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Cation and leaving group effects in isosorbide alkylation under microwave in phase transfer catalysis

Saber Chatti, Michel Bortolussi and André Loupy*

Laboratoire des Réactions Sélectives sur Supports, ICMO, UMR 8615, Bât. 410, Université Paris-Sud, 91405 Orsay Cedex, France

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Abstract—We have studied cation, salt, leaving group effects and influence of catalyst under phase transfer catalysis conditions using concomitant microwave irradiation during di-*n*-octylation of isosorbide. A small amount of solvent was necessary to control temperature and to provide good yields within a few minutes. The yields were dramatically improved when compared to conventional heating under the same conditions, in spite of similar profiles of raising in temperature. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

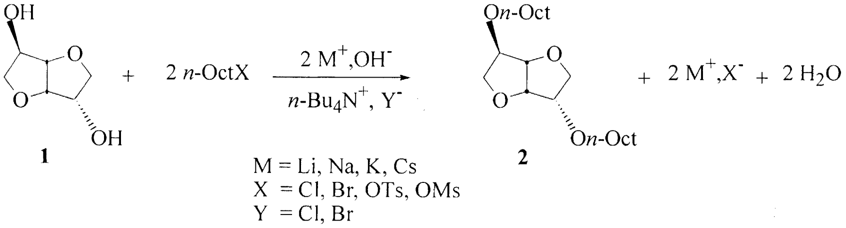
Biomass constitutes a renewable source of natural products able to be used as unfailing starting materials for access to less polluting new compounds able to substitute petroleum derivatives. Among the important derivatives of biomass, we found dianhydrohexitols and especially isosorbide (1,4:3,6-dianhydrosorbitol),[1–4]obtained from starch by dehydration of sorbitol. Recently we have described the alkylation of isosorbide[5] under microwave (MW) irradiation in phase transfer catalysis (PTC) as well as the reaction of mono-benzylated derivatives with α,ω-dihalides and ditosylates.[6] These diols could be interesting starting monomers for the synthesis of biodegradable polyethers. A main goal in our laboratory is to upgrade these derivatives and to involve them in some polyalkylations.[7]

We have previously shown that in order to minimize the competitive elimination, halide was changed to tosylate[6,8–10] allowing great improvement in the case of alkylation of mono-benzylated isosorbide. So in order to optimize experimental conditions and to evaluate MW effects on the polymerization,[11]we have studied cation and leaving group effects as well as other parameters[12,13] (salt and solvent, influence of catalyst[14]) under PTC conditions, using concomitant MW irradiation. during di-*n*-octylation of isosorbide **1** (Scheme 1).

2. Dialkylation of 1 with *n*-octyl chloride

It is of interest to use preferentially alkyl chlorides, generally cheaper and easily available, when compared to corresponding alkyl bromides in spite to their lower reactivity.[15]

Reactions with *n*-octyl chloride were studied under PTC conditions in *p*-xylene at 140°C using KOH as a base either under MW irradiation or by classical heating (Δ) using an oil bath thermostated at 140°C for the same time (10 min). The effect of counter-ion of tetra-*n*-butylammonium (PTA) was first studied (Table 1).



Scheme 1.

Keywords: cation and leaving group; alkylation; phase transfer catalysis; microwave.

* Corresponding author. Fax: +331 6915 4679;
e-mail: aloupy@icmo.u-psud.fr

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Table 1. Alkylation of **1** with *n*-octyl chloride under MW or Δ in PTC conditions (**1**; KOH; *n*-octyl chloride; *p*-xylene: 1; 3; 3; 0.5 mL)

PTA	% PTA	Yields **2** (%)[a]	
		MW	Δ
–	0	0	0
n-Bu$_4$NCl	10	7	0
	15	24	0
	20	39	0
n-Bu$_4$NBr	10	24	12
	15	34	12
	20	54	18

[a] g.c. yields using an internal standard (dioctyl phthalate).

In the absence of catalyst no reaction occurred. Addition of *n*-Bu$_4$NY is necessary to induce the formation of a strong base (eq. (1))

$$K^+, OH^- + n\text{-}Bu_4N^+, Y^- \rightleftharpoons n\text{-}Bu_4N^+, OH^- + K^+, Y^- \quad (1)$$

Increasing the amount of catalyst was logically favorable, shifting equilibrium to the right side (eq. (1)). Bromide seemed to be a better counter-ion when compared to chloride. This could be the result of an halogen exchange reaction on *n*-octyl chloride with formation of *n*-octyl bromide, a more efficient electrophile[6,15] (eq. (2))

$$\begin{tikzcd}
n\text{-OctCl} \arrow[d, "k_1"] & + & n\text{-}Bu_4N^+, Br^- & \rightleftharpoons & n\text{-OctBr} \arrow[d, "k_2"] & + & n\text{-}Bu_4N^+, Cl^- \\
{} & & & k_2 > k_1 & {} & &
\end{tikzcd} \quad (2)$$

Comparison of the results obtained under MW and Δ under the same conditions showed clearly that specific (non thermal) MW effect was more pronounced in the case of *n*-Bu$_4$NCl when compared to *n*-Bu$_4$NBr although in the last case the yields are higher in both conditions. This effect will be discussed later.

Consequently, because both cation and halide effects seemed to be of importance, the effects of addition of several alkaline salts as bromides or chlorides were studied (Table 2).

From this table, it was obvious that salt effects are important and numerous. In the case of common ions effects (MCl and/or *n*-Bu$_4$NCl), two phenomenas could be involved:

Table 2. Alkylation of **1** with *n*-octyl chloride under MW or Δ in PTC conditions (**1**; KOH; *n*-octyl chloride; PTA; MY; *p*-xylene: 1; 3; 3;20%; 3; 0.5 mL)

MY	Yields **2** (%)[a]			
	n-Bu$_4$NCl		*n*-Bu$_4$NBr	
	MW	Δ	MW	Δ
–	39	0	54	18
LiCl	20	0	44	17
NaCl	33	0	49	16
KCl	50	0	65	26
CsCl	62	0	66	14
NaBr	45	0	69	50
KBr	65	0	57	36

[a] g.c. yields using an internal standard (dioctyl phthalate).

(i) An ion exchange between alkaline salt and base (eq. (3))

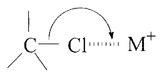
$$K^+, OH^- + M^+, Cl^- \rightleftharpoons M^+, OH^- + K^+, Cl^- \quad (3)$$

A bulkier cation M$^+$ generates a stronger base M$^+$OH$^-$, formed by ion exchange equilibrium. The following experimental sequence was compatible with such an assumption: LiCl < NaCl < KCl < CsCl. The subsequent exchange with *n*-Bu$_4$NCl (eq. (4)) is completely favoured when the energy is reduced, i.e. when the cation is bulkier

$$M^+, OH^- + n\text{-}Bu_4N^+, Cl^- \rightleftharpoons n\text{-}Bu_4N^+, OH^- + M^+, Cl^- \quad (4)$$

Lattice energy[16] (kJ/mol) LiOH: 1021; NaOH: 887; KOH: 789; CsOH 721.

(ii) An electrophilic assistance to carbon–chloride bond breaking by cation[11] (eq. (5))



(5)

This effect is increased with the hardness of cation (Li$^+$>Na$^+$>K$^+$). It is certainly involved when we consider the acceleration resulting from addition of KCl using KOH as a base where no ion exchange was concerned.

It was also obvious that specific MW effects were also more important in the case of reactions promoted by *n*-Bu$_4$NCl when compared to bromide equivalent.

Yields were always increased with *n*-Bu$_4$NBr as a transfer agent, certainly in connection with halogen exchange between *n*-OctCl and *n*-Bu$_4$NBr and formation of better electrophile *n*-OctBr (eq. (2)). In these cases, specific MW effects were less pronounced.

3. Dialkylation of 1 with *n*-octyl bromide

To confirm the preceding hypotheses, effects of salt addition and counter-ion in the case of tetra-*n*-butylammonium catalyst were studied and results are given in Table 3.

Table 3. Alkylation of **1** with *n*-octyl bromide under MW or Δ in PTC conditions (**1**; KOH; *n*-octyl bromide; PTA; MY; *p*-xylene: 1; 3; 3;10%; 3; 0.5 mL)

PTA	MY	Yields **2** (%)[a]	
		MW	Δ
n-Bu$_4$NBr	–	96[b]	10
	NaBr	60	27
	NaCl	69	1
	KCl	83	8
	CsCl	66	12
n-Bu$_4$NCl	–	68	3
	NaCl	65	0
	NaBr	50	0
	KBr	78	0
	CsBr	60	0

[a] g.c. yields using an internal standard (dioctyl phthalate).
[b] Isolated product: 90%.

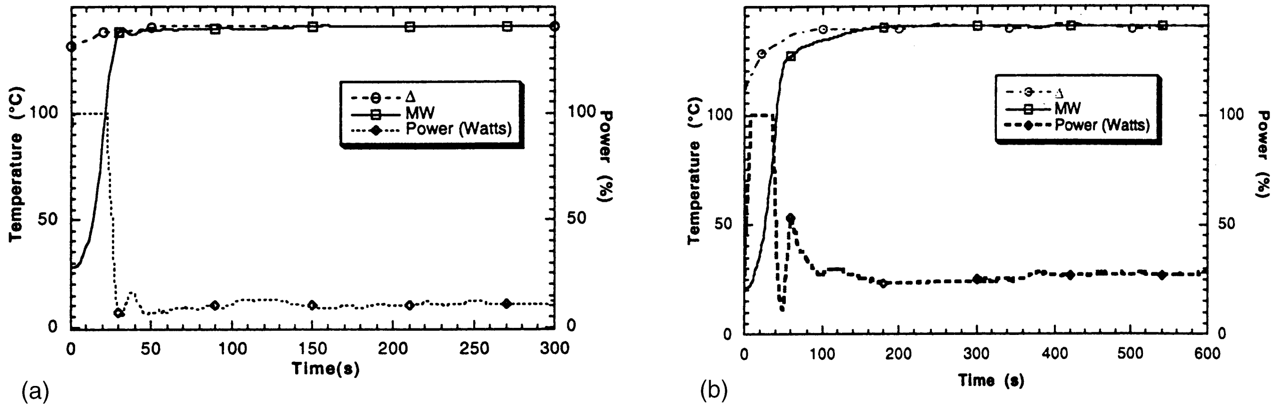


Figure 1. (a) Profile of raising temperature and in emitted power for the reaction of **1** and n-octBr (n-NBu$_4$Br). (b) Profile of raising temperature and in emitted power for the reaction of **1** and n-octCl (n-NBu$_4$Cl).

The best result was obtained with n-Bu$_4$NBr as the transfer agent in the absence of added salt. Salt effects were always negative and indicate the establishment of an ion exchange equilibrium.

In all cases, very important specific MW effects were evidenced when we consider quite close profiles of raising in temperature either under MW irradiation or under conventional heating in the same conditions (Fig. 1(a) and (b)).

They were even more important with n-octCl when compared to n-octBr as reaction proved to be always unproductive with the first alkylation agent.

4. Dialkylation of 1 with *n*-octyl sulphonates

We have previously shown[6] that arylsulphonates as leaving groups are of interest in order to minimize competitive elimination[6,8] reaction during alkylation of mono-benzylated isosorbide by dialkylating agents. Thus, before future polymerization, we have studied the behavior of n-octyl tosylate and mesylate. Main results are given in Table 4 (Scheme 2).

Table 4. alkylation of **1** with n-octyl tosylate and mesylate under MW or Δ in PTC conditions (**1**; KOH; n-Oct-OSO$_2$R; n-Bu$_4$NBr: 1; 3; 3;10%)

R=	T (°C)	Solvent	Yields 2 (%)[a]	
			MW	Δ
pCH$_3$ C$_6$H$_4$	80	cyclohexane	25	0
	110	toluene	30	0
	140	none	56	32
	140	p-xylene	50	8
	160	mesitylene	62	20
	190	decaline	51	32
CH$_3$	80	cyclohexane	87	49
	110	toluene	78	76
	≈100	none	95	–

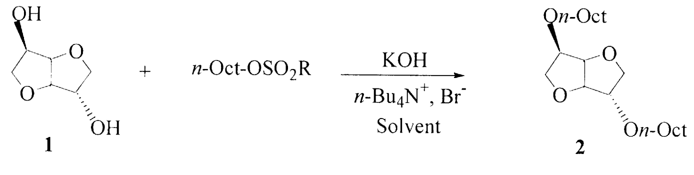
[a] g.c. yields using an internal standard (dioctyl phthalate).

The behavior of the two sulphonates is quite different as tosylate needed a significantly higher temperature to give satisfactory yields (62% in mesitylene at 160°C). The presence of a solvent had only little influence (56% in solvent-free condition at 140°C). Yields were lower by conventional heating under the same conditions. The limited yields were due to competitive tosylate hydrolysis leading therefore to significant amounts of n-octanol and dioctyl ether as evidenced by g.c. (eq. (6)):

$$n\text{-OctOTs} + \text{M}^+, \text{OH}^- \longrightarrow n\text{-OctOH} + \text{M}^+, \text{OTs}^-$$
$$n\text{-OctOH} + \text{M}^+, \text{OH}^- + n\text{-OctOTs} \longrightarrow n\text{-Oct}_2\text{O} + \text{M}^+, \text{OTs}^- + \text{H}_2\text{O} \quad (6)$$

Mesylate behaviour was more interesting. Reaction occurred with higher yields at lower temperature. A quasi-quantitative yield was obtained in the absence of organic solvent at an imposed temperature of 100°C under MW (in fact, the temperature raised momently to 120°C) within 15 min.

A rather important specific MW effect was evidenced when the reaction was performed in refluxing cyclohexane (80°C) whereas it is masked by the temperature increase level when it was conducted in toluene at 110°C. Such a specific MW increasing effect as the temperature is decreased (i.e. when the reactivity is reduced) was described by us recently in



Scheme 2.

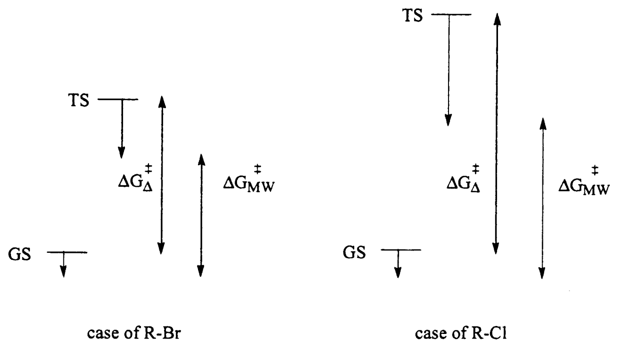
heterogeneous system[6] and by Radoiu et al. in liquid phase.[17]

5. Specific MW effects

The specific (non-purely thermal) MW effects are here of high importance and clearly dependent on the leaving group: *n*-OctCl$>$*n*-OctBr$>$*n*-OctOMs

It is interesting to note that such an intrinsic effect of MW occurs in the most difficult cases as yet observed for other types of reactions under solvent-free conditions.[18] Such an observation is consistent with a remark of Lewis[19] who underlined some years ago a generalization which has become obvious recently, stating that 'slower reacting systems tend to show greater effect under MW radiation than faster reacting systems'.

A possible explanation to this observation may lie in the consideration of relative stabilization of transition state (TS) when compared to ground state (GS). It is well known that more efficient MW-materials interactions are involved when the polarity of materials is increased as a result of dipolar polarization.[20] So it seems evident that an acceleration of a reaction under MW is the result of a better interaction of MW and TS when compared to GS if TS is more polar that GS. Another consequence of such an assumption is that one can observe stronger MW effect if TS occurs later along the reaction coordinates (more prone to develop increased polarity from initial state). When a reaction is more 'difficult'—i.e. needing high activation energy—its transition state is more product-like whereas an 'easy' one, more reactant-like, i.e. with slight modification in polarity (Scheme 3).



Scheme 3. Relative stabilization of ground state (GS) and transition state (TS) of reactions with either R–Br or R–Cl due to interaction with MW.

6. Conclusion

In the first part, we have studied the alkylation of isosorbide with *n*-octyl chloride under PTC conditions. In the absence of catalyst, no reaction occurred so it was necessary to induce the formation of a strong base. Increasing the amount of catalyst was of course favorable by shifting equilibrium to the right side. Bromide seemed to be a better counter-ion when compared to chloride. This could be the result of an halogen exchange reaction on *n*-octyl chloride with formation of *n*-octyl bromide as a more efficient electrophile. The addition of several alkaline salts have important and several effects. To confirm the hypotheses, we have studied the alkylation of isosorbide with *n*-octyl bromide and effects of salt addition and influence of catalyst.

In the second part, we have studied the alkylation of isosorbide with *n*-octyl tosylate and mesylate. Tosylate needed a significantly higher temperature to give a satisfactory yield. Mesylate behaviour is more interesting. Reaction occurred with higher yields at a lower temperature.

In all cases, comparison of reactions under microwave with conventional heating in the same conditions shows clearly a specific (non-thermal) microwave effect.

7. Experimental

7.1. Reactants and equipment

The different starting materials involved were purchased from Aldrich or Acros, and were used without any purification. Only isosorbide [gift from Société Roquette-Frères (Lestrem, France)] was previously crystallized from acetone.

The microwave reactor was a monomode system (Synthewave 402 from Société Prolabo) with focused waves operating at 2.45 GHz. The temperature was controlled all along the reaction and evaluated by an infrared detector which indicated the surface temperature (the IR lecture was calibrated by tuning the emissivity factor using a thermo-couple introduced into the reaction mixture). Temperature was maintained constant at a choosen value by modulation of emitted power. Mechanical stirring all along the irradiation provided a good homogeneity (power and temperature) and a data treatment which was followed by a computer. All reactions were performed in cylindrical Pyrex open vessels. There is no need to use an upright condenser as only small amounts of solvent are involved and as the vessel walls remain at ambient temperature.

In order to compare microwave irradiation with conventional heating, the reactions were performed under similar experimental conditions (weight of reactants, time and temperature). Using a thermostated oil bath, the temperature was measured with a Quick digital thermometer inserted into the reaction mixture and the rate of the temperature rise was adjusted to be similar to that measured under microwave irradiation.

Flash column chromatography was performed using 35–70μ silica gel 60 purchased from S.D.S. company. ^{1}H and ^{13}C NMR spectra were recorded at 200 MHz and 51.32 MHz and at 250 MHz and 62.91 MHz (Bruker WP 200, WP 250, respectively). Chemical shifts are given in ppm downfield from internal standard tetramethylsilane (δ=0.00 ppm).

7.1.1. Tosylation of *n*-octanol. *p*-Toluenesulfonyl chloride (23 g, 120 mmol) was added over a period of 30 min to a stirred solution of pyridine (31.6 g, 400 mmol) and *n*-octanol (13 g, 100 mmol) maintained at 0°C. The reaction mixture was allowed to stirr for 3 additional hours and then quenched with H_2O (200 mL) and extracted with CH_2Cl_2 (3×60 mL), and the combined organic layers were washed with 3 M HCl (3×80 mL) followed by 10% $NaHCO_3$ (1×80 mL). The organic layer was dried over Na_2SO_4 and concentrated under vacuum and the crude product purified by silica gel chromatography.

n-octyl 4-*p*-toluenesulphonate:[21] colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.90 (t, 3H, J=7.2 Hz), 1.08–1.82 (m, 12 H), 2.44 (s, 3H), 4.03 (t, 2H, J=6.9 Hz), 7.36 (d, 2H, J=8.3 Hz), 7.90 (d, 2H, J=8.3 Hz).

7.1.2. Mesylation of *n*-octanol. A stirred solution of CH_2Cl_2 (240 mL), *n*-octanol (10.53 g, 81 mmol), and triethylamine (12.33 g, 121.8 mmol) was stirred in an ice-bath, and methanesulfonyl chloride (10.2 g, 90 mmol) was added via a syringe at a rate of 0.23 mL/min. The reaction was allowed to stirr for 1 h at this temperature and then quenched with 250 mL of ice-water. The mixture was washed successively with 1.5 M HCl (200 mL), 10% $NaHCO_3$ (200 mL). The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel chromatography.

n-Octyl methanesulphonate:[21] colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.90 (t, 3H, J=6.80 Hz), 1.08–1.82 (m, 12 H), 2.97 (s, 3H), 4.16 (t, 2H, J=6.51 Hz).

7.1.3. General procedure for the synthesis of 2. Synthesis of **2** was performed under microwave irradiation or conventional heating. In a Pyrex cylindrical open reactor adapted to the Synthewave reactor, 3.42 mmol (0.5 g) of **1** were mixed with 10.26 mmol of *n*-octyl halide, tosylate or mesylate, 10.26 mmol of MY, 0.01 mmol (0.322 g) of TBAB, 10.26 mmol of powdered KOH (0.665 g) [containing about 15% of water] and 0.5 mL of solvent. The mixture was then homogenized and submitted to microwave irradiation under mechanical stirring. At the end of irradiation, the reaction mixture was cooled and extracted with methylene chloride. The extracts were evaporated under reduced pressure, analyzed by g.c. (with internal standard of dioctyl phthalate). Pure products **2** were isolated by liquid chromatography on silica gel using pentane/ethyl acetate as eluant.

D-sorbitol 1,4:3,6-dianhydro,2,5-di-*O*,*O*-octyl **2**: isolated as a syrup; R_f 0.42 (pentane/EtOAc 1/1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.90 (t, 6H, H_{14}, J=7.8 Hz), 1.5–1.15 (m, 20H, H_9–H_{12}), 1.6 (m, 4H, H_8), 3.55 (m, 5H, H_7 H_{6a} H_{6b}), 3.90 (m, 5H, H_2 H_5 H_7 H_{1a} H_{1b}), 4.45 (d, 1H, H_3, J=4.3 Hz), 4.65 (dd, 1H, H_4, J=4.85 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.1 (CH_3,C-14), 22.7 (CH_2, C-13), 26.0 (CH_2, C-12), 29.2 (CH_2, C-11), 29.4 (CH_2, C-10), 29.8 (CH_2, C-9), 32.2 (CH_2, C-8), 69.9 (C-7), 71.0 (C-1), 73.5 (C-6), 80.2 (C-4), 80.5 (C-5), 84.5 (C-2), 86.4 (C-3). Anal. Calcd for $C_{22}H_{42}O_4$: C, 71.35; H, 11.35; O, 17.29. Found: C, 71.30; H, 11.46; O, 17.24.

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