Alkylation of Carbonyl Compounds in Water: Formation of C–C and C–O Bonds in the Presence of Surfactants

Giorgio Cerichelli,*[a] Simona Cerritelli,[a] Marco Chiarini,[a] Paolo De Maria,[b] and Antonella Fontana[b]

Abstract: The formation of C–C and C–O bonds by the reaction of enolate intermediates with electrophilic substrates commonly requires strong bases, aprotic solvents and very low temperatures. A way of performing the same reactions with sodium hydroxide at moderate temperatures in aqueous surfactant solutions is presented. Different halides, ketones and surfactants (cationic, zwitterionic and anionic) have been used. The results obtained show that the amount of ketone alkylation is much higher and that the reactions are faster in the presence than in the absence of surfactant aggregates. The hydrolysis of the halide is minimised in the presence of cationic or zwitterionic surfactants.

Keywords: alkylation · aqueous solutions · carbonyl compounds · C–C coupling · C–O bond formation · micelles

Introduction

Enolate ions are important intermediates in C–O and C–C bond-formation reactions[1] as they can behave effectively as ambident nucleophiles towards many electrophiles. However, simple monocarbonyl compounds bearing α-hydrogens generally have pKa values[2] (of $\approx$20) which are too high to allow quantitative deprotonation in an aqueous base. Instead the corresponding enolates are commonly obtained[1] by the use of very strong bases in aprotic solvents at low temperatures [e.g. LDA (or LICA; LHMDS, LTMP)[3] in THF or DME at $-78\,^{\circ}$C]. Alternatively, enamines, hydrazones or oximes can be used as the equivalent of enolate ions in Stork-type reactions.[4]

We have recently shown[5] that the acidity of arylbenzylketones in water can be considerably enhanced by the addition of micelles from cationic surfactants, such as CTAB (cetyltrimethylammonium bromide), on account of a strong interaction of the enolate ions with the micellar aggregates. We have suggested[5] that this fact might offer a way of generating enolate ions from suitable monocarbonyl compounds to be used in aqueous solutions for synthetic purposes.

In this work we have performed some alkylation reactions of enolate ions obtained from the parent ketones in aqueous sodium hydroxide in the presence of micellar aggregates. Obvious advantages of working in aqueous solutions are that there are no polluting organic solvents to dispose of, water-insoluble reaction products can be isolated by simple filtration and the micellar catalyst can generally be recovered by ultrafiltration. Provided that the reactant electrophile is associated with the nucleophilic enolate within the micelle and separated from the aqueous region containing the hydroxide ion, side products from the reaction of the electrophile with the base or solvent can also be avoided. For example, benzyl alcohol was not obtained[6] during formation of new C–C bonds in reactions of benzyl bromide with β-dicarbonyl compounds performed in aqueous solutions in the presence of cationic micelles.

The investigated ketones are: benzyl phenyl ketone, cyclohexanone, γ-phenylcyclohexanone and α-tetralone. The investigated alkyl halides are: benzyl chloride, benzyl bromide, methyl iodide, cyclohexyl bromide and cyclohexyl iodide. These starting materials have been chosen for the following reasons: benzyl phenyl ketone has a molecular structure and a pKa value[7] ($\approx$15 in water) which are very similar to those of 2-phenylacetylthiophene, whose keto–enol interconversion has been kinetically investigated[5] in the presence of micelles of CTAB and the binding constant of its enolate with the micelle has been accurately measured. Cyclohexanone and γ-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Tables S1 and S2 provide NMR data, theoretical calculations and corresponding exhaustive discussion on the stereochemistry of α-benzyl-γ-phenylcyclohexanone.

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phenylcyclohexanone have quite different hydrophobic properties, but presumably very similar acidities. In the case of α-tetralone there can be competition between position 2 and 4 as the site of the C-monoalkylation reaction. For all of the above-mentioned ketones there is also the possibility of a competitive O-alkylation reaction and the investigation of this possibility, as a function of the structure of the substrate and reaction conditions, is of some additional interest.

As for the alkyl halides, benzyl and methyl derivatives are both known[1] to be reactive in S_N2-type reactions; however, they differ significantly in their hydrophobicities. On the other hand, cyclohexyl halides are usually less reactive because they are sterically hindered substrates.

Micelles from cationic surfactants are expected to be best-suited[8] for inducing a decrease in the p*K*a of a suitable enolizable ketone, while changing the counterion can modify the competition of the different anions (counterions, hydroxide and enolate ion) on the surface of the aggregate. However, a description of the system under the adopted conditions in terms of the ion exchange model is hardly worth attempting because of the very high ion concentrations and of the strong binding of the highly polarisable enolate ions to the micellar surface. Moreover, to the best of our knowledge, no ion exchange constants have been measured thus far when the micellar surface is overcrowded by neutral reagents (in the present case the ketone and the alkyl halide).

On the other hand, zwitterionic surfactants are known[9–11] to strongly interact with polarisable and/or hydrophobic anions. Moreover, with zwitterionic surfactants there is not the complication arising from the introduction into the reaction medium of anions other than those involved in the stoichiometric reaction.

Results

The general process involves formation of an enolate ion from the parent ketone (0.05 – 1.00 mol dm^{-3}) by (1 or 2 mol dm^{-3}) NaOH in an aqueous solution of 5×10^{-2} mol dm^{-3} surfactant, and the subsequent reaction of the enolate with the alkyl halide, R^2X, (0.1 – 1.0 mol dm^{-3}). In all cases, the surfactant concentration is at least one order of magnitude higher than its cmc (critical micelle concentration) and reactant concentrations are equal to or in excess of the surfactant (when present).

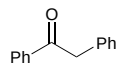
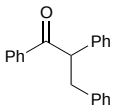
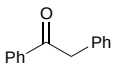
The results for the alkylation of benzyl phenyl ketone are collected in Tables 1 and 2, those for the alkylation of the other ketones are collected in Table 3 and are discussed below.

Discussion

The various factors which affect the investigated reactions can be analysed separately as follows.

Type of surfactant: The effect of varying the surfactant can be interpreted in the light of the results obtained for reactions of benzyl phenyl ketone with benzyl chloride and bromide (Table 1), with cyclohexyl bromide and iodide (Table 2) and with methyl iodide (see the Experimental Section).

Table 1. Reaction of benzyl phenyl ketone with benzyl halide: molar concentration of reagents, experimental conditions, yields and product distribution in the reaction mixture.

 [M]	Halide	Halide [M]	NaOH [M]	Surfactant (0.05 M) (or catalyst)	T[°C]	t[h]	Reacted ketone [mol %]	Product distribution in the reaction mixture[a] [mol %]				
									$PhCH_2OH$	$(PhCH_2)_2O$		$PhCH_2X$
0.1	$PhCH_2Cl$	0.1	1	CTAB[b]	25	16	99.0	98	1	0	1	0
0.05	$PhCH_2Cl$	0.05	1	CTAB	80	1	100	100	0	0	0	0
0.1	$PhCH_2Cl$	0.2	1	CTAB	25	41	100	60	21	19	0	0
0.1	$PhCH_2Cl$	0.2	1	CTAB	80	1	100	58	27	12	0	3
1	$PhCH_2Br$	1	1	CTAB	25	12	95.0	96	2	0	2	0
0.1	$PhCH_2Cl$	0.1	1	$C_{16}(CH_2CH_2OH)_2MeNB$[c]	25	1	94.0	94	0	0	6	0
0.1	$PhCH_2Cl$	0.1	1	$C_{16}(CH_2CH_2OH)_2MeNB$	80	1	100	95	5	0	0	0
0.1	$PhCH_2Br$	0.1	2	SB3-12[d]	25	1	100	99	1	0	0	0
0.1	$PhCH_2Cl$	0.1	2	SB3-12	25	1	100	99	1	0	0	0
0.1	$PhCH_2Cl$	0.1	1	SB3-12	25	1	97.0	94	3	0	3	0
0.1	$PhCH_2Cl$	0.2	2	SDS[e]	60	20	40	16	58	2	24	0
0.1	$PhCH_2Br$	0.2	2	SANa[f]	25	20	98.0	53	43	3	1	0
0.1	$PhCH_2Br$	0.1	2	SANa	60	1	45.0	29	35	1	35	0
0.1	$PhCH_2Br$	0.2	2	SANa	60	1	51.0	20	59	2	19	0
0.05	$PhCH_2Br$	0.2	5	absent	25	20	38.1	8	78	1	13	0
0.1	$PhCH_2Br$	0.2	2	absent	25	16	18.4	7	23	2	31	37
0.1	$PhCH_2Br$	0.2	2	absent	25	24	22.0	8	43	3	28	18
0.5	$PhCH_2Br$	0.5	1	TBAB[g]	25	1	67.0	50	11	0	25	14
0.5	$PhCH_2Br$	0.5	1	TBAB	25	16	84.0	72	14	0	14	0

[a] Product distribution [mol %] determined experimentally by gas chromatography analyses. [b] CTAB = cetyltrimethylammonium bromide. [c] $C_{16}(CH_2CH_2OH)_2MeNB$ = bis(2-hydroxyethyl)cetylmethylammonium bromide. [d] SB3-12 = 3-(dimethyldodecylammonium)propansulfonate. [e] SDS = sodium dodecylsulfate. [f] SANa = sodium *N*-lauroylsarcosinate. [g] TBAB, tetrabutylammonium bromide, has been used as an example of non-micelle forming, phase-transfer catalyst

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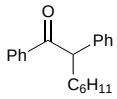
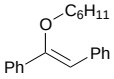
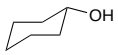
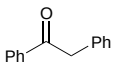
Table 2. Alkylation of benzyl phenyl ketone (0.1M) with cyclohexylhalide (0.1M) in an aqueous solution of surfactant (0.05M) and NaOH (1M): experimental conditions, yields and product distribution of the reaction mixture.

Halide	Surfactant	t [h]	Reacted ketone [mol %]	Product distribution in the reaction mixture[a] [mol %]			
							
			60 °C				
CyI	CTAI	24	79	52.5	12.5	17.5	17.5
CyB	CTAB	48	59	26.7	15.5	28.9	28.9
CyI	SB3-12	48	55	31.1	6.9	31.0	31.0
CyB	SB3-12	72	28	11.0	5.2	41.9	41.9
			80 °C				
CyI[b]	CTAI[c]	2	59	32.6	9.2	29.1	29.1
CyB[d]	CTAB[e]	4	49	36.6	16.0	23.7	23.7
CyI	SB3-12[f]	4	54	24.8	11.8	31.7	31.7
CyB	SB3-12	24	30	11.9	5.5	41.3	41.3

[a] Product distribution [mol %] determined experimentally by gas chromatography analyses. [b] CyI = cyclohexyl iodide. [c] CTAI = cetyltrimethylammonium iodide. [d] CyB = cyclohexyl bromide. [e] CTAB = cetyltrimethylammonium bromide. [f] SB3-12 = 3-(dimethyldodecylammonium)-propansulfonate.

The major effect appears to concern the distribution of the products. In the presence of cationic or zwitterionic surfactants and with equimolar reagents, the amount of benzyl alcohol produced by hydrolysis of the benzyl halide (and the amount of dibenzyl ether obtained from reaction of benzyl alcohol) is very small and the reaction goes to completion in a few hours. On the other hand, if the reaction is carried out in the presence of anionic surfactants [sodium dodecyl sulfate (SDS) or sodium *N*-lauroyl sarcosinate (SANa)], substantial amounts of benzyl alcohol and unreacted ketone are observed.

The reaction mixture is a heterophase system where the concentration of the surfactant is similar to or lower than that of the reagents, but it is always higher than its cmc. According to other studies in aqueous micelles and similar association colloids,[12] in the present system it is assumed that the transfer of reactants is a crucial but fast equilibrium process[13] and that the reaction region is the micellar aqueous solution. Consequently, the obtained results can be interpreted in the light of current ideas on micellar catalysis[14] and of previous[5] data obtained with surfactant/substrate ratios $\gg 1$.

Thus, the results of Table 1 can be accounted for by the fact that, in the presence of cationic or zwitterionic micelles, the highly polarisable and hydrophobic enolate anion and the benzyl halide are both located in a region of the aggregate where the water activity is low, while the hydrophilic hydroxide ion is strongly hydrated in a water-rich region.[15, 16] On the contrary, in the presence of anionic micelles (SDS or SANa), the enolate anion cannot be fully compartmentalised with respect to the hydroxide anion because of electrostatic repulsion. Moreover, it is known[17] that the surface of SDS micelles is "water-rich" and that water activity is not much lower than in the bulk reaction medium. The benzyl halide is therefore extensively hydrolysed while reacting with the enolate in the presence of anionic micelles (Table 1).

Interestingly enough, we did not observe any surfactant alkylation product in the case of $C_{16}(CH_2CH_2OH)_2MeNB$, bis(2-hydroxyethyl)cetylmethylammonium bromide. The amount of NaOH present in the reaction mixture is probably enough to partly dissociate a choline-type hydroxide group transforming it into a good nucleophile. The fact that this surfactant did not react with benzyl chloride may depend on the location of the benzyl phenyl ketone in the surface of the aggregate, or on a very large reactivity difference between the enolate and the alkoxide ion. It is worth mentioning that the preference of the benzyl halide for a soft carbon nucleophile over a hard O-nucleophile is in agreement with all the experimental data of Table 1.

Comparison of the results obtained in the presence and in the absence of surfactant shows that the amount of ketone alkylation is much higher and that reactions are faster in the presence of micelles. The main reaction in the absence of surfactant is the (slow) hydrolysis of the benzyl halide to benzyl alcohol.

In the case of cyclohexyl halides (Table 2), the reaction is much slower (and more selective) than that of the benzyl halides. A somewhat different behaviour of cationic and zwitterionic surfactants can be envisaged with cyclohexyl halides. Thus, the higher reactivity in the presence of cationic surfactants can be understood in view of the higher electrostatic affinity of the enolate for the cationic head-groups of CTAX (cetyltrimethylammonium halide)[9, 18, 19] and the consequently higher binding constants[8] of the enolate with cationic than with zwitterionic [3-(dimethyldodecylammonium)propansulfonate (SB3-12)] micelles. Furthermore, the interfacial region of zwitterionic micelles is quite open[20] and accessible to water, and thus favours the hydrolysis of the cyclohexyl halide.

Phase-transfer catalysis: In order to check that the micelle-forming surfactants were not behaving as simple phase-transfer catalysts, benzyl phenyl ketone (0.5 mol dm^{-3}) was treated with an equimolar amount of benzyl bromide in the presence of non-micellizing tetrabutylammonium bromide (0.05 mol dm^{-3}) at 25 °C. After 1 h, only 67 % of the ketone had reacted, but in the reaction mixture the molar ratio of

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alkylation product and product of hydrolysis of the halide was only 4.5 (50/11). After 16 h, 84% of the ketone had reacted but the alkylation/hydrolysis ratio was essentially unchanged (72/14 = 5.0). The extensive hydrolysis of the halide observed in the presence of tetrabutylammonium bromide provides evidence that CTAB and SB3-12 promote the reaction in a way which is different from simple phase-transfer catalysis.

Temperature: The major effect produced by an increase in temperature on the reaction of both benzyl and cyclohexyl halides with benzyl phenyl ketone is an increase in the rate of hydrolysis of the halides (see Tables 1 and 2) according to known effects of temperature on micellar aggregates. Ion mobilities generally increase with increasing temperature, and hydration of the micelles also increases at high temperatures[21] thereby favouring reactions that occur in regions that are relatively richer in water.

Reagent ratios: α,α-(Dibenzyl)benzyl phenyl ketone was not detected in the product mixture of the reactions of Table 1. In other words, an excess of benzyl halide or of NaOH over benzyl phenyl ketone does not cause dialkylation of the ketone, probably because of steric reasons. An experiment performed at 25 °C with equimolar quantities of the reagents and reagent/CTAB ratio up to 20:1 (the fifth reaction in Table 1) did not show any appreciable change in product distributions [i.e., after 12 hours the molar composition of the reaction mixture was: α-(benzyl)benzyl phenyl ketone 96%, benzyl alcohol 2% and benzyl phenyl ketone 2%] with respect to the first reaction in Table 1. This fact suggests that the surfactant aggregates do behave as "true catalysts".

Structure of the alkyl halide: Benzyl chloride and benzyl bromide react very similarly with benzyl phenyl ketone (Table 1) and, in the presence of cationic and zwitterionic surfactants, give α-(benzyl)benzyl phenyl ketone as the major product. With methyl iodide (see the Experimental Section), which is sterically less hindered than benzyl halides, again only a monoalkylation product was observed, even if a large excess of MeI was used, probably as a consequence of the lower hydrophobicity of MeI as compared to benzyl halide and of the fact that methanol (the hydrolysis product) is effective in disturbing the aggregation of the zwitterionic surfactant.[21] The isolated α-methylbenzyl phenyl ketone did not undergo further reaction with methyl iodide (under the same reaction conditions) and only hydrolysis of the halide could be observed. It should be noted that α-methylbenzyl phenyl ketone has only one, less acidic, α-hydrogen and is sterically more hindered than benzyl phenyl ketone.

Cyclohexyl bromide and cyclohexyl iodide were, as expected,[1] much less reactive than the benzyl halides towards benzyl phenyl ketone under similar experimental conditions (compare the results of Tables 1 and 2).

However, it is noteworthy that with the cyclohexyl halides, in addition to the C-alkylation product, a large amount of O-alkylation of benzyl phenyl ketone was observed, probably as a result of steric hindrance between the electrophilic carbon atom of the halide and the soft carbon atom of the enolate anion in the transition state of the alkylation reaction. An increase of temperature from 60 to 80 °C only slightly changed the amount of O- versus C-alkylation products. Cyclohexyl iodide, as expected, reacted faster than cyclohexyl bromide and more C-alkylation product was obtained.

Alkylation of cyclohexanone, γ-phenylcyclohexanone and α-tetralone: Taking into account that with benzyl phenyl ketone "best results" had been obtained in the presence of CTAB, the reactions with the cyclohexanones and α-tetralone were carried out only in the presence of aggregates of CTAB (Table 3).

For both cyclohexanones the reactions were slower and alkylation yields lower than those with benzyl phenyl ketone. The product mixture contained a large percentage of benzyl alcohol (an average of 24% for cyclohexanone and 15% for γ-phenylcyclohexanone) and dibenzyl ether (an average of 16% for cyclohexanone and 10% for γ-phenylcyclohexanone). This is probably caused by the higher p*K*a of cyclohexanone (18.09)[2] and γ-phenylcyclohexanone compared with that of benzyl phenyl ketone (14.75).[22] Less enolate was formed under the experimental conditions used, more hydrolysis and/or etherification product was observed.

However, comparison of the results obtained for cyclohexanone with those for the more hydrophobic γ-phenylcyclohexanone (see Table 3) shows a higher alkylation yield (and less hydrolysis and etherification of benzyl halides) for the latter ketone. The O-alkylation products were present only in trace amounts for both ketones. The high hydrophobicity of γ-phenylcyclohexanone suggests that this ketone and the corresponding enol are located, together with the halide, in a region of the aggregate where water activity is low, namely away from the region where the hydrophilic hydroxide ion resides. This should enhance the probability for the halide to react with the enolate (whose nucleophilicity should be higher in less polar environments) rather than with the hydroxide ion or the solvent to give the hydrolysis product. Moreover, the higher amount of bis-alkylation products observed for γ-phenylcyclohexanone could be attributed to the fact that this compound is sterically more hindered than cyclohexanone. Steric hindrance stabilizes[23] the enol of γ-phenylcyclohexanone and, to a greater extent, the enol of α-benzyl-γ-phenylcyclohexanone. This increases the concentration of the latter enol in the Stern layer of the micelles.

Let us finally look at the results obtained from the reaction of α-tetralone with benzyl chloride (Table 3).

With regard to competition between positions 2 and 4 of α-tetralone as the alkylation sites, we have observed that, under the experimental conditions used, the C-monoalkylation reaction occurred exclusively in position 2. The yield in alkylation products (C-alkylation plus O-alkylation) was only about 53% as the process was accompanied by extensive hydrolysis and etherification of benzyl chloride. C-Alkylation largely prevailed over O-alkylation, again presumably because of the higher nucleophilicity of the soft carbon atom, as compared to the hard oxygen atom of the enolate ion. Interestingly, the O-alkylation product underwent subsequent aromatisation to give benzyl naphthyl ether as the final product.

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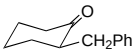
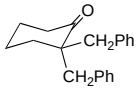
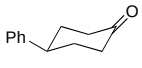
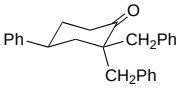
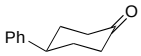
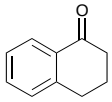
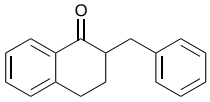
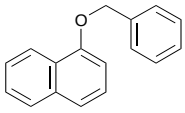
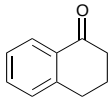
Table 3. Alkylation of cyclohexanone (0.1 mol dm^{-3}), γ-phenylcyclohexanone (0.1 mol dm^{-3}) and α-tetralone (0.1 mol dm^{-3}) with benzyl halide (0.1 mol dm^{-3}) in an aqueous solution of CTAB (0.05 mol dm^{-3}) and NaOH (1 mol dm^{-3}): concentration of reagents, experimental conditions, yields and product distribution in the reaction mixture.

Ketone	Halide	T [°C]	t [h]	Reacted ketone [mol %]	Product distribution in the reaction mixture [mol %][a]				
							$PhCH_2OH$	$(PhCH_2)_2O$	
	$PhCH_2Br$	25	48	41	18	8	22	15	37
	$PhCH_2Cl$	25	72	33	16	4	24	16	40
	$PhCH_2Br$	60	12	30	15	3	25	16	41
	$PhCH_2Cl$	60	48	25	13	1	26	17	43
							$PhCH_2OH$	$(PhCH_2)_2O$	
	$PhCH_2Br$	25	48	73	45	12	13	9	22
	$PhCH_2Cl$	25	72	69	47	5	14	10	24
	$PhCH_2Br$	60	12	69	41	11	14	10	24
	$PhCH_2Cl$	60	48	55	37	2	19	12	31
							$PhCH_2OH$	$(PhCH_2)_2O$	
	$PhCH_2Cl$	25	20	53	31	4	17	17	31

[a] Product distribution [mol %] determined experimentally by gas chromatography analyses.

Reactions in non-aqueous solvents: Analogous alkylation reactions of the less reactive γ-phenylcyclohexanone with benzyl halides have been attempted in non-aqueous solvents. In ethanol/ethoxide ion, and with the same reactant ratios and temperature as in aqueous surfactant (Table 3), the only isolated product was benzyl ethyl ether. However, in anhydrous DMSO and with KOH as the base, reaction yields and products were similar to those obtained in aqueous solutions of CTAB or the zwitterionic surfactants.

Experimental Section

Materials: 3-(Dimethyldodecylammonium)propansulfonate (SB3-12) and cetyltrimethylammonium bromide (CTAB) were commercial samples (Fluka) purified by recrystallisation from acetone and ethanol/diethyl ether, respectively. Benzyl bromide, benzyl phenyl ketone, cyclohexyl iodide, sodium *N*-lauroylsarcosinate (SANa), sodium dodecylsulfate (SDS) were commercial samples from Fluka; cyclohexyl bromide, cyclohexanone, γ-phenylcyclohexanone, tetrabutylammonium bromide were from Aldrich; α-tetralone was from Janssen; benzyl chloride and methyl iodide were from Carlo Erba. These compounds were used without further purification. Bis(2-hydroxyethyl)hexadecylmethylammonium bromide [$C_{16}(CH_2CH_2OH)_2MeNB$] was synthesized following a described procedure.[24]

Instruments: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC200E (Bruker, Ettlingen, Germany) spectrometer and are reported in ppm (δ) relative to $CDCl_3$ as the internal reference. Gas chromatographic analyses, on a HP5890 gas chromatography system equipped with a flame-ionisation detector (FID), were performed with a fused-silica wide-bore column (30×0.53 mm), using poly(5 % diphenyl/95 % dimethylsiloxane) (CP = 8) or poly(dimethylsiloxane) (CP = 5) as the stationary phase. The melting points were determined on a Büchi 510 melting point apparatus. Mass spectra were recorded on a GC/MS Varian Saturn 2000.

Alkylation of enolate ions: The reactions were performed either in an aqueous solution containing the surfactant or in bidistilled water. The temperature was kept constant in a thermostatted silicone bath. The reaction mixture was then extracted with diethyl ether ($4 \times$ 10 mL), and when more than one product was obtained the separation was achieved by silica gel chromatography with an hexane/ethyl acetate mixture as the eluent. The product distribution was determined by gas chromatography. The yields were calculated as percentage of reacted ketone. The measured yields were in good agreement with those calculated according to ref. [25]. The products gave satisfactory ^{1}H and ^{13}C NMR and/or GC-MS spectra.

Alkylation of benzyl phenyl ketone: Benzyl phenyl ketone and the halide (benzyl and cyclohexyl halide) were added with stirring to an aqueous solution (10 mL) of 5×10^{-2} mol dm^{-3} surfactant and NaOH (1 or 2 mol dm^{-3}). No surfactant was added when the blank reaction was performed. Product distribution in the reaction mixture, temperatures and times of reaction are reported in Tables 1 and 2. The reagent molar ratio ketone/halide was kept constant [1:1 (in the case of benzyl halides also the ratio 1:2 was studied)] but the concentrations were varied in the range 0.05 – 1 mol dm^{-3} in order to test the effect of the surfactant when the ratio substrate/surfactant was increased from 1:1 to 20:1.

Halide: **methyl iodide**: Benzyl phenyl ketone (1 mmol) and methyl iodide (1 mmol) were added with stirring to an aqueous solution (10 mL) of 5×10^{-2} mol dm^{-3} SB3-12 and 1 mol dm^{-3} NaOH. After 30 minutes, the recovered product was identified as α-methylbenzyl phenyl ketone (yield: 97 %). SB3-12 was used as the surfactant because CTAI is insoluble in the reaction mixture at room temperature.

Benzylation of cyclohexanone: Cyclohexanone (1 mmol) and benzyl halide (1 mmol) were added with stirring, to an aqueous solution (10 mL) of 5×10^{-2} mol dm^{-3} CTAB and 1 mol dm^{-3} NaOH. The product distribution in the reaction mixture and the experimental conditions are collected in Table 3. A small amount of α,ε-dibenzylcyclohexanone was also isolated. No difference in product distribution was found when the concentration of the starting material was increased.

Benzylation of γ-phenylcyclohexanone: γ-Phenylcyclohexanone (1 mmol) and benzyl halide (1 mmol) were added with stirring to an aqueous solution (10 mL) of 5×10^{-2} mol dm^{-3} CTAB and 1 mol dm^{-3} NaOH. The product distribution in the reaction mixture and the experimental conditions are

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collected in Table 3. Further NMR experiments on a Varian Inova 500 MHz (the data are available in Table S1 of the Supporting Information) and some theoretical calculations (Table S2 of the Supporting Information) show that only the *cis* diastereomer is obtained from the alkylation reaction under the experimental conditions used. An exhaustive discussion on this point can be found in the section "Structural analysis of α-benzyl-γ-phenylcyclohexanone" in the Supporting Information.

Benzylation of α-tetralone: α-Tetralone (1 mmol) and benzyl halide (1 mmol) were added with stirring to an aqueous solution (10 mL) of 5×10^{-2} mol dm^{-3} CTAB and 1 mol dm^{-3} NaOH. The product distribution in the reaction mixture, recovered after 20 h at room temperature, is reported in Table 3.

Identification of the products: Compounds were identified by their ^{1}H and ^{13}C spectra (see below). A software package from Advanced Chemistry Development Inc. that calculates ^{13}C NMR spectra was used to check the assignments of the chemical shifts.

***α*-(Benzyl)benzyl phenyl ketone**:[26] White crystalline solid; m.p. 121.5–122.5 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 3.06$ (dd, $^3J(H,H) = 7.0$, $^2J(H,H) = 13.8$ Hz, 1H; CH_aH_b), 3.56 (dd, $^3J(H,H) = 7.5$, $^2J(H,H) = 13.8$ Hz, 1H; CH_aH_b), 4.81 (t, $^3J(H,H) = 7.3$ Hz, 1H; C*H*), 7.03–7.47/7.85–7.95 (m, 15H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta =$ 40.12 (*C*H$_2$), 55.91 (*C*H), 126.13 (Ph^2 C_{sp^2}H4), 127.15 (Ph^3 C_{sp^2}H4), 132.85 (Ph^1 C_{sp^2}H4), 128.23 (Ph^3 C_{sp^2}H3,5), 128.30 (Ph^2 C_{sp^2}H3,5), 128.48 (Ph^1 C_{sp^2}H3,5), 128.69 (Ph^1 C_{sp^2}H2,6), 128.90 (Ph^3 C_{sp^2}H2,6), 129.14 (Ph^2 C_{sp^2}H2,6), 136.72 (Ph^2 C_{sp^2}H1), 139.08 (Ph^1 C_{sp^2}H1), 139.78 (Ph^3 C_{sp^2}H1), 199.23 (*C*O).

***α*-Cyclohexylbenzyl phenyl ketone**: White crystalline solid; m.p. 119–120 °C (hexane) [lit.:[27] m.p. 118–119 (petroleum ether)]; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.70$–2.00 (m, 10H; CH_2 cyclohexane), 2.37 (qt, $^3J(H,H) = 3.3$ Hz, $^3J(H,H) = 10.6$ Hz, 1H; C*H* cyclohexane), 4.38 (d, $^3J(H,H) = 10.3$ Hz, 1H; C*H*), 7.10–8.05 (m, 10H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 26.05$, 26.10, 26.40 (cyclohexane *C*H$_2$ 3,4,5), 30.64, 32.51 (cyclohexane *C*H$_2$ 2,6), 41.10 (cyclohexane *C*H), 59.94 (*C*H), 126.84 (Ph^2 C_{sp^2}H4), 132.67 (Ph^1 C_{sp^2}H4), 128.24, 128.38, 128.55, 128.77 (C_{sp^2}H2,3;5,6), 137.66 (Ph^2 C_{sp^2}H1), 137.93 (Ph^1 C_{sp^2}H1), 200.54 (*C*O).

Cyclohexyl α[α,β-diphenylethenyl] ether: Colourless liquid; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.90$–2.0, (m, 10H; CH_2 cyclohexane), 3.65–3.85 (m, 1H; C*H* cyclohexane), 5.95 (s, 1H; C*H*), 7.10–8.05 (m, 10H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 26.05$, 26.10, 26.40 (cyclohexane *C*H$_2$ 3,4,5), 30.64, 32.51 (cyclohexane *C*H$_2$ 2,6), 41.10 (cyclohexane *C*H), 59.94 (*C*H), 126.84 (Ph^2 C_{sp^2}H4), 132.67 (Ph^1 C_{sp^2}H4), 128.24, 128.38, 128.55, 128.77 (C_{sp^2}H2,3;5,6), 137.66 (Ph^2 C_{sp^2}H1), 137.93 (Ph^1 C_{sp^2}H1), 200.54 (*C*O); MS (70 eV): *m*/*z* (%): 278 (8) $[M]^+$, 196 (100), 118 (24), 67 (53), 39 (34).

***α*-Benzylcyclohexanone**:[28] Colourless liquid (b.p.[28a] 110 °C at 1 mm Hg); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.10$–2.60 (m, 10H; CH_2), 3.19 (dd, $^3J(H,H) = 4.6$, $^2J(H,H) = 13.6$ Hz, 1H; CH_aH_b), 7.05–7.35 (m, 5H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 24.48$ (cyclohexane *C*H$_2$ 4), 27.46 (cyclohexane *C*H$_2$ 5), 32.82 (cyclohexane *C*H$_2$ 3), 34.95 (*C*H$_2$), 41.50 (cyclohexane *C*H$_2$ 6), 51.73 (*C*H), 125.35 (C_{sp^2}H4), 127.70 (C_{sp^2}H3,5), 128.57 (C_{sp^2}H2,6), 139.82 (C_{sp^2}H1), 211.20 (*C*O).

α,α-Dibenzylcyclohexanone: White crystalline solid; m.p. 63–65 °C (hexane) [lit.:[29] 64.5–65 °C (PhH/EtOH)]; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.60$–2.60 (m, 8H; CH_2), 2.77 (d, $^2J(H,H) = 13.3$ Hz, 2H; CH_2), 3.17 (d, $^2J(H,H) = 13.3$ Hz, 2H; CH_2), 7.12–7.40 (m, 10H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 20.48$ (cyclohexane *C*H$_2$ 4), 25.46 (cyclohexane *C*H$_2$ 5), 33.37 (cyclohexane *C*H$_2$ 6), 39.43 (cyclohexane *C*H$_2$ 3), 41.88 (*C*H$_2$), 53.65 (*C*), 126.08 (C_{sp^2}H4), 127.73 (C_{sp^2}H3,5), 130.50 (C_{sp^2}H2,6), 137.36 (C_{sp^2}H1), 213.72 (*C*O).

α,ε-Dibenzylcyclohexanone: White crystalline solid; m.p. 115–117 °C (hexane); m.p. 120–121 °C (methanol) [lit. [29] m.p. 121–122 °C (methanol)]; *cis*-α,ε-dibenzylcyclohexanone[30] m.p. 124–125 °C; *trans*-α,ε-dibenzylcyclohexanone[30] m.p. 49–51 °C); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.20$–2.21 (m, 6H; cyclohexane CH_2), 2.40 (dd, $^3J(H,H) = 8.7$, $^2J(H,H) = 13.8$ Hz, 2H; CH_aH_b), 2.49–2.65 (m, 2H; C*H*), 3.21 (dd, $^3J(H,H) = 4.7$, $^2J(H,H) = 13.8$ Hz, 2H; CH_aH_b), 7.12–7.32 (m, 10H; $C_{sp^2}H$); *^{13}C NMR (200 MHz, $CDCl_3$, 25 °C)*: $\delta = 25.36$ (cyclohexane *C*H$_2$ 4), 34.87 (cyclohexane *C*H$_2$ 3,5), 35.51 (*C*H$_2$), 52.92 (*C*H), 125.93 (C_{sp^2}H4), 128.30 (C_{sp^2}H3,5), 129.18 (C_{sp^2}H2, 6), 140.60 (C_{sp^2}H1), 212.90 (*C*O).

***α*-Benzyl*γ*-phenylcyclohexanone**: White crystalline solid; m.p. 92–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) $\delta = 1.63$ (q, $J(H,H) = 12.85$ Hz, 1H; H_{3a}) 1.92 (m, 1H; H_{5a}) 2.14–2.24 (m, 2H; H_{5e}, H_{3e}), 2.41 (dd, $^3J(H,H) = 9.0$ Hz, $^2J(H,H) = 14.1$ Hz, 1H; CH*H*Ph), 2.53 (m, 2H; H_6), 2.75 (m, 1H; H_2), 3.00 (tt, $^3J(H,H) = 3.5$ Hz, $^3J(H,H) = 12.45$ Hz, 1H; H_4), 3.32 (dd, $^3J(H,H) = 4.6$ Hz, $^2J(H,H) = 14.1$ Hz, 1H; CH*H*Ph), 7.10–7.30 (m, 10H; $C_{sp^2}H$); ^{13}C NMR (500 MHz, $CDCl_3$, 25 °C, TMS) $\delta = 34.93$ (cyclohexane *C*H$_2$ 5), 35.10 (*C*H$_2$), 40.34 (cyclohexane *C*H$_2$ 3), 41.55 (cyclohexane *C*H$_2$ 6), 43.14 (cyclohexane *C*H4), 51.55 (cyclohexane *C*H2), 125.84 (C_{sp^2}H4), 126.40 (C_{sp^2}H4′), 126.53 (C_{sp^2}H2′,6′), 128.18 (C_{sp^2}H3,5), 128.38 (C_{sp^2}H3′,5′), 128.98 (C_{sp^2}H2,6), 139.96 (C_{sp^2}H1), 144.42 (C_{sp^2}H1′), 211.18 (*C*O); MS (70 eV): *m*/*z* (%): 264 (89) $[M]^+$, 146 (25), 131 (29), 117 (46), 115 (39), 91 (100), 78 (36), 77 (32), 65 (43), 39 (25).

α,α-Dibenzyl-γ-phenylcyclohexanone: White crystalline solid; m.p. 91–92 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.41$ (qd, $J(H,H) = 5.15$, $J(H,H) = 12.45$ Hz, 1H) 1.80–3.20 (m, 9H; CH_2, C*H*), 3.35 (d, $J(H,H) = 13.3$ Hz, 1H) 7.00–7.40 (m, 15H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 32.24$ (cyclohexane *C*H$_2$ 5), 38.54 (cyclohexane *C*H4), 39.79, 41.02 (*C*H$_2$), 42.00 (*C*H$_2$ 3 cyclohexane), 44.80 (cyclohexane *C*H$_2$ 6), 54.08 (cyclohexane *C*H2), 125.84 and 126.14 (C_{sp^2}H4), 126.59 (C_{sp^2}H4′), 126.30 (C_{sp^2}H2′,6′), 128.23 (C_{sp^2}H3′,5′), 127.60/128.00 (C_{sp^2}H2,6), 130.03/130.90 (C_{sp^2}H3,5), 136.79/137.92 (C_{sp^2}H1), 145.18 (C_{sp^2}H1′), 213.86 (*C*O); MS (70 eV): *m*/*z* (%): 354 (5) $[M]^+$, 264 (23), 263 (100), 65 (24).

***α*-Methylbenzyl phenyl ketone**:[31a] White crystalline solid; m.p. 49–50 °C (hexane) [lit.[31b] 53 °C (ethanol); m.p.[31c] 50–51 °C (methanol)]; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.65$ (d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 4.80 (q, $^3J(H,H) = 6.9$ Hz, 1H; C*H*), 7.15–7.55 and 8.05–8.15 (m,10H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 19.91$ (*C*H$_3$), 48.13 (*C*H), 127.25 (Ph^2 C_{sp^2}H4), 128.11 (Ph^2 C_{sp^2}H2,6), 128.82 (Ph^2 C_{sp^2}H3,5), 129.11 (Ph^1 C_{sp^2}H3,5), 129.34 (Ph^1 C_{sp^2}H2,6), 133.12 (Ph^1 C_{sp^2}H4), 136.76 (Ph^2 C_{sp^2}H1), 141.87 (Ph^1 C_{sp^2}H1), 200.48 (*C*O).

***β*-Benzyl-*α*-tetralone**:[32] White crystalline solid; m.p. 50–51 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.67$–1.86, 2.03–2.16, 2.58–3.00 (m, 6H; CH_2), 3.51 (dd, $J(H,H) = 3.8$ Hz, $^3J = 13.3$ Hz, 1H; C*H*), 7.17–7.35 (m, 7H; $C_{sp^2}H$), 7.47 (td, $J(H,H) = 1.4$, $^3J(H,H) = 8.2$ Hz, 1H; $C_{sp^2}H$) 8.68 (dd, $J(H,H) = 1.1$ Hz, $^3J(H,H) = 8.5$ Hz, 1H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 27.63$ (tetralone *C*H$_2$ 3), 28.60 (tetralone *C*H4), 35.65 (*C*H$_2$), 49.43 (*C*H), 126.11 (C_{sp^2}H4), 126.60 (tetralone C_{sp^2}H7), 127.51 (tetralone C_{sp^2}H5), 128.70 (tetralone C_{sp^2}H6), 133.26 (tetralone C_{sp^2}H8), 128.38 (C_{sp^2}H3,5), 129.25 (C_{sp^2}H2,6), 132.44 (tetralone C_{sp^2}H4a), 140.02 (C_{sp^2}H1), 144.00 (tetralone C_{sp^2}H8a), 199.36 (*C*O).

Benzyl naphthyl ether:[33] White crystalline solid; m.p. 75–77 °C (hexane) [lit.[33] 76–77 °C (ethanol)]; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 5.26$ (s, 2H; CH_2), 6.85–6.95, 7.30–7.60, 7.75–7.90, 8.30–8.45 (m, 12H; $C_{sp^2}H$); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 70.07$ (*C*H$_2$), 105.18 (naphthalene C_{sp^2}H2), 120.50 (naphthalene C_{sp^2}H4), 122.21 (naphthalene C_{sp^2}H5), 125.25 (naphthalene C_{sp^2}H8), 125.78 (naphthalene C_{sp^2}H4a), 125.84 (naphthalene C_{sp^2}H3), 126.46 (naphthalene C_{sp^2}H7), 127.38 (benzene C_{sp^2}H3,5), 127.47 (naphthalene C_{sp^2}H6), 127.93 (benzene C_{sp^2}H4), 128.60 (benzene C_{sp^2}H2,6), 134.56 (naphthalene C_{sp^2}H8a), 137.17 (benzene C_{sp^2}H), 154.51 (*C*O).

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