

and recycled for 1.5 h. This process was repeated for the addition of the next three amino acids, Fmoc-glycine-Pfp, **5**, and Fmoc-glycine-Pfp. After completion of the fifth coupling the resin was washed with  $\text{CH}_2\text{Cl}_2$  for 15 minutes, and the beads were removed from the synthesizer and dried overnight. 4-Å Molecular sieves (5 beads) and  $\text{CH}_2\text{Cl}_2$  (1 mL) were added to the resin beads, and the suspension was agitated for 1 h. TfOTMS solution (160  $\mu\text{L}$  of a 16% v/v solution in  $\text{CH}_2\text{Cl}_2$ ) was added to a solution of NIS (400 mg, 1.78 mmol in THF (4 mL) and  $\text{CH}_2\text{Cl}_2$  (1 mL). A 1.25-mL aliquot of the resulting mixture was added to the resin beads, and the suspension was agitated for 18 h. The solution was then removed by filtration, and the resin was washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 2.5$  mL). The resin was treated with 20% piperidine in  $\text{CH}_2\text{Cl}_2$  (2 mL), and the mixture was agitated for 15 min. The solvent was drained and the resin was washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 2.5$  mL). A solution of NaOH (10 mg, 0.25 mmol) in THF (0.5 mL) and methanol (2 mL) was transferred to the resin beads. The mixture was then agitated for 1 h, after which the solution was filtered from the resin and the filtrate concentrated to dryness under reduced pressure. The crude products were dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL), washed with water ( $2 \times 5$  mL), and dried ( $\text{MgSO}_4$ ), and the major  $\alpha$  isomer was purified by preparative HPLC on an Alltech Econosil Silica normal-phase preparative column (10  $\mu\text{m}$ ,  $250 \times 22$  mm) with a flow rate of 10 mL min $^{-1}$  and gradient elution (0 min: hexane 95%, 2-propanol 5%; 20 min: hexane 65%, 2-propanol 35%; then isocratic for 5 min) to give **9a** (14 mg).  $R_f = 0.77$  (petroleum:EtOAc, 1:1);  $[\alpha]_D^{25} = -5.69$  ( $c = 0.67$  in  $\text{CHCl}_3$ ); IR (thin film):  $\bar{\nu} = 3494$  (OH), 3057, 3030, 2990, 2942, 1461, 1409 cm $^{-1}$ ;  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.33$ –7.26 (m, 15H; aromatic protons), 5.70 (d,  $^3J(\text{H,H}) = 3.8$  Hz, 1H; H-1), 4.92 (d,  $^2J(\text{H,H}) = 10.9$  Hz, 1H;  $3\text{OCH}_a\text{H}_b\text{Ph}$ ), 4.85 (d,  $^2J(\text{H,H}) = 10.9$  Hz, 1H;  $3\text{OCH}_a\text{H}_b\text{Ph}$ ), 4.84 (d,  $^2J(\text{H,H}) = 11.4$  Hz, 1H;  $4\text{OCH}_a\text{H}_b\text{Ph}$ ), 4.83 (d,  $^2J(\text{H,H}) = 12.1$  Hz, 1H;  $2\text{OCH}_a\text{H}_b\text{Ph}$ ), 4.80 (d,  $^2J(\text{H,H}) = 12.1$  Hz, 1H;  $2\text{OCH}_a\text{H}_b\text{Ph}$ ), 4.71 (d,  $^3J(\text{H,H}) = 3.5$  Hz, 1H, H-1'), 4.59 (d,  $^2J(\text{H,H}) = 11.4$  Hz, 1H;  $4\text{OCH}_a\text{H}_b\text{Ph}$ ), 4.32 (t,  $^3J(\text{H,H}) = 9.4$  Hz, 1H; H-3'), 4.09 (t,  $^3J(\text{H,H}) = 9.4$  Hz, 1H; H-4'), 3.97 (t,  $^3J(\text{H,H}) = 9.0$  Hz, 1H; H-3), 3.91 (dd,  $^2J(\text{H,H}) = 12.3$  Hz,  $^3J(\text{H,H}) = 3.0$  Hz, 1H; H-6a'), 3.87 (dd,  $^2J(\text{H,H}) = 11.6$  Hz,  $^3J(\text{H,H}) = 2.4$  Hz, 1H; H-6b), 3.83–3.77 (m, 2H; H-6b' & 5), 3.74 (dd,  $^2J(\text{H,H}) = 10.3$  Hz,  $^3J(\text{H,H}) = 3.5$  Hz, 1H; H-2'), 3.73–3.69 (m, 1H; H-5), 3.61 (dd,  $^2J(\text{H,H}) = 11.6$  Hz,  $^3J(\text{H,H}) = 5.9$  Hz, 1H; H-6a), 3.56 (dd,  $^2J(\text{H,H}) = 9.0$  Hz,  $^3J(\text{H,H}) = 3.8$  Hz, 1H; H-2), 3.42 (t,  $^3J(\text{H,H}) = 9.0$  Hz, 1H; H-4), 3.39 (s, 3H;  $\text{OCH}_3$ ), 3.24 (s, 3H;  $\text{OCH}_3$ ), 3.09 (s, 3H;  $\text{OCH}_3$ ), 1.30 (s, 3H;  $\text{CH}_3$ ), 1.22 (s, 3H;  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 138.6$  (aromatic C-1), 138.0 (aromatic C-1), 128.5–127.6 (aromatic C-1, 2, 3, 4, 5, 6), 99.7 (C-BDA), 99.3 (C-BDA), 98.0 (C-1'), 97.1 (C-1), 82.0 (C-3), 79.3 (C-2), 78.4 (C-4), 75.6 ( $3\text{O}-\text{CH}_2\text{Ph}$ ), 75.2 ( $4\text{O}-\text{CH}_2\text{Ph}$ ), 73.9 ( $2\text{O}-\text{CH}_2\text{Ph}$ ), 72.2 (C-5), 70.8 (C-5'), 70.3 (C-3'), 69.5 (C-4'), 68.4 (C-2'), 62.2 (C-6), 61.2 (C-6'), 55.0 (C-1- $\text{OCH}_3$ ), 48.1 (BDA- $\text{OCH}_3$ ), 48.0 (BDA- $\text{OCH}_3$ ), 17.8 (BDA- $\text{CH}_3$ ), 17.7 (BDA- $\text{CH}_3$ ); MS ( $\text{ES}^+$ ):  $m/z$  (%): 763 (100%) [ $M+\text{Na}^+$ ]; HR-MS: calcd for  $\text{C}_{40}\text{H}_{52}\text{O}_{13}\text{Na}$ : 763.3306; found: 763.3302.

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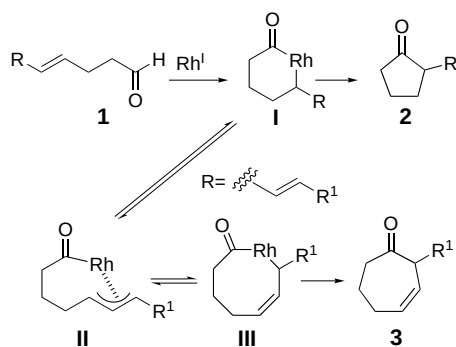
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## A New Method for the Synthesis of Cycloheptenones by $\text{Rh}^{\text{I}}$ -Catalyzed Intramolecular Hydroacylation of 4,6-Dienals

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The development of methodology for the synthesis of cyclic compounds is important in modern synthetic organic chemistry, not least because there are many biologically active compounds with complicated cyclic structures. The construction of a medium-sized ring is relatively difficult due to unfavorable entropy and nonbonding interactions occurring at the transition state during the cyclization. Transition metal catalyzed cyclization is one of the most promising strategies for the construction of such medium-sized ring compounds.<sup>[1]</sup>  $\text{Rh}^{\text{I}}$ -mediated cyclization of 4-alkenals to give cyclopentanone derivatives was first reported by Sakai et al. in 1972,<sup>[2]</sup> and this hydroacylation has subsequently been developed into a catalytic process<sup>[3]</sup> and asymmetric reaction.<sup>[4]</sup> On the basis of results of mechanistic studies,<sup>[5]</sup> it is thought that the reaction proceeds as follows (Scheme 1): a C–H bond of the aldehyde moiety of **1** is oxidatively added to a  $\text{Rh}^{\text{I}}$  complex followed by insertion of a C=C bond of an olefin to give the rhodacycle intermediate **I**. Reductive elimination from **I** occurs to produce cyclopentanone **2** along with regeneration of the  $\text{Rh}^{\text{I}}$  complex. We speculated that if a

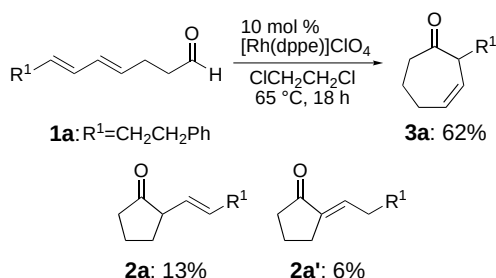
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Scheme 1. Proposed mechanism of the Rh<sup>I</sup>-catalyzed reaction of 4-alkenals to give cyclopentanone derivatives **2** and cycloheptanone derivatives **3**.

double bond is conjugated to a Rh–C bond in rhodacycle **I**, another rhodacycle intermediate **III** would be formed via a π-allylrhodium intermediate **II**. If reductive elimination from **III** occurs, cycloheptanone derivative **3** would be formed. Herein, we report a novel Rh<sup>I</sup>-catalyzed cyclization of 4,6-dienals to give a seven-membered-ring compound by a hydroacylation process.<sup>[6]</sup>

Initially, we investigated the cyclization of 4,6-dienal **1a** (Scheme 2). Treatment of **1a** with 10 mol % of [Rh(dppe)]ClO<sub>4</sub> (dppe = 1,2-bis(diphenylphosphanyl)ethane), generated in situ from [Rh(nbd)(dppe)]ClO<sub>4</sub> (nbd = norbornadiene)



Scheme 2. Cyclization of 4,6-dienal **1a**.

under an atmosphere of hydrogen,<sup>[3d]</sup> in dichloroethane at 65 °C for 18 h gave cycloheptanone **3a** in 62 % yield along with cyclopentanones **2a** and **2a'** in 13 and 6 % yields, respectively. It was thought that cycloheptanone **3a** was produced through reductive elimination from rhodacyclooctenone **III** (see Scheme 1), which was formed from rhodacyclohexanone **I** via π-allylrhodium intermediate **II**. The cyclization of **1a** using other ligands instead of dppe, such as 1,3-bis(diphenylphosphanyl)propane (dppp), 1,2-bis(diphenylphosphanyl)butane (dppb), and PPh<sub>3</sub>, gave no or only trace amounts of cyclized products **2a**, **2a'**, and **3a** along with recovery of the starting material **1a** in 54–73 %. Interestingly, the use of (*R*)-BINAP ([1,1'-binaphthalene]-2,2'-diylbis(diphenylphosphane)) in this cyclization gave only **2a** in 75 % yield, although the enantiomeric excess of **2a** was very low (3 % ee).<sup>[7]</sup>

Next, the influence of the olefinic geometry of substrate **1a** on the reactivity of this cyclization was carefully examined, and the results are summarized in Table 1. The cyclization of (*4E,6E*)-**1a** and that of (*4Z,6E*)-**1a**, both of which have an *E*

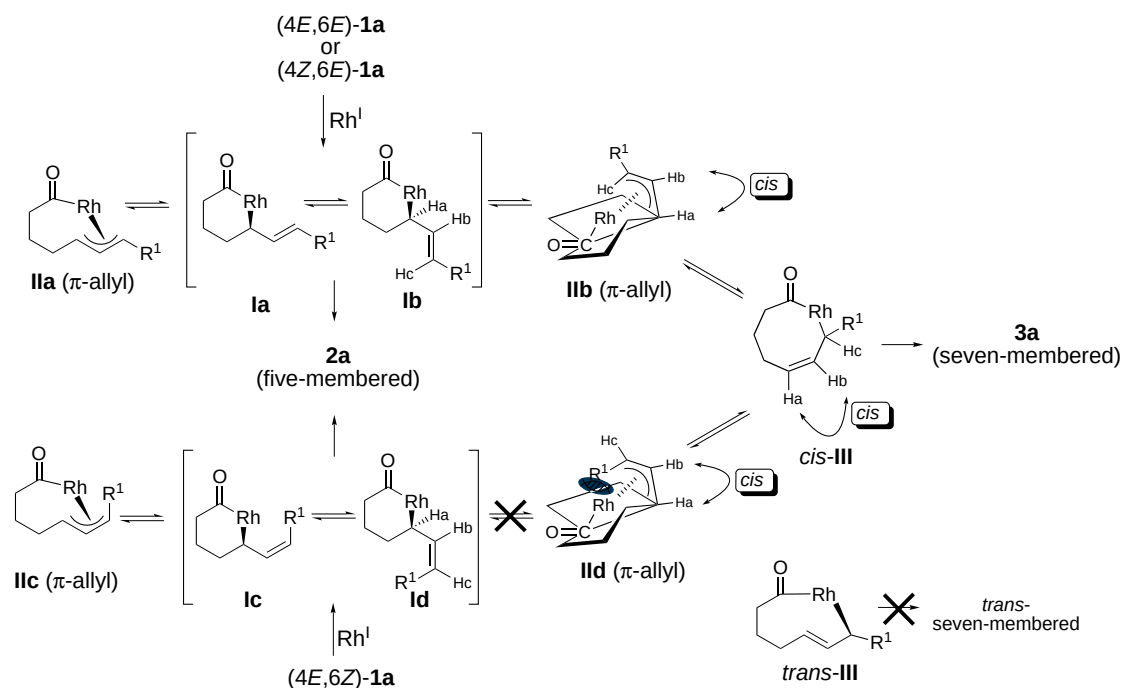
Table 1. Influence of the stereochemistry of **1a** on reactivity.

| Substrate                   | <i>t</i> [h] | <b>3a</b> [%] | <b>2a</b> [%]     | <b>2a'</b> [%] | Starting material recovered [%] |
|-----------------------------|--------------|---------------|-------------------|----------------|---------------------------------|
| ( <i>4E,6E</i> )- <b>1a</b> | 18           | 62            | 13 <sup>[a]</sup> | 6              | –                               |
| ( <i>4Z,6E</i> )- <b>1a</b> | 16           | 65            | 11 <sup>[a]</sup> | 5              | –                               |
| ( <i>4E,6Z</i> )- <b>1a</b> | 18           | trace         | 49 <sup>[b]</sup> | trace          | 38                              |

[a] *E* alkene. [b] *Z* alkene.

olefin at the C6 position, gave cycloheptanone **3a** as the major product in 62 and 65 % yields, respectively. On the other hand, the cyclization of (*4E,6Z*)-**1a**, which contains a *Z* olefin at the C6 position, gave cyclopentanone **2a** as the major product. These results indicate that the olefinic geometry of the diene moiety in 4,6-dienals strongly affects the reaction course. Thus, the cyclization of substrates with an *E* olefin at the C6 position produced cycloheptanone derivatives as the major product, while a cyclopentanone derivative was obtained from a substrate with a *Z* olefin at the C6 position. A plausible reaction mechanism in accord with these results is outlined in Scheme 3. The reaction of (*4E,6E*)-**1a** or (*4Z,6E*)-**1a** with a Rh<sup>I</sup> catalyst gives rhodacycle intermediates **Ia** and **Ib**, which might be in equilibrium with π-allylrhodium intermediates **IIa** and **IIb**. The cycloheptanone **3a** should be produced through reductive elimination from rhodacyclooctenone *cis*-**III**, while the cyclopentanone **2a** should be formed through reductive elimination from **Ia** or **Ib**. In the cyclization of (*4E,6E*)-**1a** and (*4Z,6E*)-**1a**, cycloheptanone **3a** was produced in preference to cyclopentanone **2a**. These results indicate that the equilibrium among the intermediates **Ia**, **Ib**, **IIa**, **IIb**, and *cis*-**III** would lie towards *cis*-**III** although the reason is not clear. On the other hand, in the cyclization of (*4E,6Z*)-**1a**, rhodacycle intermediates **Ic** and **Id** should be produced (see Scheme 3), which might be also in equilibrium with π-allylrhodium intermediates **IIc** and **IId**. It was thought that π-allylrhodium intermediate **IId** was unstable due to steric repulsion between the R<sup>1</sup> substituent at the C7 position and the rhodium metal center in the complex, resulting in the preferential formation of cyclopentanone **2a** in the cyclization of (*4E,6Z*)-**1a**. In all cases, the rhodacyclooctenone *trans*-**III** might be formed via π-allylrhodium intermediate **IIa** or **IIc**. However, it is apparent that a *trans*-seven-membered-ring compound cannot be produced due to its lability.

Cyclization of various 4,6-dienals was investigated under similar conditions (Table 2). The reaction of 4,6-dienal **1b** gave cycloheptanone **3b'** in 66 % yield along with cyclopentanone **2b'** in 9 % yield. In the reaction of **1c**, the cycloheptanone derivatives **3c** and **3c'** were produced in 60 % total yield as the major product. The existence of an olefinic moiety in the side chain is tolerated in this cyclization, and the

Scheme 3. A plausible reaction mechanism that accounts for the different products obtained in the cyclization of **1a**.Table 2. Cyclization of various dienals.<sup>[a]</sup>

| Substrate                                     | <i>t</i> [h] | Yield [%]                     |                 |                                |
|-----------------------------------------------|--------------|-------------------------------|-----------------|--------------------------------|
| <b>1b</b> : R <sup>1</sup> =                  | 24           | <b>3b</b> : –                 | <b>3b'</b> : 66 | <b>2b'</b> : 9                 |
| <b>1c</b> <sup>[b]</sup> : R <sup>1</sup> =   | 24           | <b>3c</b> : 45                | <b>3c'</b> : 15 | <b>2c'</b> : 3                 |
| <b>1d</b> <sup>[c]</sup> : R <sup>1</sup> =   | 18           | <b>3d</b> : 70                | <b>3d'</b> : –  | <b>2d'</b> : –                 |
| <b>1e</b> <sup>[d]</sup> : R <sup>1</sup> = H | 17           | <b>3e</b> : 7                 | <b>3e'</b> : –  | <b>2e'</b> <sup>[e]</sup> : 45 |
| <b>1f</b> :                                   | 16           | <b>2f</b> <sup>[f]</sup> : 60 |                 |                                |
| <b>1g</b> : R <sup>2</sup> = CH <sub>3</sub>  | 17           | <b>3g</b> <sup>[f]</sup> : 10 | <b>3g'</b> : 58 | <b>2g</b> <sup>[f]</sup> : 18  |
| <b>1h</b> <sup>[g]</sup> : R <sup>2</sup> = H | 15           | <b>3h</b> : 9                 | <b>3h'</b> : –  | <b>2h</b> <sup>[h]</sup> : 46  |

[a] All reactions were carried out in the presence of [Rh(dppe)]ClO<sub>4</sub> (10 mol %) in ClCH<sub>2</sub>CH<sub>2</sub>Cl at 65 °C. [b] Reaction temperature was 45 °C. [c] (4*Z*,6*E*)-**1d** was used as the substrate. [d] The yields were determined by GC. [e] *E/Z* = 1/2.5. [f] The cyclized products were obtained as a single isomer although the stereochemistry has not been determined. [g] The reaction was carried out at 65 °C for 12 h, then at reflux for 3 h. [h] *E/Z* = 1/1.6.

reaction of **1d** gave cycloheptenone **3d** in 70 % yield. On the other hand, the cyclization of **1e** and that of **1f**, having no substituent at the C7 position, gave the cyclopentanone **2e'** and **2f'** in 45 and 60 % yields, respectively, as the major

product. The same tendency was observed in the cyclization of **1g** and **1h**; that is, the cyclization of **1g** under similar conditions gave the bicyclic cycloheptenone derivatives **3g** and **3g'** in 68 % total yield along with bicyclic cyclopentanone **2g'** in 18 % yield, whereas the cyclization of **1h**, having no substituent at the terminus of the diene moiety, preferentially afforded the bicyclic cyclopentanone **2h'**. In all cases, a cycloheptenone derivative should be produced through an unstable eight-membered rhodacycle intermediate such as *cis*-**III** (Scheme 3). It seems likely that a substituent (R<sup>1</sup> or R<sup>2</sup>) plays an important role as a donating group to stabilize the buildup of positive charge on the terminal carbon atom of the diene moiety in *cis*-**III**, which might promote the formation of cycloheptenone derivatives.

We have succeeded for the first time in extending Rh<sup>I</sup>-catalyzed intramolecular hydroacylation to the synthesis of seven-membered rings. The cyclization of 4,6-dienals with a substituent at the C7 position produced cycloheptenone derivatives as the major product, while the cyclization of 4,6-dienals with no substituent at the terminus of the diene moiety preferentially gave cyclopentanone derivatives. The olefinic geometry of the diene moiety in 4,6-dienals also affected the reaction course. Thus, the cyclization of substrates having an *E* olefin at the C6 position produced cycloheptenone derivatives as the major product, while a cyclopentanone derivative was obtained from a substrate with a *Z* olefin at the C6 position. Further studies along this line are in progress.

### Experimental Section

Typical procedure for cyclization of (4*E*,6*E*)-**1a**: A solution of [Rh(dppe)(nbd)]ClO<sub>4</sub> (18.0 mg, 0.026 mmol) in degassed ClCH<sub>2</sub>CH<sub>2</sub>Cl (1.0 mL) was stirred under a H<sub>2</sub> atmosphere at room temperature for 1 h. The reaction vessel was flushed with argon gas, and a solution of (4*E*,6*E*)-

**1a** (55.0 mg, 0.26 mmol) in degassed  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (1.6 mL) was added to the mixture. The reaction mixture was stirred at  $65^\circ\text{C}$  for 18 h. After removal of the solvent, the residue was purified by column chromatography on silica gel to afford **3a** (0.16 mmol, 62%) along with **2a** (0.034 mmol, 13%) and **2a'** (0.015 mmol, 6%). Selected spectral data of **3a**: IR (neat):  $\bar{\nu} = 3024, 2934, 1708, 1654, 1496, 1456\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.67\text{--}1.82$  (m, 2H),  $2.03\text{--}2.18$  (m, 2H),  $2.31\text{--}2.76$  (m, 6H),  $3.63$  (m, 1H)  $5.23$  (dddd,  $J = 11.1, 3.2, 2.0, 2.0\text{ Hz}$ , 1H),  $5.76$  (dddd,  $J = 11.1, 6.7, 6.7, 1.9\text{ Hz}$ , 1H),  $7.16\text{--}7.31$  (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 21.8, 29.4, 31.8, 33.2, 44.0, 48.4, 125.7, 125.8, 126.8, 128.2, 128.3, 128.4, 131.2, 141.8, 208.9$ ; EI-LRMS:  $m/z$ : 214 [ $M^+$ ], 123, 110, 104, 91; EI-HRMS calcd for  $\text{C}_{15}\text{H}_{18}\text{O}$  214.1358, found 214.1346. **2a**: IR (neat):  $\bar{\nu} = 2960, 2854, 1740, 1453, 1149\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.68\text{--}1.88$  (m, 2H),  $2.00\text{--}2.42$  (m, 6H),  $2.68\text{--}2.76$  (m, 3H),  $5.47$  (dd,  $J = 15.6, 6.1\text{ Hz}$ , 1H),  $5.60$  (dt,  $J = 15.6, 6.3\text{ Hz}$ , 1H),  $7.17\text{--}7.38$  (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 20.7, 29.8, 34.4, 35.7, 37.7, 52.2, 125.8, 126.6, 128.2, 128.2, 128.4, 128.4, 132.4, 141.8, 218.9$ ; EI-LRMS:  $m/z$ : 214 [ $M^+$ ], 123, 110, 105, 91; EI-HRMS calcd for  $\text{C}_{15}\text{H}_{18}\text{O}$  214.1358, found 214.1362. **2a'**: IR (neat):  $\bar{\nu} = 2924, 2856, 1718, 1648, 1096\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.81$  (tt,  $J = 7.6, 7.6\text{ Hz}$ , 2H),  $1.93$  (dddd,  $J = 7.6, 7.6, 7.6, 7.6\text{ Hz}$ , 2H),  $2.18$  (dt,  $J = 7.6, 7.6\text{ Hz}$ , 2H),  $2.34$  (dd,  $J = 7.6, 7.6\text{ Hz}$ , 2H),  $2.52\text{--}2.57$  (m, 2H),  $2.67$  (t,  $J = 7.6\text{ Hz}$ , 2H),  $6.57$  (dddd,  $J = 7.6, 7.6, 2.7, 2.7\text{ Hz}$ , 1H),  $7.15\text{--}7.32$  (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 20.0, 26.9, 29.3, 30.1, 35.6, 38.7, 125.7, 128.1, 128.1, 128.2, 128.2, 135.4, 137.4, 141.5, 206.7$ ; EI-LRMS:  $m/z$ : 214 [ $M^+$ ], 130, 123, 110, 91; EI-HRMS calcd for  $\text{C}_{15}\text{H}_{18}\text{O}$  214.1358, found 214.1365.

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## Super-Hydrophobic Surface of Aligned Polyacrylonitrile Nanofibers\*\*

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The wettability of solid surfaces is a very important property that is governed by both the chemical composition and the geometrical microstructure of the surface.<sup>[1-3]</sup> Super-hydrophobic surfaces, with a water contact angle (CA) greater than  $150^\circ$ , have attracted much interest because of potential practical applications.<sup>[4]</sup> Conventionally, super-hydrophobic surfaces have been produced mainly in two ways: One is to create a rough surface (e.g., with a fractal structure)<sup>[5]</sup> and the other is to modify the surface with materials of low surface free energy, such as fluorinated or silicon compounds.<sup>[6]</sup>

Recently, we have succeeded in preparing densely packed aligned carbon nanotubes (ACNTs).<sup>[7]</sup> The water contact angle on this nanostructured ACNT film was  $(158.5 \pm 1.5)^\circ$ , that is, the ACNT film has super-hydrophobic properties. The water contact angle increased to  $(171 \pm 0.5)^\circ$  after modification with a fluoroalkylsilane. This high value is believed to be due to the nanostructure and the presence of fluoroalkylsilane groups. Here we describe a novel method to synthesize aligned polyacrylonitrile (PAN) nanofibers, which have a nanostructure similar to that of the ACNTs but a much lower density. The surface of the as-synthesized PAN nanofibers shows super-hydrophobicity (CA =  $(173.8 \pm 1.3)^\circ$ ). This is the first report of a water contact angle greater than  $170^\circ$  without any modification of the surface. We also note that the density of the aligned nanostructures is very important for the super-hydrophobicity.

Compared with other template syntheses,<sup>[8-10]</sup> the method used here to synthesize PAN nanofibers is very simple. Only extrusion of the PAN precursor solution into the solidifying solution under pressure is necessary.<sup>[11]</sup> The template was an anodic aluminum oxide membrane, prepared according to ref. [12], with a diameter of 13 mm, a thickness of 60  $\mu\text{m}$ , and a porosity consisting of an array of parallel, straight channels. Aligned nanofibers with different diameters and densities can be easily obtained by using templates with different pore diameters, and the alignment process can be applied to different polymer precursors such as poly(vinyl alcohol), polystyrene, polyesters, and polyamides.

Figure 1a shows a scanning electron microscopic (SEM) image of the surface of the as-prepared anodic aluminum oxide membrane used as template. The pores are arranged in a regular hexagonal pattern with an average pore diameter of

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