Reductions of α,β-Unsaturated Ketones by $NaBH_4$ or $NaBH_4$ + $CoCl_2$: Selectivity Control by Water or by Aqueous Micellar Solutions

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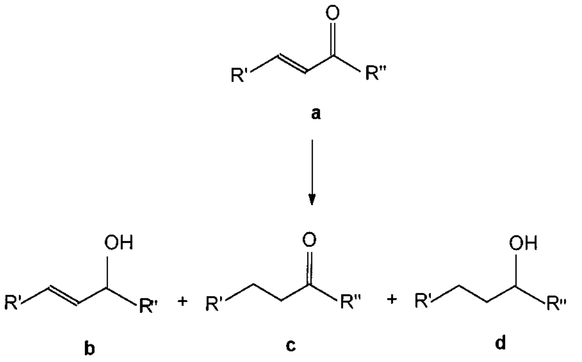
Operationally simple and environmentally benign procedures have been developed to selectively reduce different α,β-unsaturated ketones, 4,4-dimethylcyclohex-2-ene-1-one (**1**), isophorone (**2**), benzylideneacetone (**3**), chalcone (**4**) by $NaBH_4$ or by the system $NaBH_4$ + $CoCl_2$. Alternative reaction media to the extensively used MeOH have been explored, and new procedures take advantage of the acceleration and chemoselectivity induced by water or by aqueous micellar solutions. It was possible to selectively and quantitatively afford pure products of 1,2 and of 1,4 reduction as well as the totally reduced compounds (yield and selectivity > 90%) by simple changes in the experimental conditions.

Introduction

Since the discovery of the reducing properties of borohydride, sodium borohydride has received considerable attention as a selective and mild reducing agent; it is particularly attractive for general use thanks to its ease of handling. However, reduction of conjugated aldehydes and ketones is generally complicated by competing 1,2 and 1,4 processes, (Scheme 1) and the clean reduction of α,β-unsaturated aldehydes and ketones by hydride reagents has offered considerable difficulty: $NaBH_4$ predominantly reduces the C=O bond of conjugated systems in most cases, but substantial amounts of fully saturated alcohols have been found in general,[1,2] and the selectivity depends on several factors such as steric hindrance of the double bond, as well as the ring size in cyclic systems, and the solvent used.[1]



Scheme 1. Possible products from reductions of α,β-unsaturated ketones

The selective reduction of α,β-unsaturated aldehydes and ketones is of interest as this problem is often encountered in synthetic schemes. For the selective reduction of the carbonyl function considerable progress has been made in the development of reducing agents derived from $NaBH_4$: good selectivity has been achieved by addition of lanthanide ions[3] or $CaCl_2$,[4] by use of $Zn(BH_4)_2$[5] or $NaBH_4$ in carboxylic acid as reaction medium.[6] The selective reduction of the C=C bonds has been achieved by addition of $CoCl_2$ or $NiCl_2$ to solutions of $NaBH_4$, with formation of solid borides and of H_2, which acts as the reducing agent.[7] This kind of reaction is usually carried out in MeOH, but since $NaBH_4$ reacts with MeOH at a rapid rate, and metal borides further accelerate this breakdown,[8] and since $NaBH_4$ is considerably more stable in water than in MeOH,[9] the use of water as solvent was explored. Ganem et al.[10] have already explored the use of aqueous tetrahydrofuran, but only to carry out the reduction of nitriles to amines by $NaBH_4$ in the presence of $CoCl_2$: they found that the presence of water provides advantages in terms of reactivity with respect to methanol. Moreover, the use of water as solvent is particularly attractive for developing mild, cheap, and environmentally benign reaction conditions, and there is considerable interest in water as a reaction medium.[11]

Furthermore, aqueous association colloids are alternatives to the use of organic solvents in that they provide reaction media distinct from bulk water in terms of polarity, and they can also compartmentalize reagents so that they can provide chemo-, regio-, or stereoselectivity.[12] Attention has also been devoted to the selective reduction of enones in surfactant-rich media with $NaBH_4$ where it seems that they affect regioselectivity.

An improvement in the selectivity for products of 1,4 reduction with cationic micelles of CTABr or CTA(BH_4) for several enones was reported by Sukeninik:[13a] only the totally reduced products **d** or the 1,2 reduction product **b** were produced, and only for one of them was the selectivity in product **d** up to 70%; no attempts to rationalize the results based on substrate structure or to improve conditions for the other substrates have followed these preliminary studies. The use of hydrotopes[13b] in heterogeneous conditions has been shown to lead to totally reduced products **d** with high selectivity (90%), but only one substrate, isophorone, has been investigated.

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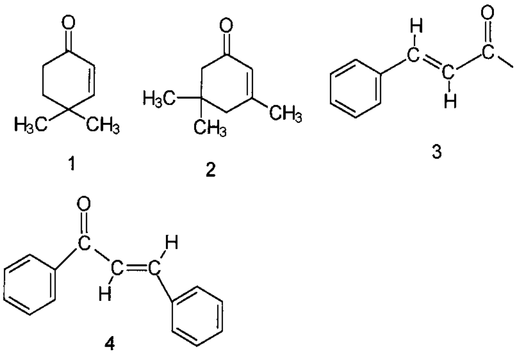
Several examples have concerned improvements in the selectivity of the 1,2 product.[14] Fargues-Sakellariou et al.[14a] reported a high efficiency (95%) for the formation of product **b** with selectivity induced by microemulsions of sodiumdodecyl sulfate (SDS) or CTABr; this study, however, was limited to one substrate (isophorone) and the organic solvent must be in a large excess, more than water, when microemulsions are used: the same reaction in aqueous micelles of the same surfactants gives lower selectivities dependent on the surfactant structure. Jaeger[14b] also used microemulsions to induce selective formation of product **b** for benzylideneacetone; he found high selectivity (92%), but with no advantage over the use of organic solvents, that give 100%. Attempts to use only aqueous media have recently been more successful: aggregates of anionic surfactants (SDS)[14c] or of special ones such as nonionic glycosidic surfactants or amphiphilic carbohydrates[14d] give the products of 1,2 reduction with selectivities >90%.

Our aim in the present work is to afford selectively and quantitatively each of the possible products using aqueous reaction media. In particular the products of 1,2 reduction are generally obtained in high selectivity in MeOH, and we investigated the possibility of using water as an alternative medium; however, most attention was devoted to the more difficult problem of selective production of each of the two other products. We now report our results with four α,β-unsaturated ketones of different steric and electronic requirements (Scheme 2): 4,4-dimethylcyclohex-2-ene-1-one (**1**), isophorone (**2**), benzylideneacetone (**3**) and chalcone (**4**) whose reduction can lead to three different products according to Scheme 1.



Scheme 2. α,β-Unsaturated ketones studied

Results and Discussion

Reduction by $NaBH_4$ in Various Media

Reductions by $NaBH_4$ were carried out in different media and the results are collected in Table 1. In the absence of surfactants, methanol (homogeneous conditions) was compared with water (heterogeneous conditions). The use of water as reaction medium provided enhanced reactivity and selectivity, for isophorone **(2)** and it was possible to prepare selectively **2b**. Isophorone is known to be relatively unreactive toward reduction in MeOH,[2,15] but in water 92% allylic alcohol formed with 84% conversion (entry 7). For the other substrates compounds **b** were conveniently prepared in MeOH.

Table 1. Reactions of substrates **1–4** with $NaBH_4$ in various media

Entry	Substrate	Medium[a]	Conversion (mol-%)	b	c (mol-%)	d
1	**1**	MeOH	100	95	–	5
2		H_2O[b]	100	76	–	24
3		CTEABr	100	48	–	52
4		CTBABr	100	48	–	52
5		SB3–12	99	62	–	38
6	**2**	MeOH[c]	12	73	9	18
7		H_2O[b,c]	84	92	2	6
8		CTEABr[c]	92	73	9	18
9		CTBABr[d][e]	100	76	9	15
10		SB3–12[c]	69	82	6	12
11		CTAMs[d]	100	69	6	20
12	**3**	MeOH	100	99	–	1
13		H_2O[b]	100	67	–	33
14		CTEABr	100	83	–	17
15		CTBABr	100	81	–	19
16		SB3–12	100	91	–	8
17	**4**	MeOH	96	93	–	7
18		H_2O[b]	34	85	–	15
19		CTABr	97	58	–	42
20		CTEABr	97	58	–	42
21		CTPABr	97	44	–	56
22		CTBABr	99	32	–	68
23		SB3–12	97	41	–	59
24		TBABr[b]	12	70	–	30

[a] At 25 °C with 0.010 M [substrate], 0.011 M [$NaBH_4$] and 0.1 M [surfactant]; reaction time 1 h unless otherwise noted; mol-% determined by GC analysis. – [b] Heterogeneous conditions. – [c] Reaction time 24 h. – [d] Reaction time 12 h. – [e] 0.1 M and 0.05 M [surfactant] give the same result.

A screening for the use of cationic and zwitterionic aqueous micellar solutions was carried out with changes in surfactant structure. The surfactants used were the cationic cetyltrialkylammonium salts $nC_{16}H_{33}N^+R_3X^-$ [R = Me, (CTAX), Et (CTEAX), *n*Pr (CTPAX), *n*Bu (CTBAX), X = Br (bromide), Ms (methansulfonate)] and zwitterionic 3-(*N*,*N*-dimethyldodecyl-ammonium) propanesulfonate $nC_{12}H_{25}N^+Me_2(CH_2)_3SO_3^-$ (SB3–12). Aqueous micellar solutions provided enhanced reactivity with respect to reaction in the absence of surfactants, and a certain chemoselectivity control, dependent on the hydrophobic character of the substrate.

The reactivity of **2** further increased in cationic micellar solutions, especially when CTAMs and CTBABr were used (entries 9, 11). Zwitterionic sulfobetaine micelles are not as effective as the cationic in accelerating the reaction (entry 10). This can be easily understood in terms of the electrostatics of the micellar surface. Also, for chalcone **(4)**, a significant increase in the reactivity is observed in micellar solution, relative to water, but with no advantages compared to methanol.

As regards chemoselectivity, the surfactants generally induced an increase in the 1,4 process to afford the saturated alcohols (products **d**); this effect is significant with the most hydrophobic substrate, **4**, and it increases with increasing bulk of the surfactant head group reaching a value of 68 mol-% of saturated alcohol (entries 19–22). The use of SB3–12 provides chemoselectivity (entry 23), while the nonmicellizing quaternary ammonium salt tetrabutyl ammonium bromide (TBABr) is neither effective in accelerating the reaction nor in providing chemoselectivity (entry 24). The preference for the 1,4 reaction pathway in micellar solution can be related to a greater stabilization by the soft ammonium ion of the surfactant for the transition state which bears the more disperse negative charge: this effect is more significant with big-head surfactants which provide a softer ammonium centre, as consistent with studies upon S_N2-E2 competition from both a preparative[16] and a physicochemical point of view,[17] and studies upon attack at the C or S atoms in aryl esters of sulfonic acids.[18] This extensive screening shows that the use of aqueous micellar solutions of $NaBH_4$ does not provide advantages over the other media (water and MeOH) in selectively and quantitatively affording pure products.

Reduction by the System $NaBH_4 + CoCl_2$ in Various Media

Reductions by the system $NaBH_4 + CoCl_2$, to afford saturated ketones **c**, were carried out in various media and the results are shown in Table 2.

Table 2. Reactions of substrates **1–4** with $NaBH_4 + CoCl_2$ in various media

Entry	Substrate	Medium[a]	[substrate]/[$NaBH_4$]/[$CoCl_2$]	Conversion	**c** (mol-%)
1	**1**	MeOH	1/2.5/2	88	90
2		H_2O	1/2.5/2	83	93
3		H_2O[b]	1/2.5/2	82	90
4		SDS	1/3.5/3	47	43
5	**2**	MeOH[c]	1/2.5/2	38	98
6		H_2O[d]	1/6/3	95	98
7		SDS[c]	1/3.5/3	38	100
8	**3**	MeOH	1/2.5/2	96	77
9		H_2O	1/2.5/2	>99	51
10		SDS	1/3.5/3	91	86
11	**4**	MeOH	1/2.5/2	99	96
12		H_2O	1/6/3	8	73
13		SDS	1/3.5/3	83	80

[a] At 30 °C with 0.010 M [substrate], 0.011 M [$NaBH_4$] and 0.1 M [surfactant]; reaction time 1 h unless otherwise noted; the difference from 100 in product composition is compounds **b** and **d**; mol-% determined by GC analysis. – [b] $NiCl_2$ was used instead of $CoCl_2$. – [c] Reaction time 24 h. – [d] Reaction time 15 h.

As observed by various authors for other reactions with the system $NaBH_4 + CoCl_2$ in MeOH,[7] we also experimentally observed that the ratio of $NaBH_4$/$CoCl_2$ is important; for all reaction media the optimized ratios used are reported in Table 2. Substrates **1, 2** and **4,** but not **3,** afford products **c** in high selectivity in MeOH. For substrates **1** and **2** the selectivity is also good in water, with the reaction being somewhat faster in water for **2**. On the other hand, for substrate **4**, reaction is slower in water, although use of the anionic surfactant sodium dodecylsulfate (SDS) accelerates the reaction (entry 13).

The preparation of pure product **3c** was not possible in either MeOH or water, and only use of aqueous solutions of SDS afforded it in good yield (entry 10). It seems that this surfactant "protects" the micellar-bound substrate from attack by the reactive anion BH_4^-, the main reduction pathway being, therefore, the one carried out by H_2.

One-Pot Multiple-Step Reductions

The totally reduced products **d** were easily achieved by control of the ratio $NaBH_4$/$CoCl_2$ reducing in a stepwise manner (but in one pot) the double bond and the carbonyl function, or vice versa, as shown in Table 3, and explained in detail in the Experimental Section. For substrate **1** the reaction is best carried out in water, and the two-fold addition of $NaBH_4$ leads to an increased selectivity (Table 3, entries 1–3). The use of methanol with the same procedure is not as effective as water (entry 4). Product **3d** can be afforded by increasing the ratio up to 1:6:3 (entries 5–7), in only one step. The use of methanol instead of water (entry 8) is not as effective at selectively affording **3d**.

Table 3. Effects of ratios of $NaBH_4$/$CoCl_2$ upon formation of **c** and **d** in various media

Entry	Substrate	Medium[a]	[substrate]/[$NaBH_4$]/[$CoCl_2$]	Conversion (mol-%)	**c** (mol-%)	**d** (mol-%)
1	**1**	H_2O	1/6/3	100	28	70
2		H_2O	1/8/3	100	7	89
3		H_2O	1/8/3[b]	100	4	96
4		MeOH	1/8/3[b]	100	4	85
5	**3**	H_2O	1/2/3	88	73	13
6		H_2O	1/4/3	100	20	80
7		H_2O	1/6/3	100	3	97
8		MeOH	1/6/3	100	10	90
9	**4**	CTABr 0.09 M	1/8.1/3[c]	100	–	98
10		MeOH	1/8.1/3[c]	100	8	75

[a] At 30 °C with 0.010 M [substrate], 0.011 M [$NaBH_4$]; reaction time 1 h unless otherwise noted; the difference from 100 in product composition is compounds **b**; mol-% determined by GC analysis. – [b] Reaction in one pot, two steps as described in the Experimental Section; total reaction time 1 h. – [c] Reaction in one pot, three steps as described in the Experimental Section; total reaction time 2 h.

For substrate **4** the reactions do not proceed at a reasonable rate in water (cf. Table 1), and are conveniently carried out in aqueous solutions of CTABr. The initial reduction of **4** in this medium leads to **4b** and **4d** (cf. Table 1, entry 19); the allylic alcohol **4b** is thereafter reduced using the system $NaBH_4 + CoCl_2$ with optimized ratios (second step); further addition of $NaBH_4$ (third step) is then carried out to afford **4d** quantitatively (entry 9). The use of methanol instead of aqueous surfactant is not particularly effective to afford **4d** due to the rapid decomposition of the catalyst cobalt boride (entry 10). Attempts to obtain product **2d,** with either procedure, did not succeed.

Conclusions

An investigation about the use of water or aqueous solutions of different kinds of surfactant for the reduction of four different α,β-unsaturated ketones by $NaBH_4$ or by the system $NaBH_4 + CoCl_2$ allowed us to set up procedures to control product composition by simple changes in the experimental conditions. A summary of the best results of our control is in Table 4. Although MeOH is thoroughly used in the literature, we showed that it should be preferred over water in a few cases, to lead to products **1b, 3b, 4b, 4c**. Several products (**1d, 2b, 2c, 3d**) that could not be obtained pure or speedily in MeOH were conveniently obtained in water. For some other products, that were not conveniently obtained either in MeOH or in water, the use of aqueous surfactant solutions of CTABr or SDS provides good selectivity and conversion, and still operationally simple procedures: pure **3c** and **4d** could be obtained only by taking advantage of the peculiar properties of proper surfactant solutions. Environmentally benign media, cheap material, and mild reaction conditions are features of the new procedures.

Table 4. Summary of the best results to obtain pure products, **b, c,** or **d** from substrates **1–4** in various media

Substrate	Medium[a]	Conversion (mol-%)	Main product (mol-%)			[Sub.]/[NaBH$_4$]/[CoCl$_2$]
			b	c	d	
1	MeOH	100	95	–	–	1/1.1
	MeOH (H$_2$O)	88 (83)	–	90 (93)	–	1/2.5/2
	H$_2$O	100	–	–	96	1/8/3[b]
2	H$_2$O	84	92	–	–	1/1.1
	H$_2$O	95	–	98	–	1/6/3
3	MeOH	100	99	–	–	1/1.1
	SDS 0.1 M	91	–	86	–	1/3.5/3
	H$_2$O	100	–	–	97	1/6/3
4	MeOH	100	93	–	–	1/1.1
	MeOH	99	–	96	–	1/2.5/2
	CTABr 0.09 M	100	–	–	98	1/8.1/3[c]

[a] For details see Table 1, Table 2 and Table 3; the difference from 100 in product composition is the other compounds, mol-% determined by GC analysis. – [b] Reaction in one pot, two steps as described in the Experimental Section. – [c] Reaction in one pot, three steps as described in the Experimental Section.

Experimental Section

General Remarks: The preparation and purification of surfactants has been described previously.[19] The α,β-unsaturated ketones were purchased from Aldrich and used without further purification. The following internal standards were commercial and used without further purification: acetophenone (Janssen), anisole (Aldrich) diphenyl ether (Fluka). 1,2-(4,4′-Dimethoxy)diphenylethane was kindly provided by Dr. Del Giacco of our department.

^{1}H NMR were measured on a 200 MHz FT Bruker instrument, in CDCl$_3$ if not otherwise specified, and chemical shifts are relative to internal TMS. Melting points are uncorrected, and registered on a Buchi 510 instrument.

Reaction Conditions: Reactions were carried out in 50-mL round-bottom flasks with 0.1 mmol of substrate in 10 mL of solvent or surfactant solution. Mild sonication was used initially to disperse the substrates and mixtures were heterogeneous only in pure water. Solid NaBH$_4$, or an aqueous solution, was then added to the magnetically stirred solutions at 30 °C. When CoCl$_2$ was used, it was added as its solid hexahydrate salt to the magnetically stirred solutions containing the substrate; the solutions turned deep pink. As NaBH$_4$ was added a black precipitate formed. Stirring was maintained over the course of the reactions, which were followed by TLC (petroleum ether/diethyl ether 80:20 as eluent). After convenient time intervals 10 mL of water and a known amount of internal standard was added to the reaction mixture, and products were extracted with Et$_2$O (3 × 20 mL). The combined extracts were washed with water and dried over Na$_2$SO$_4$ before analysis by GLC. Tests were made with mixtures of the products to ensure the quantitative isolation and to optimize extraction conditions.

One-Pot Multiple-Step Procedures Leading to Pure Saturated Alcohols

A) For substrate **1** the reaction was initially carried out as described previously for the reaction in the presence of CoCl$_2$, in water or in MeOH, with a NaBH$_4$/CoCl$_2$ ratio of 6:3. After the substrate had completely converted into products (TLC, ca. 30 min) further NaBH$_4$ was added to the solution until only one compound was detectable by TLC. Further elaboration was as described above.

B) For substrate **4** the reaction was initially carried out in CTABr (0.09 M) or in MeOH, as described for the reaction in the absence of CoCl$_2$, with a ratio of substrate/NaBH$_4$ of 1:1.1. After the substrate had completely converted into products (ca. 1 h) CoCl$_2$ was added to the solution, which turned pink, and then NaBH$_4$ was added (the ratio NaBH$_4$/CoCl$_2$ being 3.5:3, with respect to substrate), upon which a black precipitate formed, which slowly changed to deep green as the reaction proceeded (by TLC). Further NaBH$_4$ was then added (ratio of 3.5:1 with respect to substrate) which allowed for a complete conversion into the totally reduced product. Further elaboration was as described above.

Product Analysis

Reaction products were analyzed quantitatively by GLC on an HP 5890 instrument (FID) with on-column injection, equipped with a 30 m × 0.25 mm capillary column, HP5, 1.5 μm film thickness for substrates **2** and **3**, and equipped with a 15 m × 0.26 mm capillary column HP INNOVAX 1μm film thickness for substrates **1** and **4**. Internal standards were acetophenone for substrate **1**, anisole for substrate **2,** diphenyl ether for substrate **3**, 1,2-(4,4′-dimethoxy)diphenylethane for substrate **4**, and were added as solutions in toluene (1 mL). Response factors were determined by using known mixtures of the products. All analysis were made in duplicate, and differences were <5 mol-%.

Preparation and Characterization of Products

Allylic alcohols **b** were prepared by reaction of substrates **1–4** with NaBH$_4$ in MeOH (in water **2b**), as described previously, starting from 0.3 mmol substrate. Compound **1b** was purified on a silica gel column to afford pure liquid compound in 82% yield. ^{1}H NMR: δ = 0.95 (s, 3 H, CH$_3$), 1.00 (s, 3 H, CH$_3$), 1.40–1.90 (m, 4 H, 2CH$_2$), 4.12 (m, 1 H, CH), 5.42–5.61 (m, 2 H, CH=CH).

Compound **2b** was purified on a silica gel column to afford pure liquid compound in 80% yield. The ^{1}H NMR spectrum was identical to that of a commercial sample (Aldrich).

Compound **3b** was obtained pure in 99% yield. ^{1}H NMR: δ = 1.37 (d, J = 6.39 Hz, 3 H, CH$_3$), 4.47 (m, 1 H, CH), 6.25 (dd, J = 15.92 Hz, J = 6.29 Hz, 1 H, CH), 6.59 (d, J = 15.92 Hz, 1 H, CH), 7.23–7.40 (m, 5 H, C$_6$H$_5$).

Compound **4b** was purified by crystallization from petroleum ether, affording pure white crystalline compound in 80% yield. M.p. 58–59 °C. – ^{1}H NMR (CD$_3$OD): δ = 5.34 (d, J = 6.45 Hz, 1 H, CH), 6.42 (dd, J = 15.95 Hz, J = 6.45 Hz, 1 H, CH), 6.69 (d, J = 15.95 Hz, 1 H, CH), 7.20–7.48 (m, 10 H, 2C$_6$H$_5$).

The saturated ketones **c** were prepared by reaction of substrates **1–4** with $NaBH_4/CoCl_2$ in the specified reaction medium, with optimized ratios of substrate/$NaBH_4/CoCl_2$ as reported in Table 2 and Table 4, starting form 0.3 mmol substrate. All compounds were purified on a silica gel column.

1c: Solvent: water; 82% yield. – M.p. 38–40 °C (ref.[20] 39–40 °C). – ^1H NMR: $\delta = 1.10$ (s, 6 H, $2CH_3$), 1.70 (t, $J = 6.81$ Hz, 4 H, $2CH_2$), 2.40 (t, $J = 6.81$ Hz, 4 H, $2CH_2$).

2c: Solvent: water; 98% yield. The ^1H NMR spectrum was identical to that in the literature.[21]

3c: Solvent: aqueous SDS; 77% yield. The ^1H NMR was identical to that of a commercial sample (Aldrich).

4c: Solvent: methanol; 85% yield. – M.p.: 69–70 °C (ref.[22] 67–69 °C). The ^1H NMR was identical to that of a commercial sample (Lancaster).

The saturated alcohols **d** for substrates **1** and **4** were prepared by reduction with the one-pot multiple-step procedures previously described; for substrate **3** by reduction with $NaBH_4 + CoCl_2$ with the optimized ratio reported in Table 3. Products were obtained pure, apart form **1d** which was purified on a silica gel column.

1d: 79% yield. – ^1H NMR: $\delta = 0.90$ (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3), 1.28–1.80 (m, 8 H, $4CH_2$), 3.61 (m, 1 H, CH).

2d: As mentioned we could not obtain product **2d** with our procedures. For analysis purpose, we prepared it by reduction of the ketone **2c** with $LiAlH_4$, obtaining the *cis* and *trans* saturated alcohols as a diastereomeric mixture, with 84% yield. – ^1H NMR: $\delta = 0.72$–1.12 (m, 9 H, 3 CH_3), 1.18–2.1 (m, 7 H, 3 CH_2 and CH), 3.48–4.20 (m, 1 H, CH).

3d: 97% yield. – ^1H NMR: $\delta = 1.12$ (d, $J = 6.16$ Hz, 3 H, CH_3), 1.68 (m, 2 H, CH_2), 2.64 (m, 2 H, CH_2), 3.75 (m, 1 H, CH), 7.10–7.21 (m, 5 H, C_6H_5); m.p. 70–71 °C (ref.[23] 71 °C).

4d: 92% yield. – ^1H NMR: $\delta = 2.08$ (m, 2 H, CH_2), 2.65 (m, 2 H, CH_2), 4.64 (t, $J = 6.62$ Hz, 1 H, CH), 7.19–7.45 (m, 10 H, 2 C_6H_5).

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