

Applications of surfactant-modified clays to synthetic organic chemistry

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Abstract—Two triphase catalysts (SLL) have been developed for organic phase–aqueous phase reactions catalyzed by suitable modified clay (solid phase). These triphase catalysts have been applied to nucleophilic displacement on activated (benzylic) as well as unactivated organic halides and provide a convenient and effective method of preparation of the corresponding products. Other useful transformations to, which these triphase catalysts have been successfully applied are the synthesis of 9,9-dichloro bicyclo[6.1.0]nonane, O-alkylation and C-alkylation of β -naphthol.

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1. Introduction

A significant and recurring problem in organic synthesis stems from use, or desired use, of a water-soluble reagent in chemically altering a water-insoluble organic substrate. If the reaction is conducted as a heterogeneous process (e.g., organic phase–aqueous phase reaction) observed reaction rates are normally very slow owing to the low concentration of at least one of the reactants in each phase. Techniques available to circumvent this problem rely on the use of rapid stirring, co-solvent, and phase-transfer methods. If a chemical reaction takes place at a liquid–liquid phase boundary, rapid stirring may have an accelerating effect by increasing interfacial contact.¹ Alternatively, the addition of a co-solvent can bring about a homogeneous state and thereby completely eliminate phase separation. Although this latter approach is often useful, product mixtures are necessarily made more complex and the resulting work-up made difficult. In addition, with aqueous phase–organic phase reactions, use of a co-solvent not only renders the organic substrate accessible to the reagent, but also increases the substrates contact with water and can promote competing hydrolytic pathways. Previously, another technique was developed, which appeared to have considerable potential; this method has been referred to as phase-transfer catalysis.^{2,3} In brief, an organic-soluble, partially water-soluble catalyst (most commonly a tetraalkylammonium or tetraalkylphosphonium salt) accelerate an aqueous–organic phase reaction, presumably, by extracting a given ionic

reagent out of water and into the bulk organic phase where reaction can ensue.^{4,5} One practical limitation to the phase-transfer method, however, is that many of the catalysts employed promote the formation of stable emulsions.

Regen developed a technique centering around the use of a solid phase catalyst to accelerate aqueous–organic phase reactions (triphase catalysis), which had a considerable advantages over those methods described above.⁶ In this technique, not only would catalyst recovery and product isolation be greatly simplified, but also, owing to the three-phase nature of the system, a continuous flow method could be employed, making the technique particularly attractive for industrial applications. In this respect, another promising field of application of triphase catalysis is that of certain organic clays, as triphase catalysts in nucleophilic displacement reactions. For example, the methyltrioctylammonium exchanged form of hectorite gives very high yields over a wide range of nucleophiles.⁷

We previously demonstrated the feasibility of triphase catalysis for the oxidation of 2-ethylhexanol (organic phase) by dichromate ion (aqueous phase) catalyzed by a suitable modified clay (solid phase).⁸ The work described in this paper, was carried out to expand the scope of these modified clays by applying them to a variety of useful synthetic transformations.

2. Results and discussion

2.1. Modified clays

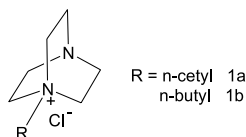
Natural bentonite from salafchegan, Iran, gray in color was

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used. It had the following chemical composition (in wt%): SiO₂ (65.04), Fe₂O₃ (1.67), MgO (1.87), Al₂O₃ (13.61), CaO (2.01), TiO₂ (0.19), Na₂O (2.26), K₂O (0.75).⁹ Since, XRD analysis revealed the presence of significant amounts of quartz and feldspar, the raw material was purified with the following procedure. A 4 wt% bentonite slurry in water was prepared and swollen at room temperature under continuous stirring. After 5 h, the concentration of the suspension was diluted to 2 wt% by addition of 0.1 M NaCl solution. The suspension was stirred overnight followed by decantation. The ion exchange procedure was repeated three times with fresh NaCl solution. Finally, the solid was washed free of chloride ions. At the last washing, stirring was stopped; the particles contained in the suspension were separated from the quartz deposits and centrifuged. The cake was dried at room temperature. The BET surface area of the unmodified Na-bentonite was 63 m²/g.

1-Cetyl-4-aza-1-azonia bicyclo[2.2.2]octane chloride (**1a**) and 1-butyl-4-aza-1-azonia bicyclo[2.2.2]octane (**1b**) were selected as the surfactants for modifying the bentonite. The reason for choosing these surfactants for modification of bentonite was that they could be synthesized very easily, and the polar heads of the surfactants have free nitrogen that is able to participate in hydrogen bonding, in addition, to electrostatic interaction between positive charge of surfactant with negative site of the bentonite surface. PTC supported on bentonite was prepared by loading 0.1 g (2.4 mmol of **1a** or 4.0 mmol of **1b**) of surfactant on 1 g of bentonite. The catalysts obtained from this modification are identified hereafter by **1a**-clay and **1b**-clay.



Based on the physical analysis of the adsorption system and adsorption process, it is recognized¹⁰ that the radical characteristics of the adsorption of surfactant at the solid/liquid interface should include two main points. First, according to the nature of adsorption there must be some attraction between surfactant molecules and the bentonite surface, which forces the surfactant molecules to transfer from bulk solution to the bentonite surface. The second one comes from the character of surfactant. It is well known that a surfactant is a kind of organic compound consisting of a hydrophilic part and a hydrophobic part. The tail exhibits the hydrophobic effect,¹¹ and in aqueous surfactant solutions above the critical micelle concentration, individual surfactant molecules will aggregate and form micelles. If the molecules of surfactant are adsorbed at the solid/liquid interface, they should also exhibit the hydrophobic effect to some extent, hence, form aggregates at solid/liquid interface with other molecules of surfactant, in the range of concentration of bulk solution. Therefore, the formation of surface aggregates can be envisaged as a superficial analogue of micellization in the bulk solution, these surface aggregates may be of different shape and size, including the so-called hemimicelles.^{12,13}

It occurred to us to develop an old technique¹⁴ centering on

the use of solid phase catalysts, which show different degree of hydrophobicity. These new phase-transfer catalysts⁸ would have considerable advantages over the previously mentioned triphase-catalysts.

2.2. Synthesis of nitriles

Nucleophilic displacement by cyanide ion on organic halides represent the most commonly used method for the preparation of nitriles. Despite the usefulness of this approach, however, the required used of water and/or other polar and potentially nucleophilic solvent needed to dissolve both the cyanide salt and the organic substrate introduces distinct limitations. In particular, competing hydrolysis and ether formation can lead to low yield of nitrile.¹⁵ Phase-transfer catalysis procedures have been successfully utilized in cyanide displacement reactions involving simple alkyl halides.^{4,5,16} Durst in the past reported that phase-transfer catalyzed cyanide displacement on activated halides, e.g., benzyl chloride (or bromide), gave significantly higher yields of nitrile when conducted as liquid–solid rather than liquid–liquid system.¹⁷

A physical phenomenon, which, if present, may make important contribution to certain triphase catalysis transformation refers to as ‘surface area catalysis’.¹⁴ On the basis of this phenomenon, it is possible that these modified clays generating microscopic aqueous and organic pools, the composition of which is either similar or identical to the external bulk phases. Modified clays used in this work may operate in part by generating extensive ‘pool/pool phase boundary’ thereby increasing the rate of interfacial reaction. We have found that by choosing an appropriate condition in the microenvironment of the reactive site in the ‘pool’, the displacement of nucleophile (e.g., cyanide ion) on alkyl halide, provides a simple and effective means for converting activated as well as unactivated organic halides to their corresponding products (Table 1). As can be seen in the Table 1, if we modify the clay material with **1a**, benzyl chloride converts very easily to benzyl cyanide at room temperature in petroleum ether. But displacement of cyanide ion on 1,6-dibromohexane does not occur in this condition. Even by changing the solvent to toluene and conducting the reaction at 90 °C, after 24 h, the displacement leads to 7-bromoheptanenitrile in less than 5%. One could help the microenvironment of the reactive site in the ‘pool’, by substituting toluene or petroleum ether with a more polar solvent. 1,6-Dibromohexane reacts with cyanide ion in the presence of **1a**-clay, in chloroform as solvent at 58 °C and produces 7-bromoheptanenitrile (37%) and 1,6-hexanedicarbonitrile (39%). Furthermore, by using a less hydrophobic environment, i.e., using **1b**-clay and increasing the polarity of microenvironment, this reaction could be done in toluene (Table 1).

2.3. Halogen exchange

Although many procedures are available for exchanging halogen in organic halides, we have found that the modified clay as the triphase catalyst furnishes a convenient method for carrying out such transformations. Examples illustrating the utility of these modified clays to catalyze halogen exchange are provided in Table 1. The fact that catalyst

Table 1. Synthetic applications of modified clay

Reactant	Product	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield ^a (%)
Cyanide displacement						
Benzyl chloride	Benzyl cyanide	1a -clay	Pet. ether	25	24	86
1,6-Dibromohexane	—	1a -clay	Pet. ether	25	24	NR
1,6-Dibromohexane	7-Bromoheptanenitrile	1a -clay	Toluene	90	24	<5
1,6-Dibromohexane	7-Bromoheptanenitrile	1a -clay	CHCl ₃	58	24	37
	1,6-Dicyanohexane					39
1,6-Dibromohexane	7-Bromoheptanenitrile	1b -clay	Toluene	90	24	18
	1,6-Dicyanohexane					50
<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl cyanide	1a -clay	Toluene	90	24	5
<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl cyanide	1b -clay	Toluene	90	24	75
Halogen exchange						
Benzyl chloride	Benzyl iodide	1a -clay	Pet. ether	25	24	50
Benzyl chloride	Benzyl bromide	1a -clay	Pet. ether	25	24	25
Benzyl chloride	Benzyl bromide	1a -clay	Toluene	90	6	80
1,6-Dibromohexane	1-Bromo-6-iodohexane	1a -clay	Pet. ether	25	24	<5
1,6-Dibromohexane	1-Bromo-6-iodohexane	1a -clay	CHCl ₃	25	24	<5
1,6-Dibromohexane	1-Bromo-6-iodohexane	1a -clay	CHCl ₃	58	24	39
	1,6-Diodohexane					41
1,6-Dibromohexane	1-Bromo-6-iodohexane	1b -clay	CHCl ₃	58	24	<5
<i>n</i> -Cetyl bromide	—	1a -clay	Pet. ether	25	24	NR
<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl iodide	1b -clay	CHCl ₃	58	24	58

^a Yields are determined by GLC based upon the reactant.

activity of the modified clays change with their hydrophilicity and the polarity of solvent, suggests that in the microenvironment of the reactive site all of the components of the system play their role.

2.4. Synthesis of dichloro bicyclo[6.1.0]nonane

Dichlorocarbene addition to the alkenes provides an attractive route to dichlorocyclopropanes.^{18,19,20} We have found that dichlorocarbene can be conveniently generated by the addition of **1a**-clay to mixture of 50% aqueous sodium hydroxide and chloroform at 58 °C. When cyclooctene is added to the mixture, the high yield of the corresponding dichlorocyclopropane is formed (Table 2).

2.5. Synthesis of thiocyanate

We have found that these modified clays provide a simple and effective means for converting organic halides to their corresponding thiocyanates (Table 2).

Table 2. Synthetic applications of modified clay

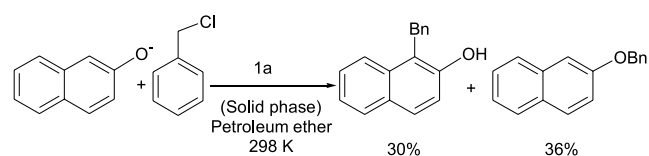
Reactant	Product	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield ^a (%)
Dichlorocarbene addition						
Cyclooctene	9,9-Dichloro-bicyclo[6.1.0]nonane	1a -clay	CHCl ₃	58	24	96
Cyclooctene	9,9-Dichloro-bicyclo[6.1.0]nonane	1a -clay	CHCl ₃	25	24	NR
Thiocyanate displacement						
<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl thiocyanate	1b -clay	Pet. ether	25	24	NR
<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl thiocyanate	1a -clay	CHCl ₃	58	24	60
	<i>n</i> -Cetyl isothiocyanate					<2
<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl thiocyanate	1b -clay	Toluene	90	24	50
	<i>n</i> -Cetyl isothiocyanate					<1
C-alkylation and O-alkylation						
2-Naphthol	1-Benzyl-2-naphthol	1a -clay	Pet. ether	25	15	30 ^b
	Benzyl-2-naphthyl ether					36 ^b

^a Yields are determined by GLC based upon the reactant.

^b Isolated yield.

2.6. C-Alkylation and O-alkylation of naphthoxide

Phenoxides undergo O-alkylation in solvents such as DMSO, DMF, ethers and alcohols. In water and trifluoroethanol, however, selective C-alkylation occurs.^{21,22} On the basis of the percentage of the C-alkylated and O-alkylated products it is possible to make a justifiable statement about the polarity of the microenvironment of the active site in our triphase system that is something between the polarity of aprotic and protic solvents, although the solvent is petroleum ether (Scheme 1).

**Scheme 1.**

An essential part of such a study was to establish the value of including the bentonite. In this respect, we compared the results obtained in the triphasic reactions with a series of

Table 3. Control experiments

Entry	Reactant	Product	Time (h)	Temperature (°C)	Solvent	Exp. condition			
						Without surfactant and clay	Clay alone	Surfactant alone	Catalysts
1	Benzyl chloride	Benzyl cyanide	24	25	Pet. ether	NR	NR	4%	86% ^a
2	1,6-Dibromohexane	7-Bromoheptanenitrile	24	58	CHCl ₃	0.5%	0.5%	21%	37% ^a
		1,6-Dicyanohexane				NR	NR	9%	39%
3	1,6-Dibromohexane	7-Bromoheptanenitrile	24	90	Toluene	6.6%	0.6%	6.6%	18% ^b
		1,6-Dicyanohexane				3.3%	NR	3.3%	50%
4	<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl cyanide	24	90	Toluene	<1%	<1%	<1%	75% ^b
5	Benzyl chloride	Benzyl bromide	6	90	Toluene	17%	21%	21%	80% ^a
6	1,6-Dibromohexane	1-Bromo-6-iodohexane	24	58	CHCl ₃	8.5%	1%	35.6%	39% ^a
		1,6-Diodohexane				0.3%	NR	8.6%	41%
7	<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl iodide	24	58	CHCl ₃	<1%	<1%	<1%	58% ^b
8	Cyclooctene	9,9-Dichloro-bicyclo-[6.1.0]nonane	24	58	CHCl ₃	4%	0.5%	80%	96% ^a
		<i>n</i> -Cetyl thiocyanate				0.5%	NR	11%	60% ^a
9	<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl thiocyanate	24	58	CHCl ₃	1%	1.1%	13%	<2%
		<i>n</i> -Cetyl isothiocyanate				<1%	<1%	<1%	50% ^b
10	<i>n</i> -Cetyl bromide	<i>n</i> -Cetyl thiocyanate	24	58	CHCl ₃	<1%	<1%	<1%	<1%

^a **1a**-clay.^b **1b**-clay.

control experiments in, which the bentonite has been omitted (i.e., a two-phase system with only the quaternary ammonium salt as the catalyst). Table 3 compares the yield, and product ratio of different control reactions on the most appropriate conditions cited in Table 1. Data in Table 3 shows that phase-transfer catalyzed displacement reactions on activated and unactivated halides gave significantly higher yields when conducted as liquid–solid rather than liquid–liquid system. An interesting point with regard to the nucleophilic substitution reactions in the presence of **1b**, was that this quaternary ammonium salt is completely soluble in water and does not show any catalytic activity in the absence of bentonite (entries 3c, 4c, 7c and 10c in Table 3). But when this quaternary ammonium salt supported on bentonite, it shows a good catalytic activity in some conditions. For example, cyanide displacement on unactivated bromide (e.g., entry 4) gave significantly higher yield of nitrile (75%) when **1b** supported on bentonite.

The results reported here demonstrate that these modified bentonites possess considerable advantages over traditional procedures for nucleophilic substitution reactions. The reactions are clean, good yielding, and work-up is simple, and the catalysts stay active for at least five times after first used.

3. Experimental

3.1. General methods

Unless stated otherwise, all reagents were obtained commercially and were used without further, purification. All alkyl and benzyl halides as well as cyclooctene and 2-naphthol were purchased from Merck Chemical Co. and used as obtained. Product mixtures were analyzed by GLC (Shimadzo Gas Chromatograph, GC 6A) flame ionization instrument using a OV-17 column (2 m) or a Carbowax 20M column (2 m) and a FID detector.

Appropriate response factors relative to an internal standard were determined for each different substance analyzed. HRMS (EI) of all new compounds were performed on a Finnigan MAT 95 double focusing mass spectrometer, equipped with an EI ion source operated at 70 eV.

3.2. Displacement of cyanide ion on organic halides

To a Morton flask (100 ml) containing 0.5 g of **1a**-clay was added a solution of 0.4 g (8.5 mmol) of sodium cyanide dissolved in 25 ml of distilled water followed by 1 ml (8.5 mmol) of benzyl chloride plus 25 ml petroleum ether. An internal standard (*n*-dodecane) was added to the reaction mixture and the mixture stirred with mechanical stirrer.

3.3. Halogen exchange

Procedure similar to that described for the conversion of benzyl chloride to benzyl iodide was followed for all of the halogen exchange reactions described in Table 1. To a Morton flask containing 0.5 g of **1a**-clay was added a solution of 1.4 g (8.5 mmol) of potassium iodide dissolved in 25 ml of distilled water followed by 1 ml (8.5 mmol) of benzyl chloride plus 25 ml petroleum ether. An internal standard (*n*-dodecane) was added to the reaction mixture and the flask heated in an oil bath maintained at 25 °C for 24 h, and the reaction mixture was stirred with a mechanical stirrer.

3.4. Naphthoxide displacement on benzyl chloride

To a Morton flask containing 0.5 g of **1a**-clay was added 5 ml of 5.2 M sodium hydroxide followed by 1.2 g (8.7 mmol) 2-naphthol in 25 ml petroleum ether, 1 ml (8.7 mmol) of benzyl chloride, and an internal standard (*n*-dodecane). The mixture was stirred with a mechanical stirrer and placed in an oil bath maintained at 25 °C for 15 h.

3.5. Dichlorocarbene addition to cyclooctene

Cyclooctene (2 ml, 7.7 mmol) dissolved in 25 ml of chloroform was added to 25 ml of 50% aqueous sodium hydroxide solution, plus **1a**-clay (0.5 g) contained in a Morton flask. After addition of an internal standard (*n*-dodecane) the mixture was stirred with a mechanical stirrer and allowed to remain at 58 °C for 24 h. Analysis of the organic phase by GLC (SE-30 column) indicated a 96% yield of 9,9-dichlorobicyclo[6.1.0]nonane.

3.6. Displacement of thiocyanate ion on organic halides

Procedures similar to that described for the conversion of *n*-cetyl bromide to *n*-cetyl thiocyanate was followed for all of the thiocyanate forming reactions described in Table 2. To a Morton flask containing 0.5 g of **1a**-clay was added a solution of 0.32 g (3.2 mmol) of potassium thiocyanate dissolved in 25 ml of distilled water followed by 1 ml (3.2 mmol) of *n*-cetyl bromide plus 25 ml chloroform. An internal standard (*n*-dodecane) was added to the reaction mixture and the flask was stirred with a mechanical stirrer, placed in an oil bath maintained at 58 °C for 24 h.

3.6.1. 9,9-Dichloro-bicyclo[6.1.0]nonane.²² ¹H NMR (300 MHz, CDCl₃): δ 1.3 (4H), 1.24 (4H), 1.13 (4H), 0.82 (2H). ¹³C NMR (75 MHz, CDCl₃): δ 23.6, 27.4, 28.2, 28.8, 66.1. MS (EI), *m/z* (%): 192 (M⁺, 10), 124 (50.7), 122 (84.9), 109 (25.9), 96 (44.3), 81 (99.9), 68 (33.9), 67 (83.6), 55 (63.9), 41 (76.7), 39 (51.6). IR (KBr): 685, 790, 875, 920, 1020, 1050, 1180, 1190, 1465, 1450, 1410, 2798, 2850, 2920 cm⁻¹. Anal. Calcd for C₉H₁₄Cl₂: C, 55.96; H, 7.25. Found: C, 55.98; H, 7.29.

3.6.2. 1-Benzyl-2-naphthol. ¹H NMR (300 MHz, CDCl₃): δ 4.25 (2H), 5.0 (1H), 6.84 (1H), 7.07 (1H), 7.14 (2H), 7.18 (1H), 7.29 (1H), 7.46 (1H), 7.6 (3H), 7.63 (1H). ¹³C NMR (75 MHz, CDCl₃): δ 118.9, 120.4, 122.5, 123.2, 126.3, 128.3, 129.3, 133.5, 133.9, 141.6, 153.5. IR (KBr): 621, 741, 813, 844, 905, 958, 1172, 1216, 1276, 1406, 1466, 1512, 1600, 1630, 2923, 3050, 3200–3500 (bs) cm⁻¹. Mp 110–112 °C (lit.²³ 110–111 °C).

3.6.3. Benzyl-2-naphthyl ether. ¹H NMR (300 MHz, CDCl₃): δ 5.3 (2H), 6.97 (1H), 7.04 (1H), 7.19 (5H), 7.21 (1H), 7.3 (1H), 7.6 (2H), 7.64 (1H). ¹³C NMR (75 MHz, CDCl₃): δ 70.9, 105.9, 118.8, 124, 126.7, 126.9, 127.2, 127.7, 127.8, 129, 129.5, 129.6, 134.8, 141.2, 157.3. IR (KBr): 632, 751, 843, 905, 959, 1277, 1378, 1466, 1511, 1630, 1701, 2922, 3055 cm⁻¹. Mp 98–100 °C (lit.²³ 98–99.5 °C).

3.6.4. *n*-Cetyl thiocyanate.²⁴ ¹H NMR (300 MHz, CDCl₃): δ 0.96 (3H), 1.29 (24H), 1.33 (2H), 1.66 (2H), 2.44 (2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.1, 22.8, 28.6, 29, 29.4, 29.7, 29.9, 31.9, 32.1, 117.3. MS (EI), *m/z* (%): 99 (13.4), 85 (43.7), 71 (63.8), 57 (99.9), 55 (24.2). Anal. Calcd for C₁₇H₃₃NS: C, 72.08; H, 11.66; N, 4.95; S, 11.31. Found: C, 72.15; H, 11.71; N, 4.91; S, 11.28.

3.6.5. *n*-Cetyl isothiocyanate.²⁵ ¹H NMR (300 MHz, CDCl₃): δ 0.96 (3H), 1.29 (24H), 1.3 (2H), 1.33 (2H), 3.6 (2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.1; 22.8, 26.6; 29;

29.4; 29.7; 30.2; 31.9, 53.8, 130.7. MS (EI), *m/z* (%): 283 (M⁺, 0.6), 251 (17.6), 250 (86.1), 115 (91.9), 83 (17), 72 (20.9), 69 (38.3), 57 (44.1), 55 (88.5), 43 (92.6), 41 (99.1), 29 (45.3). Anal. Calcd for C₁₇H₃₃NS: C, 72.08; H, 11.66; N, 4.95; S, 11.31. Found: C, 72.21; H, 11.76; N, 4.89; S, 11.26.

3.6.6. *n*-Cetyl cyanide.²⁶ ¹H NMR (300 MHz, CDCl₃): δ 0.96 (3H), 1.29 (24H), 1.33 (2H), 1.66 (2H), 2.41 (2H). ¹³C NMR (75 MHz, CDCl₃): δ 14.1, 17.5, 22.8, 25.5, 28.6, 28.9, 29.4, 29.7, 31.9, 117.7. MS (EI), *m/z* (%): 208 (9.3), 138 (13.8), 110 (27), 97 (46.1), 96 (22), 70 (26.6), 57 (74.7), 55 (52.5), 43 (99.9), 41 (89.4), 29 (57.5). IR (KBr): 718, 1471, 2245, 2873, 2915, 2948, 2977 cm⁻¹. Anal. Calcd for C₁₇H₃₃N: C, 81.27; H, 13.15; N, 5.78. Found: C, 81.30; H, 13.18; N, 5.75.

3.6.7. *n*-Cetyl iodide. ¹H NMR (300 MHz, CDCl₃): δ 0.96 (3H), 1.29 (24H), 1.33 (2H), 1.86 (2H), 3.13 (2H). ¹³C NMR (75 MHz, CDCl₃): δ 6.8, 14.1, 22.8, 28.5, 29.4, 29.7, 30.4, 31.9, 33.6. MS (EI), *m/z* (%): 225 (10.3), 85 (54.6), 71 (75.5), 57 (99.9), 43 (60.8), 29 (8.6). IR (KBr) 604, 719, 1179, 1204, 1377, 1369, 1377, 1467, 2853, 2918, 2966 cm⁻¹. Bp 130 °C/0.2 mm (lit.²⁷ 152–154 °C/0.7 mm).

3.6.8. 1,6-Diiodohexane. ¹H NMR (300 MHz, CDCl₃): δ 1.29 (4H), 1.86 (4H), 3.13 (4H). ¹³C NMR (75 MHz, CDCl₃): δ 6.8, 29.2, 33.6. MS (EI), *m/z* (%): 338 (M⁺, 0.4), 211 (29.4), 169 (28.5), 155 (45.5), 128 (12.5), 127 (24.9), 83 (61.5), 55 (99.1), 43 (18.1), 41 (88.5), 39 (46.8), 29 (29.2), 27 (60). IR (KBr): 596, 719, 1179, 1216, 1425, 1456, 2950, 2953 cm⁻¹. Bp 72–74 °C/0.2 mm (lit.²⁸ 141–142 °C/10 mm).

3.6.9. 1-Bromo-6-iodohexane. ¹H NMR (300 MHz, CDCl₃): δ 1.29 (4H), 1.79 (2H), 1.86 (2H), 3.13 (2H), 3.3 (2H). ¹³C NMR (75 MHz, CDCl₃): δ: 6.8, 26.9, 29.4, 32.7, 33.6, 33.7. MS (EI), *m/z* (%): 292 (M⁺, 1.9), 165 (25.7), 163 (25.4), 123 (17.9), 121 (19.1), 109 (16.7), 107 (17.3), 84 (16.3), 83 (98.3), 56 (16.7), 55 (99.9), 43 (80.3), 41 (83.9), 39 (68.7). Anal. Calcd for C₆H₁₂BrI: C, 24.74; H, 4.12. Found: C, 24.71; H, 4.05.

3.6.10. 1,6-Dicyanohexane. ¹H NMR (300 MHz, CDCl₃): δ 1.29 (4H), 1.66 (4H), 2.41 (4H). ¹³C NMR (75 MHz, CDCl₃): δ 17.5, 25.5, 27.8, 117.7. MS (EI), *m/z* (%): 137 (M⁺, 1.2), 96 (99.9), 83 (16.3), 82 (26.5), 69 (63.4), 68 (16.9), 55 (84.7), 54 (54.5), 42 (34.7), 41 (87.9). IR: 850, 1398, 1440, 2225, 2840, 2950 cm⁻¹. Anal. Calcd for C₈H₁₂N₂: C, 70.59; H, 8.82; N, 20.59. Found: C, 70.68; H, 8.91; N, 20.68.

3.6.11. 7-Bromoheptanenitrile. ¹H NMR (300 MHz, CDCl₃): δ 1.29 (4H), 1.66 (2H), 1.79 (2H), 2.41 (2H), 3.3 (2H). ¹³C NMR (75 MHz, CDCl₃): δ 17.5, 25.5, 27.3, 27.6, 32.7, 33.7, 117.7. MS (EI), *m/z* (%): 190 (M⁺, 0.2), 110 (99.9), 109 (10.7), 83 (44.9), 82 (44.3), 69 (92.9); 55 (66.2), 54 (47.8), 43 (15.1), 42 (22.9), 41 (87.6), 39 (44.2). Bp 96–98 °C/2 mm (lit.²⁹ 140–141 °C/14 mm).

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