



Cycloalkane-based thermomorphic systems for organic electrochemistry: an application to Kolbe-coupling

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ABSTRACT

The discovery that cycloalkanes can form thermomorphic systems with typical polar organic solvents has led to the development of less-polar electrolyte solutions. Their mixing and separation can be regulated reversibly at a moderate temperature range. The phase switching temperature can be controlled by changing the solvent compositions. While biphasic conditions are maintained below the phase switching temperature, conductive monophasic conditions as less-polar electrolyte solutions are obtained above the phase switching temperature. After the electrochemical transformations, biphasic conditions are reconstructed below the phase switching temperature, facilitating the separation of cycloalkane where hydrophobic products or designed hydrophobic platforms are selectively partitioned. Several polar organic solvents, including acetonitrile, methanol, and pyridine, can be used in this system according to the requirement of the reactions.

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Briefs

Less-polar electrolyte solutions have been constructed using cycloalkane-based thermomorphic systems.

1. Introduction

The solid-phase technique comprises a substantial fraction of current research in both the academic and industrial fields, offering a great advantage with regards to compound separation and has also proven to be effective for automated synthesis and combinatorial chemistry. Generally, reaction substrates are bound to a solid-phase, facilitating their separation from the reaction mixture to enable efficient multistep chemical transformations, especially for peptide synthesis.¹ Meanwhile, the immobilization of reaction catalysts on a solid-phase realizes their consecutive recycling to establish green chemical transformations, which also serves as promising applications in combination with a flow strategy.² From this aspect, electrodes are regarded as immobilized redox reagents in electrochemical transformations. Their potentials can be simply controlled to regulate electron transfer at their surfaces.³ Although not only various functional group transformations, but also a wide variety of carbon–carbon bond forming reactions have been accomplished, electrochemical approaches have the following essential requirements. First, a large amount of supporting electrolyte

is needed to impart electrical conductivity to polar organic solvents, which requires subsequent separation and disposal. Second, reaction substrates should be soluble in polar electrolyte solutions because electron transfer takes place only at the surface of the electrodes; thus, the use of hydrophobic substrates is restricted. Third, insoluble hydrophobic products generated during the electrochemical transformations might form polymeric films at the surface of electrodes that suppress electric current severely, known as electrode passivation.⁴ To satisfy the above criteria, several electrochemical reaction systems have been devised for improvement of the electrochemical transformation productivities.⁵

The biphasic technique has also dominated the landscape of modern synthetic chemistry to provide a facile separation of compounds by simple liquid–liquid extraction, including fluoruous⁶ and ionic⁷ systems. The fluoruous biphasic technique is based on the insolubility of perfluorinated hydrocarbons with both polar and less-polar organic solvents; thus, fluoruous compounds, including reaction substrates, products, and catalysts, or designed fluoruous platforms, are preferentially dissolved in the fluoruous phase, realizing their rapid separation. Moreover, thermomorphic systems that change thermally from biphasic conditions to monophasic conditions have also been developed to achieve unique separation techniques.⁸ For example, a 1:1 (v/v) mixture of heptane and 90% aqueous ethanol are immiscible, forming biphasic conditions at 25 °C. While heating to 70 °C is sufficient to make this system miscible, constructing monophasic conditions, the initial biphasic conditions are reformed at 25 °C. Therefore, the use of designed water soluble polymer platforms leads to a versatile scheme for

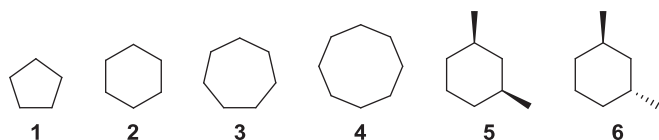
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compound separation, in which the compound can be fully recovered from a 90% aqueous ethanol phase even if it is distributed throughout the monophasic conditions at 70 °C, enabling homogeneous chemical transformations.

We have been developing various chemical transformations in cyclohexane-based thermomorphic systems, which stem from the discovery that cyclohexane can form thermomorphic systems with typical polar organic solvents and their mixing and separation can be regulated reversibly at a moderate temperature range.⁹ For example, a 1:4 (v/v) mixture of cyclohexane and nitromethane shows biphasic conditions at 25 °C, which forms monophasic conditions at 60 °C to serve as an effective homogeneous reaction field, while cooling to 25 °C reforms the initial biphasic conditions. On the basis of these findings, we have also demonstrated several electrochemical transformations in cyclohexane-based multiphase electrolyte solutions.¹⁰ In these systems, while electrolyte solutions are partially miscible with cyclohexane to construct multiphase electrolyte solutions, supporting electrolytes are selectively dissolved in polar organic solvents. Thus, hydrophobic products are continuously removed from the electrolyte solutions to suppress their overoxidations and to enable consecutive recycling of supporting electrolytes. In light of previous studies, we sought to realize less-polar electrolyte solutions assisted by cycloalkane-based thermomorphic systems so that completion of their mixing and separation would be regulated reversibly at a moderate temperature range, satisfying the above-mentioned essential requirements of electrochemical transformations.

2. Results and discussion

The present study began with the investigation of the thermomorphic properties of cycloalkanes. For this purpose, 1:3 (v/v) mixtures of several cycloalkanes (**1–6**) and acetonitrile as typical polar organic solvents were prepared (Scheme 1). All cycloalkanes (**1–6**) were immiscible with acetonitrile to form biphasic conditions at 25 °C, which were then gradually heated. It was observed that all cycloalkanes (**1–6**) exhibited thermomorphic properties and were miscible with acetonitrile to form monophasic conditions at each phase switching temperature (Table 1). The hydrophobicity of cycloalkanes (**1–6**) is expected to increase with the number of carbons. As expected, a reasonable increase in the phase switching temperatures was observed for non substituted cycloalkanes (**1–4**). On the other hand, the phase switching temperatures of both *cis*-(**5**) and *trans*-1,3-dimethylcyclohexane (**6**) were relatively low that their hydrophobic natures could be estimated to be at the same level as cyclooctane (**4**). The ring-flip of cyclohexane was supposedly responsible for the thermomorphic properties.



Scheme 1. Structures of cycloalkanes used in this study.

The thermomorphic properties of cycloalkanes (**1–4**) were also studied using methanol as a typical polar organic solvent. 1:1 (v/v) mixtures of several cycloalkanes (**1–4**) and methanol were prepared. In this case, cyclopentane (**1**) was miscible with methanol to form monophasic conditions even at 25 °C, while cyclooctane (**4**) was immiscible with methanol to form biphasic conditions even around the boiling point of the solvent (Table 2). When cyclohexane (**2**) or cycloheptane (**3**) was utilized, thermal changes at a moderate temperature range were sufficient to regulate their mixing and

Table 1

Phase switching temperatures of cycloalkane-based thermomorphic systems using acetonitrile as a typical polar organic solvent

| Cycloalkane | Phase switching temperature (°C) ^a |
|--|---|
| Cyclopentane (1) | 29 |
| Cyclohexane (2) | 53 |
| Cycloheptane (3) | 59 |
| Cyclooctane (4) | 75 |
| <i>cis</i> -1,3-Dimethylcyclohexane (5) | 60 |
| <i>trans</i> -1,3-Dimethylcyclohexane (6) | 59 |

^a Biphasic conditions composed of 1:3 (v/v) mixtures of several cycloalkanes (**1–6**) and acetonitrile as a typical polar organic solvent (20 mL) were gradually heated with stirring to form monophasic conditions at the temperature.

Table 2

Phase switching temperatures of cycloalkane-based thermomorphic systems using methanol as a typical polar organic solvent

| Cycloalkane | Phase switching temperature (°C) ^a |
|---------------------------|---|
| Cyclopentane (1) | — ^b |
| Cyclohexane (2) | 40 |
| Cycloheptane (3) | 66 |
| Cyclooctane (4) | — ^c |

^a Biphasic conditions composed of 1:1 (v/v) mixtures of several cycloalkanes (**1–4**) and methanol as a typical polar organic solvent (20 mL) were gradually heated with stirring to form monophasic conditions at the temperature.

^b Miscible even at 25 °C.

^c Immiscible even around at the boiling point of the solvent.

separation. These results provided us an incentive to construct less-polar electrolyte solutions enabled by the cycloalkane-based thermomorphic systems.

On the basis of these observations, we investigated numerous compositions of electrolyte solutions that showed practical thermomorphic properties in combination with cycloalkanes to realize less-polar electrolyte solutions. As a supporting electrolyte, potassium hydroxide was added to a 1:1:2 (v/v/v) mixture of pyridine, methanol, and acetonitrile (saturated), which was then combined with an equal volume of several cycloalkanes (**1–4**). It has been demonstrated that heating to moderate temperatures was enough to create monophasic conditions as less-polar electrolyte solutions (Table 3). Furthermore, lithium perchlorate could also be employed as a supporting electrolyte (0.1 M) to realize less-polar electrolyte solutions assisted by the cycloalkane-based thermomorphic systems, which completely reformed the initial biphasic conditions after cooling to 25 °C (Scheme 2).

Table 3

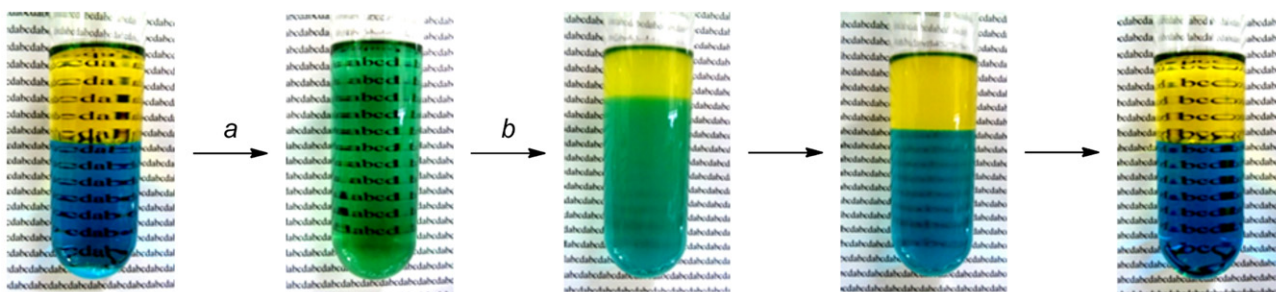
Phase switching temperatures of cycloalkane-based thermomorphic systems using an electrolyte solution composed of potassium hydroxide and 1:1:2 (v/v/v) mixtures of pyridine, methanol, and acetonitrile

| Cycloalkane | Phase switching temperature (°C) ^a |
|---------------------------|---|
| Cyclopentane (1) | — ^b |
| Cyclohexane (2) | 48 |
| Cycloheptane (3) | 55 |
| Cyclooctane (4) | 63 |

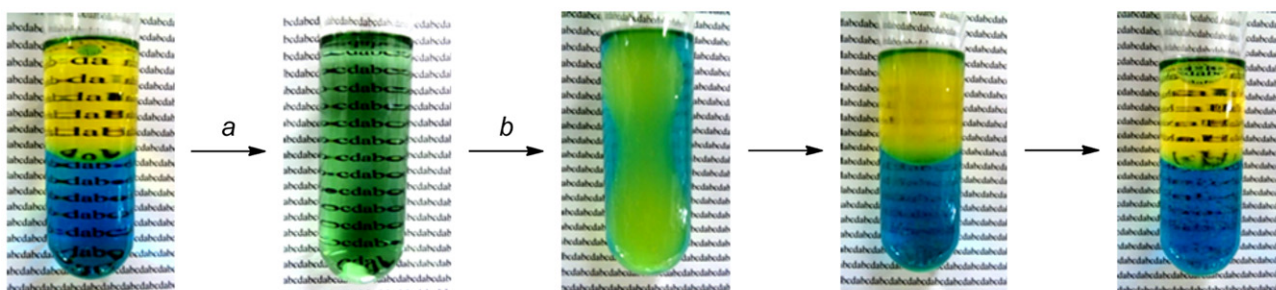
^a Biphasic conditions composed of 1:1 (v/v) mixtures of several cycloalkanes (**1–4**) and electrolyte solution (20 mL) were gradually heated with stirring to form monophasic conditions at the temperature.

^b Miscible even at 25 °C.

With these results in hand, we then turned our attention to the application of cycloalkane-based thermomorphic systems as less-polar electrolyte solutions for practical electrochemical transformations. In this context, the oxidative dimerization of carboxylate anions through decarboxylation, known as Kolbe-coupling, was chosen as a model, which is still under active investigation in

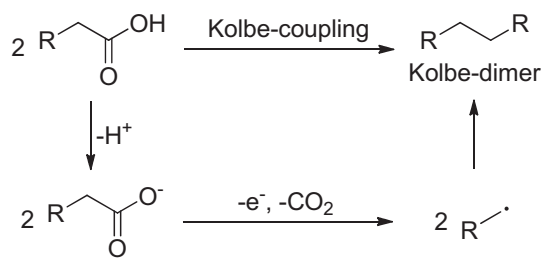


Cyclohexane-based thermomorphic systems using electrolyte solution composed of lithium perchlorate (0.1 M) and 1:1:2 (v/v/v) mixtures of pyridine, methanol, and acetonitrile. Upper cyclohexane phase was colored by coenzyme Q10 and lower electrolyte solution phase was colored by methylene blue. (a) Heating to 51 °C with stirring. (b) Cooling to 25 °C.



Cyclooctane-based thermomorphic systems using electrolyte solution composed of lithium perchlorate (0.1 M) and 1:1:2 (v/v/v) mixtures of pyridine, methanol, and acetonitrile. Upper cyclooctane phase was colored by coenzyme Q10 and lower electrolyte solution phase was colored by methylene blue. (a) Heating to 71 °C with stirring. (b) Cooling to 25 °C.

Scheme 2. Phase switching of cycloalkane-based thermomorphic systems.

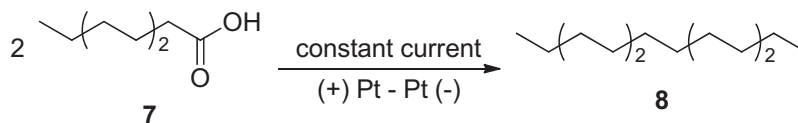


Scheme 3. Reaction mechanism of Kolbe-coupling.

both the academic and industrial fields (Scheme 3).¹¹ Initially, the anodic oxidation of octanoic acid (**7**) was carried out in a 1:1:2 (v/v/v) mixture of pyridine, methanol, and acetonitrile using potassium hydroxide (saturated) as a supporting electrolyte under constant current to give the Kolbe-dimer (**8**) in excellent yield (Scheme 4).¹² Even in the presence of an equal volume of cyclohexane (**2**), the Kolbe-dimer (**8**) was obtained in excellent yield, also realizing gram-scale production. In this case, the reaction mixture formed biphasic conditions at 25 °C, which was heated by electrical resistance to construct monophasic conditions, realizing a less-polar electrolyte solution, during the application of the current. The addition of octanoic acid (**7**) did not affect the thermomorphic properties of the system. Because of the polarity, the Kolbe-dimer

(**8**) was selectively dissolved into the less-polar cyclohexane (**2**); thus, the dimer could be immediately removed from the electrolyte solutions by only cooling to form the biphasic solutions, enabling consecutive recycling of electrolyte solutions (Scheme 5).

On the other hand, when 3-phenylpropanoic acid (**9**) was used as a substrate, the less-polar electrolyte solutions were critical for the reaction. The anodic oxidation of 3-phenylpropanoic acid (**9**) in the 1:1:2 (v/v/v) mixture of pyridine, methanol, and acetonitrile using potassium hydroxide (saturated) as a supporting electrolyte under constant current gave the Kolbe-dimer (**10**) in low yield (Scheme 6). In this case, the formation of an insoluble polymeric film was observed at the surface of the electrodes, decreasing the yield of the Kolbe-dimer (**10**). The addition of an equal volume of cyclohexane (**2**) significantly improved the reaction efficiency. The reaction mixture was heated by electrical resistance to construct monophasic conditions as less-polar electrolyte solutions during application of the current, which inhibited the formation of the insoluble polymeric film at the surface of the electrodes, affording the Kolbe-dimer (**10**) in good yield. The same reaction conditions could also be applied to the Kolbe-coupling of several carboxylic acids (**11–13**) to give the corresponding Kolbe-dimers (**14–16**) in good yields (Scheme 7). It should be noted that the monophasic conditions were formed by heating using electrical resistance to realize less-polar electrolyte solutions during the application of the current, while cooling to 25 °C was sufficient to reform the biphasic conditions, enabling the rapid separation of the Kolbe-dimers (**14–16**) from the electrolyte solutions.



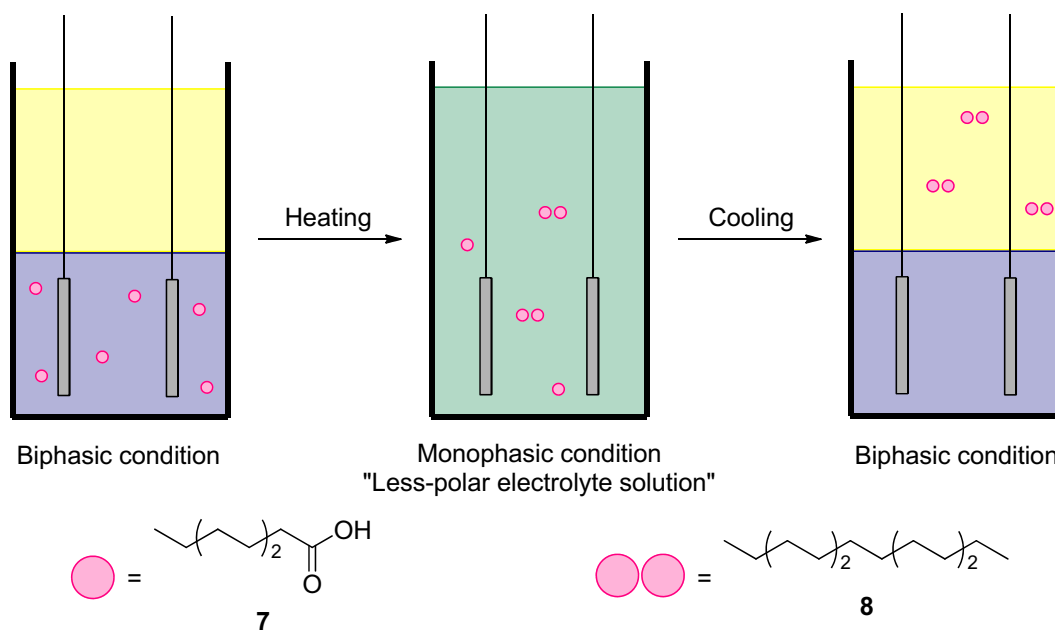
| electrolyte solution | current density | yield (%) ^a |
|--|-----------------------|-----------------------------------|
| pyridine:MeOH:MeCN = 1:1:2 without c-Hex | 25 mA/cm ² | 93 ^b |
| pyridine:MeOH:MeCN = 1:1:2 with c-Hex | 25 mA/cm ² | 95 ^b (91) ^c |

^aDetermined by NMR

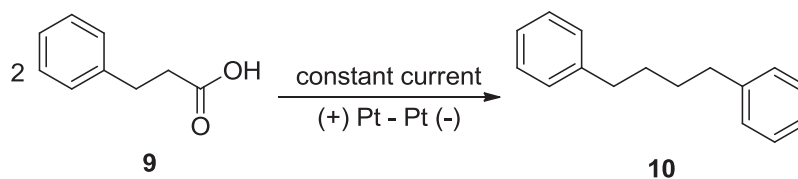
^b2.50 mmol of octanoic acid (**7**) was used

^c25.0 mmol of octanoic acid (**7**) was used

Scheme 4. Kolbe-coupling of octanoic acid (**7**).



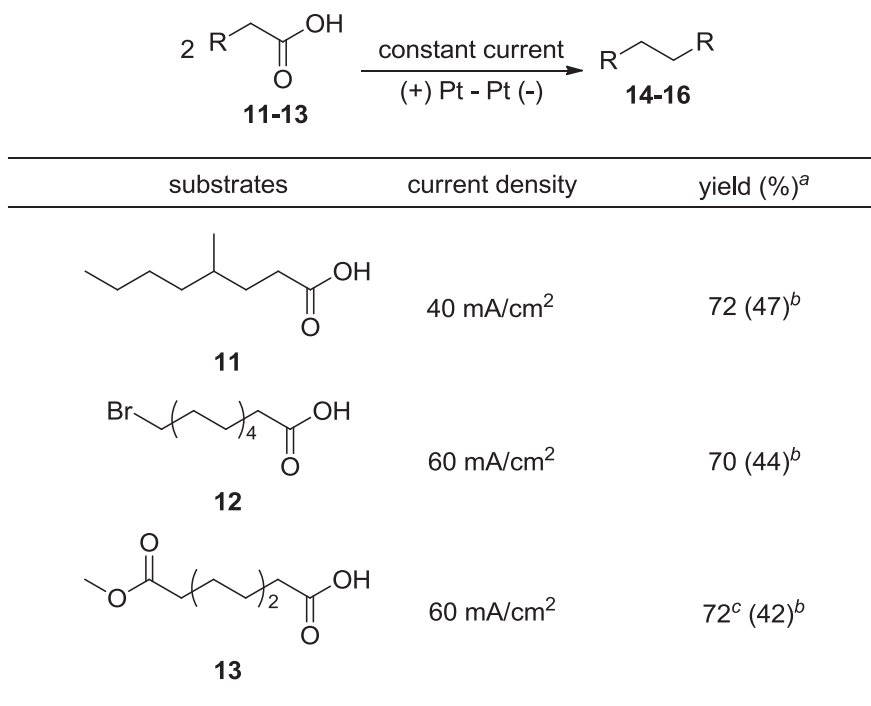
Scheme 5. Schematic illustration of the Kolbe-coupling of octanoic acid (**7**) using cyclohexane-based thermomorphic systems.



| electrolyte solution | current density | yield (%) ^a |
|--|-----------------------|------------------------|
| pyridine:MeOH:MeCN = 1:1:2 without c-Hex | 60 mA/cm ² | 45 |
| pyridine:MeOH:MeCN = 1:1:2 with c-Hex | 60 mA/cm ² | 65 |

^aDetermined by NMR

Scheme 6. Kolbe-coupling of 3-phenylpropanoic acid (**9**).

^aDetermined by NMR^bYield without *c*-Hex^cDiisopropylether was used instead of pyridine**Scheme 7.** Kolbe-coupling of several carboxylic acids (**11–13**).

3. Conclusion

In conclusion, we found that several cycloalkanes (**1–6**) showed unique thermomorphic properties in combination with several typical polar organic solvents, including acetonitrile, methanol, and pyridine, leading to the construction of less-polar electrolyte solutions. Their mixing and separation can be regulated reversibly at a moderate temperature range. We also demonstrated that cycloalkane-based thermomorphic systems as less-polar electrolyte solutions are efficient for practical electrochemical transformations using Kolbe-coupling as a model. Thus, the reaction mixtures were heated by electrical resistance to construct monophasic conditions, which inhibited electrode passivations, and the hydrophobic products can be immediately removed from the electrolyte solutions by only cooling to reform the biphasic conditions. Less-polar electrolyte solutions assisted by cycloalkane-based thermomorphic systems would be a significant aid for expanding the possibility of electrochemical transformations.

4. Experimental section

4.1. Kolbe-couplings with cyclohexane

Carboxylic acids (2.5 mmol) were added to electrolyte solutions (20 mL) using potassium hydroxide as a supporting electrolyte (saturated) in the presence of the cycloalkanes. The undivided reaction cell was capped with a septum equipped with platinum electrodes (10 mm×20 mm). The electrolysis was then performed at constant current. After completion of the reaction, the cycloalkane phase was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using *n*-hexane–EtOAc to give products. The products' yields were determined by NMR.

4.2. Kolbe-couplings without cyclohexane

Carboxylic acids (2.5 mmol) were added to electrolyte solutions (20 mL) using potassium hydroxide as a supporting electrolyte (saturated). The undivided reaction cell was capped with a septum equipped with platinum electrodes (10 mm×20 mm). The electrolysis was then performed at constant current. After completion of the reaction, the reaction mixture was poured into EtOAc, and the EtOAc solution was successively washed with brine. The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation under reduced pressure, the residue was purified by silica gel column chromatography using *n*-hexane–EtOAc to give the products. The products yields were determined by NMR.

4.2.1. Tetradecane (8, oil). ¹H NMR (600 MHz, CDCl₃) δ 1.33–1.22 (24H, m), 0.88 (6H, t, *J*=6.8 Hz) ¹³C NMR (150 MHz, CDCl₃) δ 32.0, 29.7, 29.4, 22.7, 14.1 IR (NaCl, cm⁻¹) 2902, 2733, 2677, 1464, 1381, 1302, 895, 719 MS (rel int.) *m/z* 198 (M⁺, 2), 155 (1), 141 (1), 127 (1), 113 (2), 99 (5), 85 (34), 71 (65), 57 (100) HRMS calcd for C₁₄H₃₀ 198.2347 (M–H 197.2269), found 197.2280.

4.2.2. 1,4-Diphenylbutane (10, solid). ¹H NMR (600 MHz, CDCl₃) δ 7.30–7.11 (10H, m), 2.63 (4H, t, *J*=6.8 Hz), 1.71–1.62 (4H, m) ¹³C NMR (150 MHz, CDCl₃) δ 142.5, 142.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 125.7, 125.6, 35.8, 31.1 IR (KBr, cm⁻¹) 3099, 3057, 3026, 2929, 2856, 1954, 1865, 1805, 1603, 1495, 1452, 1348, 1119, 1065, 1024, 906, 742, 696 MS (rel int.) *m/z* 210 (M⁺, 85), 195 (1), 181 (2), 167 (4), 130 (3), 117 (11), 104 (10), 91 (100), 77 (11), 65 (23), 51 (4) HRMS calcd for C₁₆H₁₈ 210.1409, found 210.1434.

4.2.3. 5,10-Dimethyltetradecane (14, oil). ¹H NMR (600 MHz, CDCl₃) δ 1.35–1.05 (22H, m), 0.90–0.83 (12H, m) ¹³C NMR (150 MHz, CDCl₃) δ 37.2, 36.8, 36.8, 32.8, 29.4, 27.5, 27.4, 27.4, 23.1, 23.1, 19.7,

19.7, 14.2, 14.1 IR (NaCl, cm^{-1}) 2958, 2927, 2852, 1468, 1373, 1153, 912, 731 MS (rel int.) m/z 211 (2), 197 (1), 169 (11), 141 (21), 127 (4), 113 (7), 99 (14), 85 (100), 71 (69), 57 (95) HRMS calcd for $\text{C}_{16}\text{H}_{34}$ ($\text{M}-\text{C}_4\text{H}_9$ 169.1956), found 169.1948.

4.2.4. *1,20-Dibromoicosane (15, solid)*. ^1H NMR (600 MHz, CDCl_3) δ 3.41 (4H, t, $J=6.8$ Hz), 1.85 (4H, quint, $J=6.8$ Hz), 1.42–1.26 (32H, m) ^{13}C NMR (150 MHz, CDCl_3) δ 34.1, 32.8, 29.7, 29.7, 29.6, 29.5, 29.4, 28.8, 28.2 IR (KBr, cm^{-1}) 2922, 2845, 1471, 1331, 1298, 1267, 1236, 1205, 717, 642 MS (rel int.) m/z 359 (2), 233 (2), 219 (3), 207 (4), 191 (4), 177 (5), 163 (5), 151 (8), 137 (25), 127 (4), 111 (6), 97 (20), 83 (44), 71 (87), 57 (100) HRMS calcd for $\text{C}_{20}\text{H}_{40}\text{Br}_2$ 438.1497 ($\text{M}-^{79}\text{Br}$ 359.2313), found 359.2295.

4.2.5. *Dimethyl tetradecanedioate (16, solid)*. ^1H NMR (600 MHz, CDCl_3) δ 3.67 (6H, s), 2.30 (4H, t, $J=7.6$ Hz), 1.62 (4H, quint, $J=7.2$ Hz), 1.29–1.26 (16H, m) ^{13}C NMR (150 MHz, CDCl_3) δ 174.3, 51.4, 34.1, 34.1, 29.5, 29.5, 29.4, 29.4, 29.2, 29.1, 29.1, 24.9 IR (KBr, cm^{-1}) 2983, 2917, 2850, 1743, 1475, 1464, 1435, 1387, 1309, 1254, 1203, 1169, 991, 881, 729 MS (rel int.) m/z 255 (35), 222 (7), 213 (37), 194 (6), 181 (26), 163 (23), 140 (8), 121 (7), 112 (25), 98 (96), 84 (62), 74 (100), 55 (77) HRMS calcd for $\text{C}_{16}\text{H}_{30}\text{O}_4$ 286.2144 ($\text{M}+\text{Na}$ 309.2042), found 309.2062.

Acknowledgements

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Supplementary data

Additional table and scheme, general information, experimental details, characterization data, and copies of ^1H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.04.112.

References and notes

- (a) Boas, U.; Brask, J.; Jensen, K. J. *Chem. Rev.* **2009**, *109*, 2092–2118; (b) Nandy, J. P.; Prakesch, M.; Khadem, S.; Reddy, P. T.; Sharma, U.; Arya, P. *Chem. Rev.* **2009**, *109*, 1999–2060; (c) Blaney, P.; Grigg, R.; Sridharan, V. *Chem. Rev.* **2002**, *102*, 2607–2624; (d) Seeberger, P. H.; Haase, W.-C. *Chem. Rev.* **2000**, *100*, 4349–4394; (e) Guillier, F.; Orain, D.; Bradley, M. *Chem. Rev.* **2000**, *100*, 2091–2158.
- (a) Ikegami, S.; Hamamoto, H. *Chem. Rev.* **2009**, *109*, 583–593; (b) Wang, Z.; Chen, G.; Ding, K. *Chem. Rev.* **2009**, *109*, 322–359; (c) Buchmeiser, M. R. *Chem. Rev.* **2009**, *109*, 303–321; (d) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401–3430; (e) Duchateau, R. *Chem. Rev.* **2002**, *102*, 3525–3542.
- (a) Yoshida, J.; Kataoka, K.; Horcajada, R.; Nagaki, A. *Chem. Rev.* **2008**, *108*, 2265–2299; (b) Sperry, J. B.; Wright, D. L. *Chem. Soc. Rev.* **2006**, *35*, 605–621; (c) Moeller, K. D. *Synlett* **2009**, 1208–1218; (d) Moeller, K. D. *Tetrahedron* **2000**, *56*, 9257–9554; (e) Little, R. D. *Chem. Rev.* **1996**, *96*, 93–114; (f) Fuchigami, T.; Inagi, S. *Chem. Commun.* **2011**, 10211–10223.
- (a) Savéant, J.-M. *Chem. Rev.* **2008**, *108*, 2348–2378; (b) Houmam, A. *Chem. Rev.* **2008**, *108*, 2180–2237; (c) Tanaka, H.; Kuroboshi, M.; Mitsudo, K. *Electrochemistry* **2009**, *77*, 1002–1009.
- (a) Tajima, T.; Nakajima, A. *J. Am. Chem. Soc.* **2008**, *130*, 10496–10497; (b) Tajima, T.; Nakajima, A.; Doi, Y.; Fuchigami, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 3550–3552; (c) Horcajada, R.; Okajima, M.; Suga, S.; Yoshida, J. *Chem. Commun.* **2005**, 1303–1305; (d) Wu, X.; Davis, A. P.; Lambert, P. C.; Steffen, L. K.; Toy, O.; Fry, A. J. *Tetrahedron* **2009**, *65*, 2408–2414; (e) Wu, X.; Davis, A. P.; Fry, A. J. *Org. Lett.* **2007**, *9*, 5633–5636; (f) Sawamura, T.; Kuribayashi, S.; Inagi, S.; Fuchigami, T. *Adv. Synth. Catal.* **2010**, *352*, 2757–2760; (g) Sawamura, T.; Kuribayashi, S.; Inagi, S.; Fuchigami, T. *Org. Lett.* **2010**, *12*, 644–646; (h) Miranda, J. A.; Wade, C. J.; Little, R. D. *J. Org. Chem.* **2005**, *70*, 8017–8026; (i) Hosoi, K.; Inagi, S.; Kubo, T.; Fuchigami, T. *Chem. Commun.* **2011**, 8632–8634.
- (a) Zhang, W. *Chem. Rev.* **2009**, *109*, 749–795; (b) Zhang, W. *Chem. Rev.* **2004**, *104*, 2531–2556; (c) Studer, A.; Hadida, S.; Ferritto, R.; Kim, S.-Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823–826; (d) Horvath, I. T.; Rabai, J. *Science* **1994**, *266*, 72–75; (e) Gladysz, J. A. *Science* **1994**, *266*, 55–56.
- (a) Parvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615–2665; (b) Fukumoto, K.; Ohno, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1852–1855; (c) Geldbach, T. J.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 8114–8115; (d) Consorti, C. S.; Aydos, G. L. P.; Ebeling, G.; Dupont, J. *Org. Lett.* **2008**, *10*, 237–240.
- (a) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev.* **2009**, *109*, 530–582; (b) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345–3384; (c) Hobbs, C.; Yang, Y.-C.; Ling, J.; Nicola, S.; Su, H.-L.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2011**, *13*, 3904–3907; (d) Bergbreiter, D. E.; Liu, Y.-S.; Osburn, P. L. *J. Am. Chem. Soc.* **1998**, *120*, 4250–4251; (e) Huang, Y.-Y.; He, Y.-M.; Zhou, H.-F.; Wu, L.; Li, B.-L.; Fan, Q. *J. Org. Chem.* **2006**, *71*, 2874–2877; (f) Barré, G.; Taton, D.; Lastécouères, D.; Vincent, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 7764–7765; (g) Rocaboy, C.; Gladysz, J. A. *Org. Lett.* **2002**, *4*, 1993–1996; (h) Wende, M.; Meier, R.; Gladysz, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 11490–11491.
- (a) Kim, S.; Ikuhisa, N.; Chiba, K. *Chem. Lett.* **2011**, *40*, 1077–1078; (b) Kim, S.; Tsuruyama, A.; Ohmori, A.; Chiba, K. *Chem. Commun.* **2008**, 1816–1818; (c) Kim, S.; Yamamoto, K.; Hayashi, K.; Chiba, K. *Tetrahedron* **2008**, *64*, 2855–2863; (d) Hayashi, K.; Kim, S.; Kono, Y.; Tamura, M.; Chiba, K. *Tetrahedron Lett.* **2006**, *47*, 171–174; (e) Chiba, K.; Kono, Y.; Kim, S.; Nishimoto, K.; Kitano, Y.; Tada, M. *Chem. Commun.* **2002**, 1766–1767.
- (a) Okada, Y.; Yamaguchi, Y.; Chiba, K. *Eur. J. Org. Chem.* **2012**, 243–246; (b) Okada, Y.; Yoshioka, T.; Koike, M.; Chiba, K. *Tetrahedron Lett.* **2011**, *52*, 4690–4693; (c) Okada, Y.; Chiba, K. *Electrochim. Acta* **2010**, *55*, 4112–4119; (d) Kim, S.; Noda, S.; Hayashi, K.; Chiba, K. *Org. Lett.* **2008**, *10*, 1827–1830.
- (a) Schmitt, M.; Qinghai, S. *Chem. Commun.* **2012**, 2707–2709; (b) Koutsaftis, D.; Marinis, D.; Karantonis, A. *Electrochim. Acta* **2012**, *59*, 376–381; (c) Shtelman, A. V.; Becker, J. Y. *J. Org. Chem.* **2011**, *76*, 4710–4714; (d) Lebreux, F.; Buzzo, F.; Marko, I. E. *Synlett* **2008**, 2815–2820; (e) Kurihara, H.; Fuchigami, T.; Tajima, T. *J. Org. Chem.* **2008**, *73*, 6888–6890.
- Mendonça, A. J.; Inês, M.; Esteves, A. P.; Mendonça, D. I.; Medeiros, M. J. *Synth. Commun.* **2011**, *41*, 820–825.