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Diastereoselective [2 + 2] Photocycloaddition of Cyclohexenone Derivative with Olefins in Supercritical Carbon Dioxide

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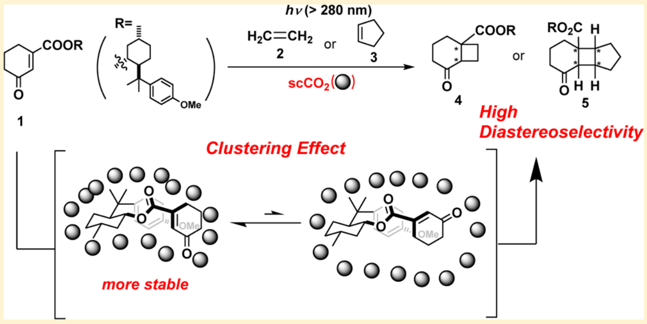

ABSTRACT: We performed diastereoselective [2 + 2] photocycloaddition of the cyclohexenone derivative with olefins in supercritical carbon dioxide ($scCO_2$). A dramatic enhancement of conversion was observed at around critical density when ethylene gas was employed as a coupling partner. Furthermore, we elucidated that the pressure dependence of the diastereomeric excess (de) was discontinuous at critical density owing to the difference of substrate solubility between near-critical carbon dioxide ($ncCO_2$) and $scCO_2$; both the reaction conversion and de values obtained were lower than those in conventional organic solvent. On the contrary, when cyclopentene (liquid) was utilized as a coupling partner, moderate conversion was always observed irrespective of CO_2 pressure, because the substrate could be dissolved in cyclopentene. Furthermore, we could accomplish de enhancement in $scCO_2$, in particular around critical density, compared to that in organic solvent. This highly selective photoreaction is due to the unique solvent property of $scCO_2$, which is called the clustering effect.

■ INTRODUCTION

The photochemical reactions *via* excited state are good synthetic methods for constructing highly strained compounds or complicated structures with ease. In particular, it is well-known that [2 + 2] photocycloaddition can afford the very strained cyclobutane skeleton easily by photoirradiation to olefins. Highly strained cyclobutane skeletons show important potential as the precursor of not only natural products but also various unique compounds, and much effort has been dedicated to this reaction in various fields.[1,2] However, it is very difficult in photoreactions to control the high regio- and stereoselectivity because the photoreaction includes the excited state's species, which are hard to control because of their very short lifetime and very high reactivity. Therefore, the stereoselective photoreaction is still a challenging problem. Many approaches such as solid-state photochemistry, supramolecular photochemistry, and using a chiral auxiliary or sensitizer[3] have led to greater achievements in highly asymmetric photoreactions. Among those approaches, the introduction of chiral auxiliaries has been widely employed as a promising method for achieving highly stereoselective photoreaction. Although this method affords some diastereomeric (not enantiomeric) products, very high selectivity can be expected using the strong interaction in the ground state. As the chiral auxiliary, a wide range of natural product derivatives, such as camphor,[3d] menthol,[4] tartaric acid,[5] and bornyl,[6] have been utilized. We also have examined the diastereoselective [2 + 2] photocycloaddition of cyclohexenone, which is attached to the menthol derivatives as chiral auxiliaries accompanied with a ester bond, with olefins as a coupling partner[7] and reported a very high diastereomeric excess (de) (max 96% de) by introducing a 8-(*p*-methoxynaphthyl) menthyl derivative.[7g] As reported previously,[7d] the diastereoselective mechanism of this photoreaction is explained by an equilibrium among the conformations of various prochiral substrates. In various conformations, stacked *s-trans* and *s-cis* conformers, in which the cyclohexenone ring and aromatic ring attached to menthyl group are located face-to-face, are very stable, and these conformers become the intermediates for photoproducts. In particular, the *s-trans* conformer is more stable than the *s-cis* conformer, and the *s-trans* one may have the smallest volume of all conformers. Therefore, the key point for enhancing diastereoselectivity should be to stabilize the most stable and smallest conformer. Although previously we have only paid attention to temperature as a stabilizing factor, these findings prompt us to utilize supercritical carbon dioxide ($scCO_2$; critical point = 31 °C, 7.38 MPa) as a reaction media for enhancing diastereoselectivity. $scCO_2$ is a unique media that form clusters owing to the density fluctuation around the critical point in particular.[8] Previously, some papers have reported highly selective photoreactions utilizing this unique property in $scCO_2$ such as photoisomerization,[9] photodimerization,[10] and Photo-Fries rearrangement;[11] however, there are few reports for asymmetric photoreaction in $scCO_2$. In both uni-[12] and bimolecular[13] enantiodifferentiating photosensitized reactions conducted in $scCO_2$, the product's ee always showed a sharp dependence on pressure observing critical density (d_c = 0.468 g cm^{-3}) at each temperature. In addition, a higher enantiomeric excess (ee) value compared to that in conventional organic solvent was observed in some cases,[12b,c,13a] only using $scCO_2$ as reaction media. They concluded that these results were accomplished by the clustering effect of $scCO_2$,

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Scheme 1. Diastereodifferentiating [2 + 2] Photocycloaddition of Cyclohexenone Having an 8-(*p*-Methoxyphenyl) Menthyl Group (1) with Ethylene (2) or Cyclopentene (3)

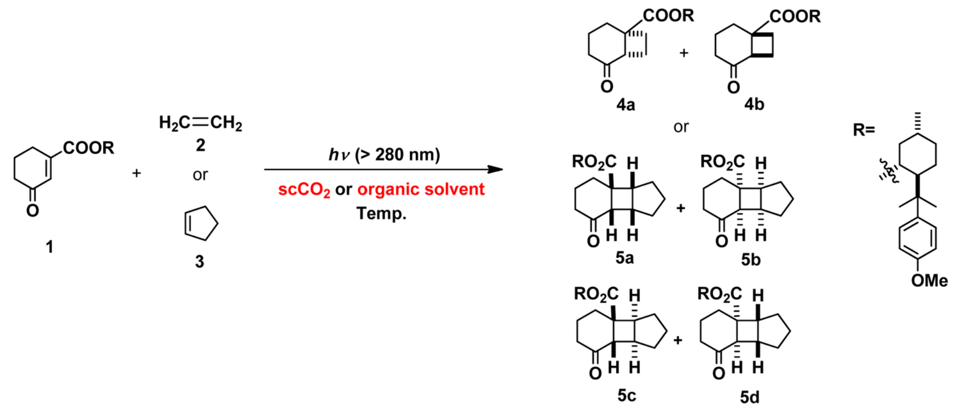

Table 1. Diastereodifferentiating [2 + 2] Photocycloaddition of 1 with 2 in $ScCO_2$ Media or Conventional Organic Solvents[a]

run	medium	temp (°C)	CO_2 pressure (MPa)	total pressure (MPa)	conv[b] (%)	de[c] (%)
1	nc- and $scCO_2$	35	3.5	6.5	4	[d]
2			4.7	7.5	4	[d]
3			4.8	7.7	7	[d]
4			5.6	8.6	88	40
5			5.7	8.7	77	41
6			6.0	9.0	93	40
7[e]			6.0	9.0	66	38
8			6.7	9.7	95	42
9			7.1	10.1	91	41
10			7.3	10.3	91	43
11			7.5	10.5	94	44
12			8.0	11.0	92	43
13			8.5	11.5	91	40
14			9.0	12.0	90	42
15			9.5	12.5	87	39
16			10.0	13.0	90	40
17			16.0	19.0	84	38
18		45	6.0	9.0	24	[d]
19			6.7	9.7	65	35
20			7.3	10.3	80	34
21			7.5	10.5	87	40
22			8.0	11.0	74	40
23			8.5	11.5	89	36
24			8.8	11.8	91	36
25			9.2	12.2	86	37
26			9.5	12.5	82	36
27			9.7	12.7	83	39
28			10.0	13.0	79	41
29			10.8	13.8	83	40
30			11.8	14.8	87	39
31			13.5	16.5	78	34
32[f]	methylcyclohexane	0	[g]	0.1	100	49
33		35	[g]	0.1	74	23
34		45	[g]	0.1	47	22
35[f]	toluene	0	[g]	0.1	100	31
36		35	[g]	0.1	57	17
37		45	[g]	0.1	47	15
38[f]	dichloromethane	0	[g]	0.1	100	19
39		35	[g]	0.1	26	−4

[a] [**1**] = 5 mM; **2** = 3.0 MPa (in nc- and $scCO_2$), or 0.1 MPa (in organic solvent); irradiated for 3 h (in $scCO_2$) or 1.5 h (in organic solvent). [b] Determined by ^{1}H NMR. [c] Diastereomeric excess of product ((**4a** − **4b**)/(**4a** + **4b**)) determined by chiral HPLC; error in de < ±1%. [d] Not determined. [e] Irradiated for 1.5 h. [f] Data from ref 7h. [g] Not contained.

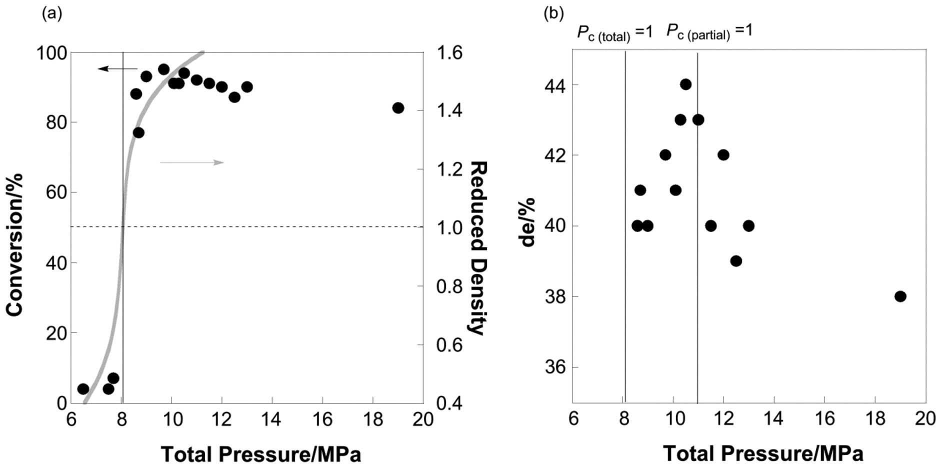

Figure 1. (a) Pressure dependence of the reduced density (gray) and the conversion and (b) de of product (**4a** and **4b**) obtained in the diastereodifferentiating photocycloaddition of **1** with **2** (3.0 MPa) in nc- and scCO$_2$ at 35 °C.

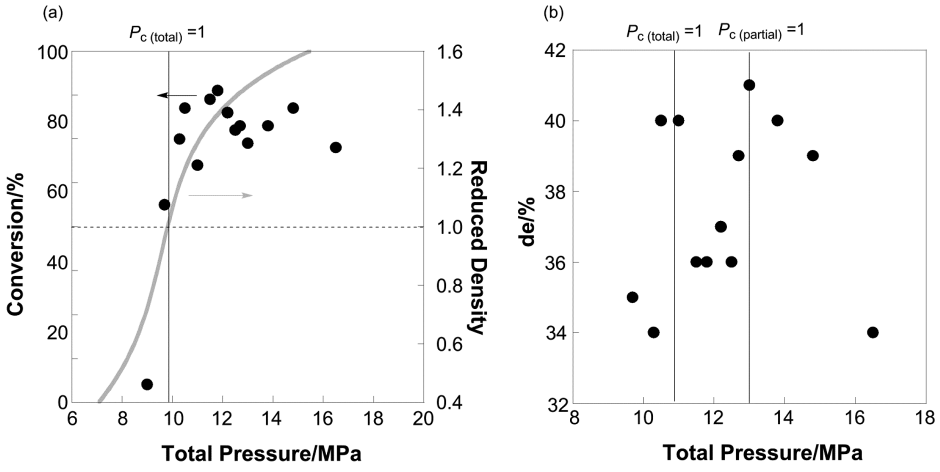

Figure 2. (a) Pressure dependence of the reduced density (gray) and the conversion and (b) de of product (**4a** and **4b**) obtained in the diastereodifferentiating photocycloaddition of **1** with **2** (3.0 MPa) in nc- and scCO$_2$ at 45 °C.

which is never observed in conventional organic solvent. However, in all mentioned photosensitized reactions in scCO$_2$, the behavior in only the excited state has been discussed in terms of fluorescence or fluorescence lifetime measurement because the excited state played an important role for determining the selectivity in those reactions. On the other hand, this clustering effect can induce a very large negative activation volume in the ground state.[14] This means that the most stable and smallest conformer (*s-trans*) in the diastereoselective photoreaction of cyclohexenone can be stabilized efficiently by the clustering effect in the ground state and therefore may afford high de values. From these viewpoints, in this work we examined the diastereodifferentiating [2 + 2] photocycloaddition of cyclohexenone having a 8-(*p*-methoxyphenyl) menthyl group as a chiral auxiliary (**1**) with some olefins (**2** or **3**) in scCO$_2$ to examine the clustering effect in this diastereoselective photoreaction (Scheme 1).

■ RESULTS AND DISCUSSION

Ethylene Gas (2) as Coupling Partner. Previously, we achieved the very highly diastereoselective [2 + 2] photocycloaddition of cyclohexenone having menthol derivatives as chiral auxiliaries with ethylene as a coupling partner in conventional organic solvent.[7a−d,g] Because ethylene gas is the smallest olefin, the high selectivity using ethylene can demonstrate a quite important significance in the field of organic synthesis. Furthermore, due to its gas-like property, scCO$_2$ can be highly miscible with gas reagents. This high miscibility may be capable of enhancing the reaction efficiency (reaction conversion) owing to the very high diffusion. Hence, at first, we examined the diastereodifferentiating [2 + 2] photocycloaddition of **1** with **2** (3.0 MPa) in ncCO$_2$, scCO$_2$, and conventional organic solvent at 35 and 45 °C. The conversion and de values obtained are listed in Table 1 and summarized in Figures 1 and 2.

The photoreaction shown in Scheme 1 proceeded smoothly and afforded only the desired photoproducts (**4a** and **4b**). In both scCO$_2$ and conventional organic solvent, high reaction temperature decreased the reaction conversion (Table 1 run 8 vs 19 and run 10 vs 20, etc. in scCO$_2$ and runs 32−34, runs 35−37, runs 38 and 39 in conventional organic solvents). This was probably due to the low solubility of ethylene gas at high temperature. As can be seen in Figures 1a and 2a, the reaction conversion was enhanced dramatically around ca. 8.0 MPa (35 °C) or ca. 10.0 MPa (at 45 °C) observed critical density (meaning reduced density = 1) in scCO$_2$ media. In scCO$_2$ media, the solubility of the substrate was enhanced generally around the pressure of observed critical density (P_c; 8.1 MPa at 35 °C, 9.8 MPa at 45 °C) owing to the clustering effect.[8] Thus, a dramatic enhancement of conversion could be observed around critical density at each temperature. In the $scCO_2$ region, the change of conversion might almost be a plateau, indicating modest pressure effects in this region. On the other hand, the best conversion in $scCO_2$ media was lower than that in methylcyclohexane for the same irradiation time (run 7 vs 33), showing that the CO_2 clustering effect could not enhance the reaction efficiency even with a gas reagent. Furthermore, the lower de values were obtained at higher temperature in both organic solvent and $scCO_2$. As mentioned before, a more stable conformer was hard to form preferentially at the high temperature. On the other hand, we could observe an enhanced diastereoselectivity in $scCO_2$ compared to that in conventional organic solvent (run 11 vs run 33 at 35 °C, run 28 vs run 34 at 45 °C). Furthermore, as can be seen from Figures 1b and 2b, the de of photoproducts is not a straightforward function of CO_2 pressure, exhibiting a distinct peak around 11.0 MPa (at 35 °C) or 13.0 MPa (at 45 °C). At these pressures, the partial pressure of CO_2 showed the critical density. If the pressure is the main factor for controlling the conformation equilibrium, the de value obtained increases along with the pressure increasing. However, the reaction outcome showed a different tendency. This means the clustering effect, which is observed most clearly around the pressure of observed critical density, can be the most important factor for controlling the product's de. Thus, although the diastereoselectivity is intrinsically independent of reaction conversion in this photoreaction, we were able to enhance both reaction conversion and the diastereoselectivity by clustering effect using $scCO_2$ as reaction media compared to levels in organic solvents at the same temperature. However, the possibility that the ethylene gas's pressure controls this photoreaction should be carefully considered. Next, we examined this photoreaction with lower pressure (1.0 MPa) ethylene gas in nc- and $scCO_2$. The data obtained were listed in Table 2 and summarized in Figure 3 and Figure 4.

Even at lower ethylene pressure, a sudden leap in reaction conversion was observed around the total pressure showing critical density at each temperature as in the case of 3.0 MPa of ethylene. Furthermore, the de peak, which was not distinct, was also observed around the partial CO_2 pressure showing critical density at 35 °C. Thus, the CO_2's clustering effect could control this photoreaction predominantly even using a low-pressure reagent. However, obviously, both the conversion and de values obtained at 1.0 MPa ethylene gas were lower than those obtained at 3.0 MPa ethylene gas (Table 1 vs Table 2). These outcomes mean the ethylene gas can also control this photoreaction critically. This observation encouraged us to examine the pressure or concentration effect of ethylene gas on this photoreaction in nc- and $scCO_2$ (Table 3).

When using the same pressure of ethylene gas, the conversion and de were mostly similar irrespective of substrate concentration (runs 1, 2, and 3). However, lower conversion and decrease in de of ca. 10% were observed using half pressurizing ethylene gas despite the same concentration ratio between substrate and ethylene (run 1 vs 4). This can be explained considering not only CO_2 pressure as reaction media but also ethylene gas pressure as a reagent that could control both the reaction conversion and the substrate's conformation equilibrium in favor of the more stable conformer. To clarify this hypothesis, we examined the ethylene gas pressure effect for this photoreaction in methylcyclohexane using a pressure-resistant reaction vessel (Table 4).

Table 2. Diastereodifferentiating [2 + 2] Photocycloaddition of 1 with 2 (1.0 MPa) in nc- and $scCO_2$[a]

run	temp (°C)	CO_2 pressure (MPa)	total pressure (MPa)	conv[b] (%)	de[c] (%)
1	35	5.5	6.5	2	*d*
2		7.5	8.5	79	31
3		8.5	9.5	79	34
4		10.0	11.0	74	31
5		17.0	18.0	68	29
6	45	8.0	9.0	14	*d*
7		9.0	10.0	58	29
8		10.0	11.0	69	28
9		10.5	11.5	67	29
10		11.5	12.5	61	29
11		11.7	12.7	61	30
12		12.5	13.5	69	29
13		14.5	15.5	64	27

[a] [1] = 5 mM; irradiated for 3 h. [b] Determined by ^1H NMR. [c] Determined by chiral HPLC; error in de < ±1%. [d] Not determined.

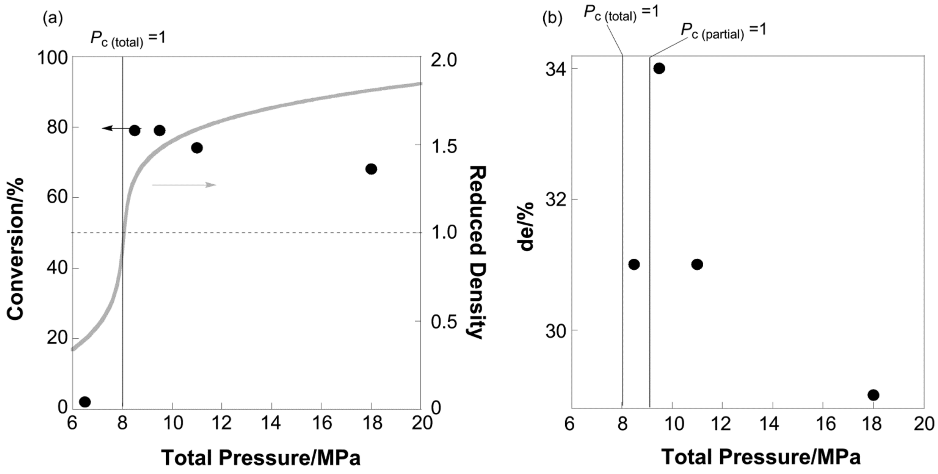

Figure 3. (a) Pressure dependence of the reduced density (gray) and the conversion and (b) de of product (**4a** and **4b**) obtained in the diastereodifferentiating photocycloaddition of **1** with **2** (1.0 MPa) in nc- and $scCO_2$ at 35 °C.

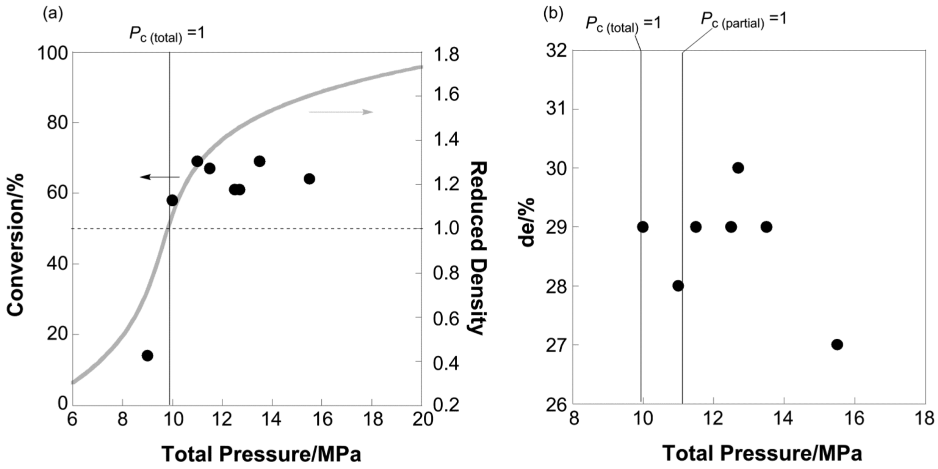

Figure 4. (a) Pressure dependence of the reduced density (gray) and the conversion and (b) de of product (**4a** and **4b**) obtained in the diastereodifferentiating photocycloaddition of **1** with **2** (1.0 MPa) in nc- and scCO$_2$ at 45 °C.

Table 3. Diastereodifferentiating [2 + 2] Photocycloaddition of 1 with 2 at Various Pressures in nc- and scCO$_2$ at 35 °C

run	concn (mM)	ethylene pressure (MPa)	CO$_2$ pressure (MPa)	total pressure (MPa)	conv[a] (%)	de[b] (%)
1	5.0	3.0	8.0	11.0	92	42
2	2.5	3.0	8.0	11.0	92	39
3	10.0	3.0	8.0	11.0	93	42
4	2.5	1.5	8.0	9.5	82	35

[a] Determined by ^{1}H NMR. [b] Determined by chiral HPLC; error in de < ±1%.

As anticipated, high pressurizing ethylene gas could afford a high conversion and de even in conventional organic solvent (Table 4, run 1). Furthermore, both the conversion and de using 3.0 MPa ethylene gas in methylcyclohexane were higher than that in scCO$_2$ (Table 4 run 1 vs Table 1 run 7). Although we could observe the distinct clustering effect of scCO$_2$ in this diastereodifferentiating photoreaction, pressure of ethylene gas as reagent could affect the conformation stability of the substrate and control both the conversion and de preferentially. Therefore, it is impossible to examine the clustering effect of this photoreaction in more detail using ethylene gas as a reagent.

Cyclopentene Liquid (3) as Coupling Partner. As mentioned before, we elucidated that the pressure of ethylene gas as a coupling partner controlled this photoreaction more than CO$_2$ pressure. Accordingly, we employed liquid cyclopentene (**3**) as a coupling partner and examined the photoreaction of **1** with **3** in both scCO$_2$ and methylcyclohexane and toluene to confirm the CO$_2$-self-clustering effect in this photoreaction by utilizing an accurate volume of **3**.

First, we examined this photoreaction in conventional organic solvent to confirm the temperature effect (Table 5). As reported previously, this photoreaction should afford the four diastereomeric products: *cis-syn-cis* products **5a**, **5b** and *cis-anti-cis* products **5c**, **5d**. However, only the three products **5a**, **5c**, and **5d** were actually obtained.[7f,h] Therefore, the de value of *syn* products was always >99%. For the reaction conversion, we could not observe the distinct difference at each temperature. In particular, slightly higher conversion was observed at higher temperature in toluene (Table 5, runs 2 and 4). This indicated that cyclopentene was fully dissolved in each solvent, unlike for ethylene. Conversely, the de value of the *anti* products decreased when the temperature was increased for both solvents (Table 5). This tendency is similar with the reaction using ethylene gas, and we could also elucidate that the conformation stability plays a key role for determining de in this photoreaction, as shown in the previous report.[7e] On the basis of these outcomes, we examined this photoreaction in scCO$_2$ media at 35 and 45 °C (Table 6).

When ethylene gas was used as a reagent, the reaction almost did not proceed at the ncCO$_2$ region owing to the very low solubility of substrate. On the contrary, a moderate conversion was observed even in the ncCO$_2$ region (Figure 5a and Figure 6a), and the dramatic enhancement could not be observed at the critical density when using cyclopentene as a reagent. This indicated that the substrate can be dissolved in cyclopentene, and

Table 4. Diastereodifferentiating [2 + 2] Photocycloaddition of 1 with 2 at Various Pressures in Methylcyclohexane at 35 °C[a]

run	ethylene pressure (MPa)	conv[b] (%)	de[c] (%)
1	3.0	90	58
2	1.0	86	54
3	0.6	78	46
4	0.3	71	39
5	0.1[d]	74	23

[a] [**1**] = 5 mM; irradiated for 1.5 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral HPLC; error in de < ±1%. [d] Ethylene gas was bubbling for 5 min.

Table 5. Diastereodifferentiating [2 + 2] Photocycloaddition of 1 with 3 at 35 or 45 °C in Conventional Organic Solvent[a]

					de[c] (%)	
run	temp (°C)	solvent	conv[b] (%)	ratio[c] *syn*:*anti*	*syn*	*anti*
1	35	methyl cyclohexane	76	33:67	>99	39
2		toluene	63	27:73	>99	27
3	45	methyl cyclohexane	74	26:74	>99	26
4		toluene	72	32:68	>99	21

[a] [**1**] = 5.0 mM, 15 equiv of **3** added; irradiated for 1.5 h. [b] Determined by ^{1}H NMR. [c] *syn*:*anti* = (**5a**:(**5c** + **5d**)); ratio and diastereomeric excess of *anti* products ((**5c** − **5d**)/(**5c** + **5d**)) determined by chiral HPLC; error in de < ±1%.

this solution can also be easily miscible with $ncCO_2$ media. Then, the reaction could proceed even in $ncCO_2$ media. Still, the obtained conversion was about 50%, which was lower than that in conventional organic solvent (Table 5 vs Table 6). On the other hand, the distinct peak of de value was observed around the pressure of critical density (ca. 8.0 MPa at 35 °C, ca. 10.0 MPa at 45 °C) similarly as mentioned previously (Figure 5b and 6b). This means that CO_2 pressure did not play a role in controlling conformation stability. Furthermore, an enhanced de (about 10% at 35 °C, about 20% at 45 °C) compared to that in methylcyclohexane was observed in $scCO_2$ (Table 6 run 2 vs Table 5 run 1 at 35 °C, and Table 6 run 11 vs Table 5 run 3 at 45 °C). These outcomes clearly showed that the clustering effect of $scCO_2$ played an inevitable role for controlling not only the solubility of substrate but also the product's selectivity

Table 6. Diastereodifferentiating [2 + 2] Photocycloaddition of 1 with 3 at 35 and 45 °C in $ScCO_2$ Media[a]

run	temp (°C)	CO_2 pressure (MPa)	conv[b] (%)	ratio[c] *syn:anti*	de[c] (%) *syn*	*anti*
1	35	7.6	48	30:70	>99	31
2		8.0	45	41:59	>99	50
3		8.4	46	37:63	>99	47
4		8.4	46	36:64	>99	45
5		8.8	39	35:65	>99	40
6		9.5	38	34:66	>99	39
7		10.8	34	32:68	>99	27
8	45	9.3	26	27:73	>99	37
9		9.5	31	30:70	>99	39
10		9.7	47	28:72	>99	43
11		10.0	51	25:75	>99	45
12		10.2	54	26:74	>99	43
13		11.3	42	25:75	>99	42
14		11.7	40	23:77	>99	37

[a] [**1**] = 5.0 mM, 15 equiv of **3** added; irradiated for 1.5 h. [b] Determined by ^{1}H NMR. [c] *syn:anti* = (**5a**:(**5c** + **5d**)); ratio and diastereomeric excess of antiproducts ((**5c** − **5d**)/(**5c** + **5d**)) determined by chiral HPLC; error in de < ±1%.

CONCLUSION

In examining the diastereodifferentiating [2 + 2] photocycloaddition of cyclohexenone with an 8-(*p*-methoxyphenyl) menthyl group as a chiral auxiliary (**1**) with olefins (gas reagent **2** or liquid reagent **3**) in $scCO_2$ media, we have revealed that the dramatic enhancement of reaction conversion and the peak of de value could be observed around critical density owing to the clustering effect, which was a specific feature in $scCO_2$ media. The conversion leap was induced by the difference in the substrate's solubility between $ncCO_2$ and $scCO_2$ media; however, the best conversion in each reaction (with **2** or **3**) was unexpectedly lower than that in conventional organic solvent. Furthermore, we elucidated that the reaction selectivity was controlled by the ethylene gas preferentially. We could not confirm the merit of using $scCO_2$ media for diastereoselectivity when adopting ethylene gas as coupling partner. However, when employing cyclopentene as a reagent, we could achieve a de higher than that in organic solvent. Apparently, this superior result depended on the clustering effect of $scCO_2$, and we could elucidate that $scCO_2$ reaction media was effective from the perspective of not only ecofriendly chemistry but also asymmetric synthetic chemistry. Now, we have expanded the scope of using supercritical fluids for achieving the compatibility of high conversion and high selectivity.

EXPERIMENTAL SECTION

General. All chemicals were used without further purifications. Spectrograde solvents were used throughout the work. Carbon dioxide of 99.99% purity was used as received. Cyclohexenone (**1**) was prepared as reported previously.[7]

Photolysis and Product Analysis. An ether solution containing a given amount of substrate **1** was placed in a high-pressure vessel, which was equipped with three sapphire windows for photoirradiation. Then, the ether was evaporated *in vacuo*. After that, the coupling partner was added under N_2 atmosphere, if necessary. Then, carbon dioxide was introduced to the vessel until the desired pressure (3.5−16.0 MPa) was reached at the fixed temperature (35.0 or 45.0 ± 0.1 °C). The light source was a 500-W ultrahigh-pressure mercury lamp, and the light passed through a water layer and pyrex filter before introduction to the reaction vessel.

After photoirradiation, the reaction vessel was placed in an ice bath to cool. Then, the pressure of CO_2 (and ethylene) was released very

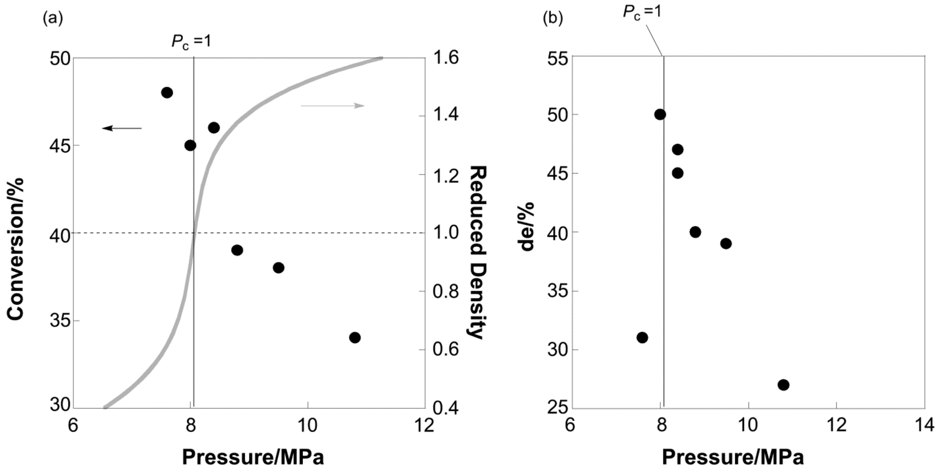

Figure 5. (a) Pressure dependence of the reduced density (gray) and the conversion and (b) de of antiproduct (**5c** and **5d**) obtained in the diastereodifferentiating photocycloaddition of **1** with **3** in nc- and $scCO_2$ at 35 °C.

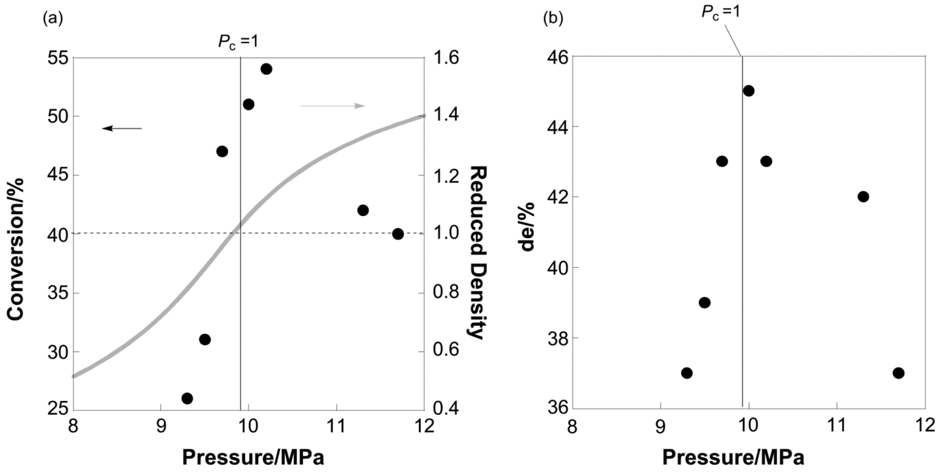

Figure 6. (a) Pressure dependence of the reduced density (gray) and the conversion and (b) de of antiproduct (**5c** and **5d**) obtained in the diastereodifferentiating photocycloaddition of **1** with **3** in nc- and $scCO_2$ at 45 °C.

slowly and gathered into ice-cooled diethyl ether using a stainless steel tube. The residue in the vessel was collected by washing several times with diethyl ether after disassembling the reaction vessel completely. In a former paper,[12c] we reported a large deviation observed in conversion or yield even after several times washing, without reaction vessel disassembly. However, we could succeed in high reproducibility (same conversion and standard deviation of 1.4% in de) adopting this washing method and therefore could discuss the conversion or de accurately in this paper. The combined ether solution was evaporated *in vacuo*, and ^{1}H NMR of residue was measured for calculating the reaction conversion. The de of **4** or **5** was determined with a chiral HPLC instrument equipped with a UV detector (detection at 277 nm). The chiral HPLC analysis for product **4** was run at 25 °C on a Chiralpak IB column (5 μm particles, 4.6 mm ϕ × 250 mm) eluted with a 98:2 mixture of *n*-hexane/isopropyl alcohol at a flow rate of 0.2 mL/min under the isocratic conditions. Each diastereomer's peaks were well separated and retention time was **4a** 45.7 min and **4b** 42.3 min; de was calculated from the integrated areas. The chiral HPLC analysis for product **5** was run as reported previously.[7f]

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Notes

The authors declare no competing financial interest.

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