Pergamon

Tetrahedron Letters 43 (2002) 5859–5861

TETRAHEDRON
LETTERS

Disproportionation of diarylmethanol derivatives by using supercritical water

Bunpei Hatano,* Jun-ichi Kadokawa and Hideyuki Tagaya

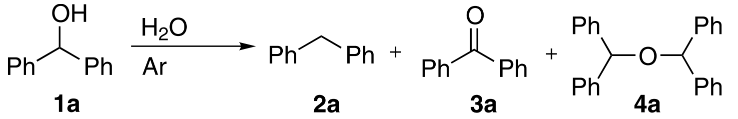
Department of Chemistry and Chemical Engineering, Faculty of Engineering, Yamagata University,
Yonezawa, Yamagata 992-8510, Japan

Received 11 March 2002; revised 12 June 2002; accepted 14 June 2002

Abstract—Non-catalytic disproportionation of diarylmethanol derivatives was found to proceed efficiently in supercritical water. This method was also applied to various diarylmethylamine derivatives to give the disproportionation products in good yields.
© 2002 Elsevier Science Ltd. All rights reserved.

Water has been attracting increased attention as a medium for chemical reactions in recent years.[1] The physicochemical properties of supercritical and near-critical water are quite different from those of ordinary water,[2] and the reactivity of organic compounds is often enhanced greatly. Early interest in supercritical water utilization was focused on waste treatment of such as polymer wastes and toxic compounds, and the complete air combustion of these wastes with little or no toxic emission is possible in supercritical water.[3] On the other hand, only a few reports have described the utility of supercritical or near-critical water from the viewpoint of organic synthesis.[4,5] We now report the first example of disproportionation[6] of diarylmethanol derivatives (**1**) in supercritical water. This transformation is applicable to various diarylmethanol and diarylmethylamine derivatives (**1**) to give the corresponding diarylmethanes (**2**) and diaryl ketones (**3**) in excellent yields, respectively.

During the course of our study to investigate the reactivity of alcohols in supercritical water, we found that



(1)

Table 1. The reaction of **1a** in high-temperature water[a]

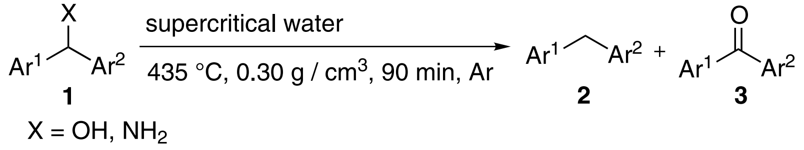
Entry	Temp. (°C)	Water (g)	Density (g/cm³)[b]	Ion product (−log *Kw*)	Reaction period (min)	Conv. (%)	Isolated yield (%)		
							2a	**3a**	**4a**
1	435	0.5	0.05	22.0	90	100	42	40	–
2	435	3.0	0.30	13.8	90	100	46	48	–
3	435	5.4	0.54	11.1	90	100	43	46	–
4	435	0	–	–	90	47	11	12	–
5	435	3.0	0.30	13.8	15	69	27	28	–
6[c]	300	3.0	–	–	90	44	15	16	Trace
7	200	3.0	–	–	90	30	–	–	27

[a] *Reaction conditions*: 2.0 mmol of **1a**, H_2O, under Ar in a tubular steel bomb reactor (10 mL), unless otherwise stated.
[b] The value of supercritical water density: water density = water (g)/the volume of reactor (10 mL).
[c] A trace amount of **4a** was detected by ^1H NMR.

---

* Corresponding author.

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)01163-2



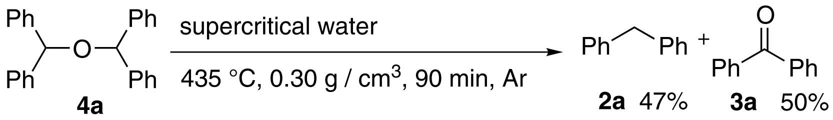
(2)

Table 2. Disproportionation of **1** in supercritical water[a]

1	Ar^1	Ar^2	X	Isolated yield (%)	
				Alkane **2**	Ketone **3**
1b	C_6H_5	3-MeC_6H_4	OH	46	43
1c	C_6H_5	4-MeC_6H_4	OH	47	42
1d	4-MeC_6H_4	4-MeC_6H_4	OH	34	34
1e	C_6H_5	2-Naphtyl	OH	39	38
1f	C_6H_5	4-Pyridyl	OH	49[b]	49[b]
1g	C_6H_5	C_6H_5	NH_2	49	49
1h	C_6H_5	4-MeC_6H_4	NH_2	41	42
1i	4-MeC_6H_4	4-MeC_6H_4	NH_2	37	38
1j	C_6H_5	Cyclohexyl	OH	Complex mixture	

[a] *Reaction conditions*: 2.0 mmol of **1**, 3.0 mL of H_2O, at 435°C, under Ar, unless otherwise stated.

[b] The yield was determined by ^{1}H NMR.



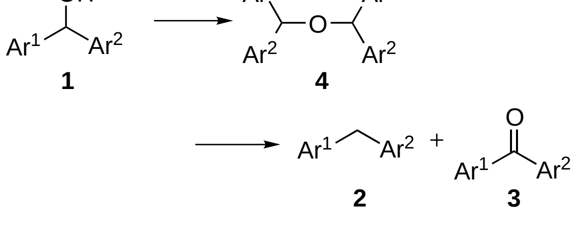
(3)

diphenylmethanol (**1a**) was transformed into diphenylmethane (**2a**) and benzophenone (**3a**). In order to reveal the scope of the present unique disproportionation, **1a** was treated under several conditions summarized in Eq. (1) and Table 1.[7] In supercritical water, the present disproportionation proceeded smoothly over the examined water density range (0.05, 0.30, and 0.54 g/cm^3) (entries 1, 2, and 3). Although change in the density of supercritical water is reported to influence ion product at the same temperature,[8,9] it did not affect the reaction. When **1a** was heated at 435°C without water, the yields of the desirable products greatly decreased (entry 4). This fact indicates that supercritical water accelerates the disproportionation. The shorter reaction time gave the corresponding disproportionation products in low yields along with unchanged **1a** (entry 5). On the other hand, the reaction temperature affected the selectivity of products. At 300°C, we detected a trace amount of bis(diphenylmethyl) ether (**4a**), along with **2a** and **3a** (entry 6). Ether **4a** was obtained in 27% yield instead of the disproportionation products at 200°C (entry 7).

This disproportionation was effected with other diarylmethanols (Eq. (2), Table 2). Similar treatment of diarylmethanols (**1b**–**d**) with supercritical water gave the corresponding disproportionation products in good yields. The substrates bearing a naphthyl (**1e**) or 4-pyridyl group (**1f**)[10] also gave the disproportionation products. In addition to the diarylmethanols, primary amines such as diphenylmethylamine derivatives (**1g**–**i**) were found to give **2** and **3** in good yields. When **1g** was treated under supercritical condition for 15 minutes, a trace amount of **1g** and **1a** (17%) was observed along with **2a** (35%) and **3a** (37%). This fact suggests the amine derivatives are first transformed to the corresponding alcohol derivatives (**1**). Cyclohexylphenylmethanol (**1j**), bearing a hydrogen atom at the α-position of the hydroxyl group, gave a complex mixture containing benzylidenecyclohexane and 1-benzylcyclohexene along with a trace amount of the disproportionation products. The unexpected products were yielded through intramolecular dehydration of **1j**. The alkenes formation from alcohols was reported to be accelerated in supercritical water.[11]

When ether **4a** was treated under the supercritical condition, the corresponding products were obtained in excellent yields (Eq. (3)).

Based on these results, the disproportionation is considered to proceed through the pathway shown in Scheme 1. It was already reported that diarylmethanols were transformed into the corresponding diarylmethanes and diarylketones in the presence of *p*-toluenesulfonic acid



Scheme 1.

or trifluoromethanesulfonic acid, and the reaction is considered to proceed via a hydride transfer mechanism from a bis(diarylmethyl) ether **4** intermediate.[12] Consequently, we consider the present disproportionation to proceed through the intramolecular hydrogen transfer of **4** to give alkane **2** and ketone **3**. During the processes, supercritical water not only works as a reaction medium but also accelerates the reaction.

In conclusion, we have developed a novel disproportionation of diarylmethanol derivatives and diarylmethylamine derivatives. In supercritical water, this disproportionation proceeds under neutral conditions efficiently. Although the present method can be applied only to limited substrates, this report reveals the synthetic utility of supercritical water as a reaction medium. More detailed study on the reaction mechanism as well as other synthetic applications of supercritical water are now in progress.

References

1. For recent reviews on green chemistry: (a) *Green Chemistry Theory and Practice*; Anastas, P. T.; Warner, J., Eds.; Oxford University Press: Oxford, 1998; (b) *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*; Anastas, P. T.; Williamson, T. C., Eds.; Oxford University Press: Oxford, 1998; (c) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025; (d) Varma, R. S. *Green Chem.* **1999**, *1*, 43; (e) Epple, M. *Chem. Ing. Tech.* **1999**, *71*, 35; (f) Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathe, D. *Synthesis* **1998**, 1213; (g) Sato, K.; Aoki, M.; Takagi, J.; Noyori, R.; Bianchini, C.; Barbaro, P. *Chemtracts* **1998**, *11*, 629.
2. (a) *High-Temperature Aqueous Solution: Thermodynamic Properties*; Fernandes, P. R. J.; Corti, H. R.; Japer, M. L., Eds.; CRC: Boca Raton, 1992; (b) Shaw, R. W.; Brill, T. B.; Clifford, A. A.; Eckert, C. A.; Franck, E. U. *Chem. Eng. News* **1991**, *69*, 26; (c) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBC/NRC Wasserdampftafeln*; Springer: Heidelberg, 1988; pp. 19–214; (d) Tödheide, K. In *Water—a Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1972; Vol. 1, p. 514.
3. (a) Hirth, T.; Franck, E. U. *Chem. Ing. Tech.* **1994**, *66*, 1355; (b) Tester, J. W.; Holgate, H. R.; Armellini, F. J.; Webley, P. A.; Killilea, W. R.; Hong, G. T.; Barner, H. E. In *Emerging Technologies for Hazardous Waste Management III*; Tedder, D. W.; Pohland, F. G., Eds.; American Chemical Society: Washington, DC, 1993; Vol. 518, Chapter 3; (c) Schilling, W.; Franck, E. U. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 631.
4. For recent reviews on organic reactions in high-temperature water: (a) Katritzky, A. R.; Nichols, D. A.; Siskin, M.; Murugan, R.; Balasubramanian, M. *Chem. Rev.* **2001**, *101*, 873; (b) Savage, P. E. *Chem. Rev.* **1999**, *99*, 603.
5. For examples of organic synthesis using high-temperature water: (a) Ikushima, Y.; Hatakeda, K.; Sato, O.; Yokoyama, T.; Arai, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 210; (b) Bröll, D.; Kaul, C.; Krämer, A.; Krammer, P.; Richter, T.; Jung, M.; Vogel, H.; Zehner, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 2998; (c) Ikushima, Y.; Hatakeda, K.; Sato, O.; Yokoyama, T.; Arai, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2910; (d) Sato, O.; Ikushima, Y.; Yokoyama, T. *J. Org. Chem.* **1998**, *63*, 9100; (e) Junk, T.; Catallo, W. J. *Tetrahedron Lett.* **1996**, *37*, 3445; (f) Yao, J.; Evilia, R. F. *J. Am. Chem. Soc.* **1994**, *116*, 11229.
6. Another type of disproportionation in supercritical water, i.e. Cannizzaro-type disproportionation, has been reported in the previous study.[5a,b]
7. A typical procedure is as follows: in a tubular steel bomb reactor (10 mL) were placed diphenylmethanol **1a** (368 mg, 2.0 mmol) and water (3.0 mL) under argon atmosphere and kept at 435°C for 90 min in a sand bath. After the reactor was cooled to room temperature in a water bath, water (20 mL) and ethyl acetate (30 mL) were added to the resulting mixture, and the two liquid layers were separated. The organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (30 g; eluent, petroleum ether:chloroform = 50:0, 48:2, 46:4, 44:6, 42:8, 40:10, 35:15, 30:20, 25:25, and 0:50, each ×50 mL), giving **2a** (162 mg, 0.96 mmol) and **3a** (168 mg, 0.92 mmol) in the yields as shown in Table 1, entry 1.
8. The ion product value ($-\log Kw$) was calculated by water density and reaction temperature. For reference see: (a) Wagner, W.; Kruse, A. *Properties of Water and Steam*; Springer-Verlag: Berlin–New York–Tokyo, 1998; (b) Marshall, W. L.; Franck, E. U. *J. Phys. Chem. Ref. Date* **1981**, *10*, 295.
9. Savage and co-worker described the effect of water density on the dehydration of cyclohexanol. Reference: Akiya, N.; Savage, P. E. *Int. Eng. Chem. Res.* **2001**, *40*, 1822.
10. In the case of **1f**, the disproportionated products could not be separated by chromatography on silica gel, and the yields of **2f** and **3f** were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard.
11. Antal, M. J.; Brittain, A.; DeAlmeida, C.; Ramayya, S.; Roy, J. C. *ACS Symp. Ser.* **1987**, *329*, 77.
12. (a) Waterlot, C.; Couturier, D.; Backer, M. D.; Rigo, B. *Can. J. Chem.* **2000**, *78*, 1242; (b) Gautret, P.; El-Ghammarti, S.; Legrand, A.; Couturier, D.; Rigo, B. *Synth. Commun.* **1996**, *26*, 707; (c) Heinisch, G. *Bull. Soc. Chem. Belg.* **1992**, *101*, 579; (d) Heinisch, G.; Waglechner, R. *J. Heterocyclic Chem.* **1984**, *21*, 1727; (e) Heinisch, G.; Luszczak, E.; Pailer, M. *Monatsh. Chem.* **1974**, *105*, 763; (f) Bartlett, P. D.; McCollum, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 1441; (g) Burton, H.; Cheeseman, G. W. H. *J. Chem. Soc.* **1953**, 986; (h) Balfe, M. P.; Kenyon, J.; Thain, E. M. *J. Chem. Soc.* **1952**, 790; (i) Kny-Jones, F. G.; Ward, A. M. *J. Chem. Soc.* **1930**, 535.