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Novel direct reduction of diaryl ketones to diarylmethanes using supercritical 2-propanol

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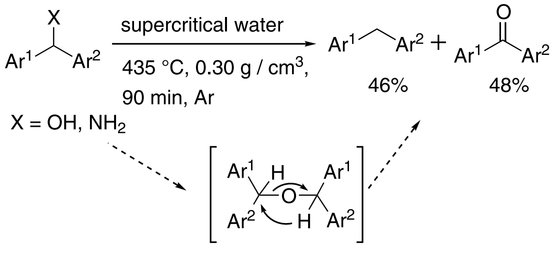
Abstract—We found that diaryl ketones reduce directly to diaryl alkanes under supercritical 2-propanol. This method was applied to one-pot synthesis of anthracene from anthraquinone derivatives by the addition of sulfur in excellent yields.

From the viewpoint of sustainable and green chemistry,[1] supercritical fluids have received considerable attention as a clean medium for organic synthesis in recent years.[2,3] The organic synthesis under supercritical fluids is valuable for simplicity in procedures as well as for ecological and economical reasons. A great number of synthetic methods have been developed under supercritical carbon dioxide,[4] while there have been only a few attempts to use supercritical water and alcohol as an organic reaction medium due to their high critical points.[5] However, the reaction in supercritical water and alcohol is of great interest and has advantages not only in green chemistry but also in synthetic chemistry since the physicochemical properties of supercritical and near-critical water and alcohol are quite different from those of ordinary liquids as they can be continuously controlled by temperature and pressure.[6] We have recently revealed that diarylmethanol derivatives transformed into diarylmethanes and diaryl ketones under supercritical water (Scheme 1).[7] This disproportionation is considered to proceed via a hydrogen transfer from bis(diarylmethyl) ether intermediate.



Scheme 1.

During the course of our studies on the reactivity of several functional groups under supercritical water and alcohols, we found that 2-propanol served as a reducing reagent under supercritical conditions,[8,9] and diaryl ketones (**1**) were directly reduced to diarylmethanes (**2**) under supercritical 2-propanol.[10] This reduction is applicable to various diarylketones (**1**) and gives the corresponding diarylmethanes (**2**) in excellent yields.

First, we examined the direct reduction of benzophenone (**1a**) in several alcohols under supercritical conditions. When **1a** and methanol or ethanol were kept at 350°C for 5 h under supercritical conditions, the reduced products (**2a** and **3a**) were obtained in poor to moderate yield (Table 1, entries 1 and 2). In the case of 2-propanol, surprisingly, the reaction system was very simple and the direct reduced product, alkane **2a**, was obtained in 90% yield without any purification (entry 3). By contrast, the reaction did not proceed in *t*-butyl alcohol at all (entry 4). This fact indicated that hydrogen of α-position of the hydroxy group of alcohol plays an important role in the present direct reduction. The temperature and pressure in the present reduction using 2-propanol affected the yield and selectivity of the reaction products. Above 350°C, **3a** was obtained as a single product under supercritical conditions (entries 5, 6, and 7). Although the reduction of the carbonyl group was achieved almost completely at 300°C under 65 kg/cm^2, the present reduction cannot be accomplished selectively to give the mixture of **2a** and **3a** (entry 8). It

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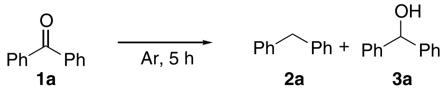


(1)

Table 1. Reaction of **1a** in several alcohols[a]

Entry	Solv.	Amount of solv. (mL)	Temp (°C)	Pressure (kg/cm^2)	Conv. (%)	Yield (%)	
						2a	**3a**
1[b]	MeOH	3	350	145	46	12	6
2	EtOH	3	350	97	76	1	74
3	*i*PrOH	3	350	76	100	90	0
4	*t*BuOH	3	350	67	9	0	0
5	*i*PrOH	5	350	137	100	96	0
6[c]	*i*PrOH	1	350	60	84	70	0
7	*i*PrOH	3	400	101	100	95	0
8[c]	*i*PrOH	3	300	65	70	34	28
9	*i*PrOH	3	250	50	0	0	0

[a] Reaction conditions: 2.0 mmol of **1**, alcohol (1–5 mL), 5 h, under Ar. The reaction product was detected by ^{1}H NMR and GC-MS.

[b] Methyl diphenylmethyl ether was obtained in 10% yield.

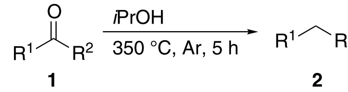
[c] A trace amount of isopropyl diphenylmethyl ether was detected by ^{1}H NMR.

is interesting to note that the present reduction did not proceed at all below supercritical conditions (entry 9). The best result was obtained when the reaction was carried out at 350°C using 5 mL of 2-propanol (entry 5).

This direct reduction to alkane was effective for other diaryl ketones (Eq. (2), and Table 2).[11] Similar treatment of diarylketones (**1b–e**) with supercritical 2-propanol gave the corresponding diarylmethanes (**2**) in excellent yields. The substrate bearing a 4-pyridyl (**1f**) or 2-naphthyl group (**1g**) also provided the desired product. The cyclic ketones such as fluoren-9-one (**1h**) and inden-1-one (**1i**) were reduced to the corresponding ketones (**2h** and **2i**) in moderate to good yields. In the case of aryl aldehyde (**1j**), the reduction proceeded slowly: after 5 hours 4-biphenylmethanol was obtained in 38% yield along with alkane **2j** (40%). The longer reaction time provided the desirable alkane **2j** in a good yield.

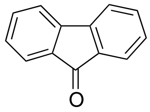
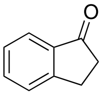
This reduction method can be applied to one-pot synthesis of anthracene from anthraquinone derivatives (Eq. (3) and Table 3). When the reaction 10H-anthracen-9-one (**1k**) was conducted in 2-propanol for 5 hours at 400°C, anthracene (**5k**) was obtained as a major product in 60% yield along with 9,10-dihydroanthracene (**2k**) and 1,2,3,4-tetrahydroanthracene (**4k**) in 29% and 8% yields, respectively. This transformation is considered to proceed via the reduction of the carbonyl group to alkane and subsequent rearrangement and aromatization. The aromatized **5k** was obtained as a single product by the addition of sulfur[12] in an excellent yield. This application can adapt to anthraquinone (**1l**), and **4l** was available in a good yield.

These results can be accounted for by the reaction pathway involving Meerwein–Ponndorf–Verley reduction[8] of **1** and disproportionation of intermediate **6** as shown in Scheme 2: diaryl ketone **1** was transformed to alcohol **3** by MPV-reduction using supercritical 2-propanol[9] and subsequent disproportionation[7] of ether **6** formed in situ from **3** and 2-propanol to produce alkane **2**.[13,14]



(2)

Table 2. Direct reduction of **1** using *i*PrOH[a]

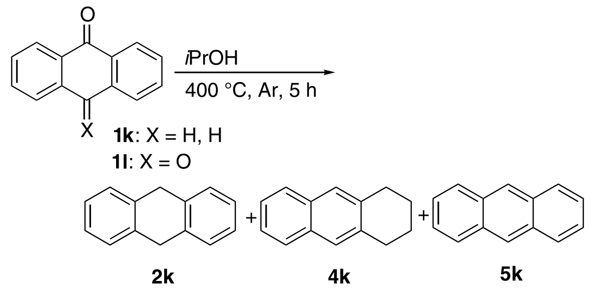
1	R^1	R^2	Yield (%) of **2**[b]
1b	C_6H_5	2-MeC_6H_4	90
1c	C_6H_5	3-MeC_6H_4	95
1d	C_6H_5	4-MeC_6H_4	92
1e	4-MeC_6H_4	4-MeC_6H_4	93
1f	C_6H_5	4-Pyridyl	89
1g	C_6H_5	2-Naphthyl	90
1h			85
1i			50
1j[c]	4-PhC_6H_4	H	85

[a] Reaction conditions: 2.0 mmol of **1**, 5 mL of 2-propanol, at 350°C, 5 h, under Ar, unless otherwise stated.

[b] The product was isolated by bulb-to-bulb distillation.

[c] The reaction was carried out for 10 h.

In conclusion, we have developed a novel direct reduction of diaryl ketones to diarylmethanes using supercritical 2-propanol. Although the present method can be applied to limited substrates, this report reveals the



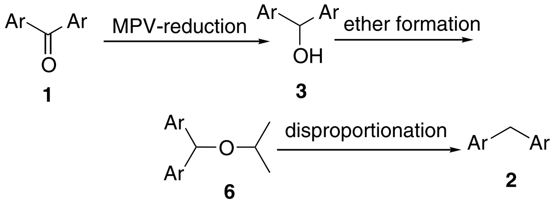
(3)

Table 3. Direct reduction of anthraquinone derivatives using *i*PrOH[a]

1	Additive	Yield (%)[b]		
		2k	**4k**	**5k**
1k	–	29	8	60
1k	Sulfur	–	–	90
1l	Sulfur	–	–	88

[a] Reaction conditions: 1.0 mmol of **1**, 5 mL of 2-propanol, at 400°C under Ar.

[b] The product was isolated by recrystallization.



Scheme 2.

synthetic utility of supercritical 2-propanol as well as the simplicity and cleanliness of procedures. More detailed studies on other synthetic applications in supercritical fluids are now underway.

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10. To our knowledge, only two attempts have been reported that 2-propanol in the presence of strong acids or hydrous tin oxide at 300°C performed as a reductant of ketones to alkanes. Reference, see: (a) Burton, H.; Cheeseman, G. W. H. *J. Chem. Soc.* **1953**, 986; (c) Takahashi, K.; Shibagaki, M.; Kuno, H.; Matsushita, H. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1107.
11. A typical procedure is as follows: in a tubular steel bomb reactor (10 mL) were placed **1** (2.0 mmol) and 2-propanol (5 mL) under argon atmosphere, and the reactor was sealed with the steel cap, and kept at 350°C for 5 h in a sand bath. After the reactor was cooled to room temperature in a water bath, the resulting mixture was extracted with ethyl acetate (10 mL) and concentrated. The residue was purified by bulb-to-bulb distillation. The yields were shown in Table 2.
12. Aromatization using sulfur is well known. Reference, see: (a) Newman, M. S.; Din, Z. U. *J. Org. Chem.* **1971**, *36*, 966; (b) Crawford, M.; Supanekar, V. R. *J. Org. Chem.* **1964**, 2380; (c) Blair, H. S.; Crawford, M.; Spence, J. M.; Supanekar, V. R. *J. Org. Chem.* **1960**, 3313.
13. Acetone, which was probably formed in disproportionation of **6**, was detected by GC-MS.
14. Using 2-propanol-d^8 instead of 2-propanol-d^0 under supercritical conditions (350°C, 134 kg/cm^2), the diphenylmethane-d^2 was obtained in 90% yield.