yields than oil bath heating reflecting the inherent inefficiency of heating under conventional conditions. Not unexpectedly, both of the primary hydroxyl groups of 1,4-butanediol were benzoylated (entry 9). However under the optimised conditions only bis-benzoylation was observed from reaction of dimethyl tartrate, whereas 2,3-butanediol was almost unreactive.

Attempts to selectively protect methyl α-D-glucopyranoside **10**, were unsuccessful due to its insolubility in toluene. It is also only very sparingly soluble in acetonitrile, and this does not facilitate the selective protection, especially if the product is more soluble. The ^1H NMR spectrum of the product mixture was complex, but was consistent with tris-protected methyl 2,3,6-tribenzoyl α-D-glucopyranoside **11** as the main product.[7a]



Scheme 2.



The use of microwave ovens to perform organic transformations has aroused increasing interest since early reports describing the significant rate enhancements that are possible.[18] The use of microwaves often results in a reduction in reaction time and gives cleaner reactions than those performed under standard conditions. Our results show that microwave ovens can be also used to precisely control heating time, to beneficial effect.

3. Mechanism

Given the myriad procedures reported for the selective monoprotection of primary alcohols it is surprising that this simple selective mono-protection protocol has not previously been described as a general procedure. Recently, Paquette noted that protection of an isotaxane tetraol was completely selective at room temperature when performed using 20 equiv. of benzoic anhydride in pyridine; only when DMAP was added were secondary and tertiary hydroxyl groups acylated.[19] However, this selectivity was not further investigated. Sharpless noted a concentration dependence during the protection of phenylethylene glycol using *p*-toluenesulfonyl chloride,[20] and also observed that the regioselectivity could be enhanced by using more sterically encumbered arenesulfonyl chlorides.[20]

We considered the different results obtained under conventional conditions using 1 and 5 equiv. of reagents (Table 2, entries 6 and 7) could only be accounted for if different mechanisms were in operation for the protection of the primary and secondary hydroxyl group. Under the conditions employed, reaction of triethylamine with benzoyl chloride could be accelerated potentially leading to the formation of a more sterically hindered acylammonium electrophile **12** which would undergo reaction selectively with the primary hydroxyl group of the diol (Scheme 2). We considered that any other benzoylation product, such as **3** (Table 2, entry 7), was formed by the direct reaction of the secondary hydroxyl group with benzoyl chloride. That this suggestion was viable was confirmed by performing the protection of 1,2-decanediol in the absence of triethylamine using 5 equiv. of benzoyl chloride.[†] The product ratio (**2**–**3**–**4**–**1**=2:1:4:0.2) showed that reaction of the secondary hydroxyl group was more favourable in the absence of triethylamine. An alternative rationale, in which R_3N acts as a Brønsted base, has been proposed by Yamamoto and co-workers to explain selectivity differences for related transformations using a variety of bases.[21]

The excellent selectivity observed compares well with that observed using tin-containing compounds, in which selectivity is compromised by post-acylation equilibrium in simple diols.[22]

4. Conclusions

In summary, we have shown that the benzoylation of 1,*n* diols can be achieved with high regioselectivity at the primary hydroxyl group by use of a fivefold excess of benzoyl chloride and triethylamine both of which are inexpensive, commercially available reagents. Careful control of heating time prevents undesired further reaction, and this is most readily achieved using microwave irradiation. The stoichiometry and mode of heating appears to have an important effect on the regiochemical outcome of the reaction.

5. Experimental

Microwave irradiation was carried out in a domestic oven (Sharp, 2450 MHz, 800 W), operated at full power that had been modified to incorporate a condenser. The diols, methyl α-D-glucopyranoside and benzoyl chloride were available commercially (from Aldrich or Lancaster) and were used as received. For all other general experimental procedures see previous work.[23]

5.1. Typical procedure for the dibutyltin oxide catalysed selective protection of diols under microwave conditions

To a mixture of 1,2-decanediol (0.174 g, 1.0 mmol) and triethylamine (0.101 g, 1.0 mmol) in toluene (30 mL) was added dibutyltin oxide (0.05 g, 0.25 mmol) and benzoyl chloride (0.141 g, 5.0 mmol). The flask was attached to a reflux condenser in an adapted microwave oven, and subjected to microwave irradiation (800 W) for 1 min. The mixture was allowed to stand for 30 s, and then subjected to a further minute of irradiation. The process was repeated until the total irradiation period was 9 min, then the mixture was allowed to cool, then filtered and concentrated at reduced pressure. Column chromatography (petroleum ether–ethyl acetate) yielded 1-benzoyloxy-2-hydroxydecane **2a** (0.214 g, 77%) as white crystals, and

[†] The reaction mixture was refluxed for 4 h, and analysed in the normal way.

2-benzoyloxy-1-hydroxydecane **3a** (0.44 g; 16%) as a colourless oil.

5.1.1. 1-Benzoyloxy-2-hydroxydecane. R_f=0.53 (4:1 petroleum ether–ethyl acetate). mp 39–40°C. ν_{max} (Nujol) 3507 (O–H), 1697 cm^{-1} (C=O). δ_H 0.88 (3H, m, CH_3), 1.0–1.5 (12H, m), 2.15 (1H, s, OH), 3.86–4.04 (1H, m, CH), 4.23 (1H, dd, J_1=7.2 Hz, J_2=11.5 Hz, O*H*CH), 4.40 (1H, dd, J_1=7.2 Hz, J_2=11.5 Hz, O*H*CH), 7.40–7.60 (3H, m, ArH), 8.02–8.10 (2H, m, ArH). δ_C 13.8, 22.4, 25.1, 29.0, 29.2, 29.3, 31.6, 33.2, 69.0 (all CH_2), 69.8 (CH), 128.1, 129.4, 129.6, 132.9, 166.5. (Found MH^+ 279.1881. $C_{17}H_{26}O_3$+H requires 279.1960.)

5.1.2. 2-Benzoyloxy-1-hydroxydecane. R_f=0.45 (4:1 petroleum ether–ethyl acetate). ν_{max} (film) 3433 (O–H), 1719 cm^{-1} (C=O). δ_H 0.88 (3H, t, J=6.7 Hz, CH_3), 1.1–1.5 (12H, m), 1.64–1.80 (2H, m, CH_2), 2.10 (1H, t, J=6.3 Hz, OH), 3.72–3.88 (2H, m, OCH_2), 5.12–5.22 (1H, m, CH), 7.42–7.62 (3H, m, ArH), 8.02–8.10 (2H, m, ArH). δ_C 13.8, 22.3, 25.1, 28.9, 29.1, 29.2, 30.4, 31.5, 64.8, 128.1, 129.4, 129.9, 132.8, 166.7. (Found MH^+ 279.1927. $C_{17}H_{26}O_3$+H requires 279.1960.)

5.2. Typical procedure for the selective protection of diols under microwave conditions

To a mixture of 1,2-decanediol (0.174 g, 1.0 mmol) and triethylamine (0.505 g, 5.0 mmol) in toluene (30 mL) was added benzoyl chloride (0.705 g, 5.0 mmol). The flask was attached to a reflux condenser in an adapted microwave oven, and subjected to microwave irradiation (800 W) for 7 min. The mixture was allowed to cool, then filtered and concentrated under reduced pressure with a minimum of heating (<40°C).[‡] Following ^{1}H NMR spectroscopic analysis, the crude mixture was washed rapidly through a short silica plug with copious petroleum ether, and the product removed from the column using ethyl acetate. A further column chromatography (petroleum ether–ethyl acetate) yielded pure 1-benzoyloxy-2-hydroxydecane (0.250 g, 90%) as white crystals.

5.3. Typical procedure for the selective protection of diols under reflux conditions

To a mixture of 1,2-butanediol (0.090 g, 1.0 mmol) and triethylamine (0.505 g, 5.0 mmol) in toluene (30 mL) was added benzoyl chloride (0.705 g; 5.0 mmol). The flask was lowered into a hot oil bath at 140°C. When the internal temperature reached 109°C, the mixture was refluxed for a further 7 min, then removed from the heat and allowed to cool. Purification was performed as above to give pure 1-benzoyloxy-2-hydroxybutane[15] **2b** (0.146 g; 82%) as a colourless oil. R_f 0.33 (4:1 petroleum ether–ethyl acetate). ν_{max} (film) 3442 (O–H), 1720 cm^{-1} (C=O). δ_H 1.04 (3H, t, J=7.4 Hz, CH_3), 1.55–1.70 (2H, m, CH_2), 2.30 (1H, bs, OH), 3.88–3.97 (1H, m), 4.22–4.28 (1H, m), 4.38–4.44 (1H, m), 7.42–7.49 (2H, m, ArH), 7.55–7.64 (1H, m, ArH), 8.03–8.08 (2H, m, ArH).

[‡] Alternatively, the crude mixture in toluene could be passed directly through a silica plug and washed with petroleum ether, then ethyl acetate. Yields were unchanged.

5.3.1. 1,2-Bis(benzoyloxy)decane 4a. Purified by column chromatography to give a colourless oil, R_f=0.74 (4:1 petroleum ether–ethyl acetate) ν_{max} (film) 1725 cm^{-1} (C=O). δ_H 0.87 (3H, t, J=6.3 Hz, CH_3), 1.00–1.55 (12H, m), 1.76–1.87 (2H, m, CH_2), 4.43–4.59 (2H, m, OCH_2), 5.48–5.53 (1H, m, OCH), 7.40–7.60 (6H, m, ArH), 8.00–8.10 (4H, m, ArH). δ_C 14.2, 22.7, 25.2, 29.2, 29.4, 29.5, 31.0, 31.8, 65.8, 72.3, 128.4, 129.7, 129.9, 130.3, 133.1, 133.1, 166.2, 166.4. (Found MH^+ 383.2226. $C_{24}H_{30}O_4$+H requires 383.2226.)

5.3.2. 1-Benzoyloxy-3-hydroxybutane.[16] Purified by column chromatography to give a colourless oil, R_f=0.25 (4:1 petroleum ether–ethyl acetate). ν_{max} (film) 3417 (O–H), 1719 cm^{-1} (C=O). δ_H 1.20 (3H, J=6.2 Hz, CH_3), 1.70–1.94 (2H, m, CCH_2C), 2.10 (1H, bs, OH), 3.86–3.96 (1H, m), 4.26–4.36 (1H, m), 4.50–4.59 (1H, m), 7.34–7.51 (2H, m, ArH), 7.46–7.53 (1H, m), 7.94–8.00 (2H, m, ArH).

5.3.3. 1-Benzoyloxy-4-hydroxypentane.[16] Purified by column chromatography to give a colourless oil, R_f=0.21 (4:1 petroleum ether–ethyl acetate). ν_{max} (film) 3418 (O–H), 1718 cm^{-1} (C=O). δ_H 1.24 (3H, d, J=6.2 Hz, CH_3), 1.57–1.65 (2H, m, CH_2CH(OH)), 1.78–1.98 (2H, m, CH_2), 2.10 (1H, bs, OH), 3.85–3.95 (1H, m, C*H*OH), 4.36 (2H, t, J=6.6 Hz, CH_2OCO), 7.38–7.47 (2H, m, ArH), 7.54–7.60 (1H, m, ArH), 8.03–8.06 (2H, m, ArH).

5.3.4. 1,4-Bis(benzoyloxy)butane.[13] Purified by column chromatography (on neutral alumina) to give white crystals, R_f=0.58 (4:1 petroleum ether–ethyl acetate on silica gel), mp 79–80.5°C (lit.13 79°C) ν_{max} (Nujol) 1721 cm^{-1} (C=O). δ_H 1.93–1.99 (4H, m, 2×CH_2), 4.36, (4H, m, 2×CH_2O), 7.40–7.48 (4H, m, ArH), 7.52–7.60 (2H, m, ArH), 8.01–8.08 (2H, m, ArH). δ_C 25.6, 64.5, 128.4, 129.5, 130.2, 132.9, 166.6.

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