Study on the Reactivity of Diarylmethane Derivatives in Supercritical Alcohols Media: Reduction of Diarylmethanols and Diaryl Ketones to Diarylmethanes Using Supercritical 2-Propanol

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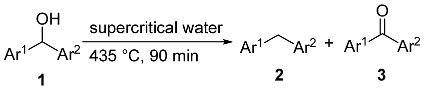
We found that diarylmethanols and diaryl ketones were smoothly reduced to the corresponding diarylalkanes using supercritical 2-propanol in good yields. Furthermore, we determined the specific reaction of fluorene using supercritical methanol at high temperature.

Key words supercritical 2-propanol; supercritical methanol; diarylmethanol; diaryl ketone; fluorene

Recently, the transformation of organic compounds using supercritical fluids as a reaction medium has received much attention in the field of organic synthesis. A great number of synthetic methods have been developed in supercritical carbon dioxide.[1,2] On the other hand, there have been only a few attempts using supercritical water and alcohol for synthetic applications due to their high critical temperature (supercritical water: $T_c=374\,°C$, supercritical methanol: $T_c=239\,°C$, supercritical 2-propanol: $T_c=235\,°C$).[3—9] However, the development of new synthetic approaches under supercritical conditions remains an attractive research area, since the use of water and alcohol is valuable not only for ecological and economical reasons but also for their unique physicochemical properties under supercritical conditions.[10,11] In our previous report, we revealed that supercritical water accelerates the disproportionation of diarylmethanol derivatives (**1**) to diarylmethanes (**2**) and diaryl ketones (**3**) (Eq. 1).[12]



1 **2** **3** (1)

During the course of our studies on the reactivity of diarylmethane derivatives in alcohols at high-temperature, we found that diarylmethanols (**1**) and diaryl ketones (**3**) were reduced to the corresponding diarylalkanes (**2**) using supercritical 2-propanol in good yields. Furthermore, we found that fluorenes were transformed into 9-methylfluorenes in the presence of sodium methoxide under supercritical methanol.

Experimental

General The ^{1}H- and ^{13}C-NMR spectra were measured by Varian Unity-Inova 500 or Mercury 200 spectrometers using TMS as the internal standard. Column chromatography was carried out using a Silica Gel 60 N (Kanto Kagaku). The TLC analysis was performed using a Kieselgel 60 F254 (Merck). All dry solvents were freshly distilled under nitrogen over the appropriate drying agent before use. The reagents were purchased from Kanto Kagaku and Aldrich Chemical Company.

Preparation of Isopropyl Diphenylmethyl Ether (4a) This compound was prepared by the literature method.[13] To a solution of benzhydrol (**1a**) (1.84 g, 10 mmol) and 2-propanol (3.8 ml, 50 mmol) in 1,2-dichloroethane (50 ml) at room temperature was added zinc chloride (8.18 g, 60 mmol). The reaction mixture was stirred at room temperature for 5 h. The usual workup and distillation with a Kugelrohr apparatus gave **4a** in 41% yield (922 mg, 4.1 mmol). **4a**: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.36—7.20 (m, 10H), 5.47 (s, 1H), 3.67 (q, 1H, $J=6.5$ Hz), 1.22 (d, 6H, $J=6.5$ Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 142.9, 128.3, 127.2, 127.0, 80.4, 69.1, 41.9, 22.2.

A Typical Procedure for Reduction of Diarylmethanols (1) to Diarylmethanes (2) Using 2-Propanol at 400 °C In a tubular steel bomb reactor (10 ml) were placed **1** (2.0 mmol) and 2-propanol (3.0 ml) under an argon atmosphere, and the reactor was sealed with a steel cap. The reactor was kept at 400 °C for 5 h in a sand bath. After the reactor was cooled to room temperature in a water bath, AcOEt (30 ml) and H_2O (20 ml) were added to the resulting mixture, and the two liquid layers were then separated. The organic layer was washed with brine (20 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation, giving **2** in the yield shown in Table 1. The pressure at 400 °C was measured using an autoclave reactor with a manometer. When **1a** (368 mg, 2.0 mmol) and 2-propanol (3.0 ml) were placed in the autoclave reactor (10 ml), the pressure was 99—110 kg/cm^2 at 400 °C. The pressure of other solvents was as follow: methanol (121—153 kg/cm^2), ethanol (104—124 kg/cm^2), *tert*-butanol (87—116 kg/cm^2). **2a**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.25—7.19 (m, 10H), 3.98 (s, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 141.1, 128.9, 128.4, 126.0, 41.9. **2b**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.28—7.06 (m, 9H), 3.91 (s, 2H), 2.93 (s, 3H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 141.3, 138.0, 135.4, 129.1, 128.8, 128.7, 128.3, 125.9, 41.4, 20.9. **2c**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.78—7.60 (m, 3H), 7.60 (s, 1H), 7.42—7.17 (m, 8H), 4.10 (s, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 140.9, 138.5, 133.6, 132.0, 129.0, 128.3, 128.0, 127.6, 127.3, 127.1, 126.7, 126.0, 125.7, 125.4, 42.1. **2d**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 8.50—8.47 (m, 2H), 7.32—7.08 (m, 7H), 3.96 (s, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 149.9, 149.6, 138.7, 128.9, 128.6, 126.5, 124.0, 41.1.

A Typical Procedure for Direct Reduction of Diaryl Ketones (3) to Diarylmethanes (2) Using 2-Propanol at 350 °C In a tubular steel bomb reactor (10 ml) were placed **3** (2.0 mmol) and 2-propanol (5.0 ml) under an argon atmosphere, and the reactor was sealed with an steel cap. The reactor was kept at 350 °C for 5 h in a sand bath. After the reactor was cooled to room temperature in a water bath, AcOEt (30 ml) and H_2O (20 ml) were added to the resulting mixture, and the two liquid layers were then separated. The organic layer was washed with brine (20 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation, giving **2** in the yield shown in Table 2. The pressure at described temperature was measured using an autoclave reactor with a manometer. When **3a** (364 mg, 2.0 mmol) and 2-propanol (5.0 ml) were placed in the autoclave reactor (10 ml), the pressure was 125—143 kg/cm^2 at 350 °C. The pressure at other temperatures was as follows: 250 °C (45—52 kg/cm^2), 300 °C (62—67 kg/cm^2). **2e**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.15—6.99 (m, 9H), 3.87 (s, 2H), 2.12 (s, 3H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 140.3, 138.9, 136.6, 130.2, 129.9, 128.9, 128.7, 128.3, 125.9, 125.7, 39.4, 19.6. **2f**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.21—6.98 (m, 9H), 3.91 (s, 2H), 2.28 (s, 3H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 141.2, 141.0, 137.9, 129.7, 128.9, 128.9, 128.4, 128.3, 126.8, 126.0, 41.8, 21.4. **2g**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.05—7.04 (m, 8H), 3.86 (s, 2H), 2.27 (s, 6H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 138.3, 135.3, 129.1, 128.7, 41.0, 20.9. **2h**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.81—7.77 (m, 2H), 7.56—7.52 (m, 2H), 7.41—7.23 (m, 4H), 3.90 (s, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 143.1, 141.6, 126.6, 126.6, 125.0, 119.8, 36.8. **2i**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.18—7.07 (m, 4H), 2.89 (m, 4H), 2.04 (m, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 144.0, 126.0, 124.3, 32.9, 25.3. **2j**: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 7.60—7.22 (m, 9H), 2.38 (s, 3H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 141.1, 138.3, 136.9, 129.4, 128.8, 128.7, 126.9, 126.9, 21.1.

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The Reaction of Isopropyl Diphenylmethyl Ether (4a) Using 2-Propanol at 350 °C In a tubular steel bomb reactor (10 ml) were placed **4a** (453 mg, 2.0 mmol) and 2-propanol (5.0 ml) under an argon atmosphere, and the reactor was sealed with an steel cap. The reactor was kept at 350 °C for 5 h in a sand bath. After the reactor was cooled to room temperature in a water bath, AcOEt (30 ml) and H_2O (20 ml) were added to the resulting mixture, and the two liquid layers were then separated. The organic layer was washed with brine (20 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane–AcOEt as the eluent) to afford **2a** (334 mg, 99%).

The transformation of Fluorenes (2h, 2k, and 2l) to 9-Methylfluorenes (5) Using Methanol at 450 °C In a tubular steel bomb reactor (10 ml) were placed **2** (2.0 mmol), sodium methoxide (270 mg, 5.0 mmol) and methanol (3.0 ml) under an argon atmosphere, and the reactor was sealed with a steel cap. The reactor was kept at 450 °C for 5 h in a sand bath. After the reactor was cooled to room temperature in a water bath, AcOEt (30 ml) and H_2O (20 ml) were added to the resulting mixture, and the two liquid layers were then separated. The organic layer was washed with saturated $NaHCO_3$ (20 ml) and brine (20 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, giving the 9-methylfluorene (**5**) in the yield shown in Table 3. **5a**: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.79—7.74 (m, 2H), 7.55—7.49 (m, 2H), 7.38—7.28 (m, 4H), 3.94 (q, 1H, J=7.6 Hz), 1.52 (d, 3H, J=7.6 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 149.1, 140.6, 127.0, 126.7, 124.0, 119.8, 42.4, 18.2. **5b**: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.69 (d, 1H, J=7.5 Hz), 7.64 (d, 1H, J=7.5 Hz), 7.46 (d, 1H, J=8.0 Hz), 7.37—7.27 (m, 3H), 7.15 (d, 1H, J=8.0 Hz), 3.83 (q, 1H, J=7.5 Hz), 2.42 (s, 3H), 1.49 (d, 3H , J=7.5 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 149.2, 148.8, 140.5, 137.8, 136.7, 127.7, 126.8, 126.6, 126.4, 124.7, 123.9, 119.5, 42.2, 21.6, 18.2. **5c**: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.62—7.58 (m, 2H), 7.45—7.40 (m, 1H), 7.33—7.14 (m, 2H), 6.86 (s, 1H), 6.77—6.61 (m, 1H), 3.87 (q, 1H, J=7.4 Hz), 3.00 (s, 6H), 1.50 (d, 3H, J=7.4 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 150.6, 150.3, 148.1, 141.1, 129.7, 125.7, 124.9, 123.6, 120.4, 118.4, 111.6, 108.1, 42.4, 41.0, 18.5.

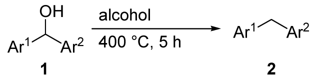
The Reaction of Fluorenes (2h) with Formaldehyde at High Temperature In a tubular steel bomb reactor (10 ml) were placed **2h** (332 mg, 2.0 mmol), sodium methoxide (270 mg, 5.0 mmol) and an aqueous solution of formaldehyde (37w%, 3.0 ml) under an argon atmosphere. The reactor was sealed with a steel cap. The reactor was kept at 450 °C for 5 h in a sand bath. After the reactor was cooled to room temperature in a water bath, AcOEt (30 ml) and H_2O (20 ml) were added to the resulting mixture, and the two liquid layers were then separated. The organic layer was washed with saturated $NaHCO_3$ (20 ml) and brine (20 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (30 g, 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 the 9-methylfluorene (**5a**) in the yield shown in Table 4, entry 1.

The Reaction of Fluorenes (2h) with Benzaldehyde Derivatives at High Temperature In a tubular steel bomb reactor (10 ml) were placed **2h** (332 mg, 2.0 mmol), sodium methoxide (270 mg, 5.0 mmol) and the benzaldehyde derivative (3 ml) under an argon atmosphere. The reactor was sealed with a steel cap. The reactor was kept at 350 °C for 5 h in a sand bath. After the reactor was cooled to room temperature in a water bath, toluene (30 ml) and H_2O (20 ml) were added to the resulting mixture, and the two liquid layers were then separated. The organic layer was washed with saturated $NaHCO_3$ (20 ml) and brine (20 ml), dried over Na_2SO_4, and concentrated under reduced pressure. After removal of the excess benzaldehyde by bulb-to-bulb distillation, the residue was purified by column chromatography on silica gel (30 g, 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 9-benzylfluorenes (**7a**, **7b**) in the yield shown in Table 4, entries 2 and 3. **7a**: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.69—7.15 (m, 13H), 4.23 (t, 1H, J=7.7 Hz), 3.10 (d, 2H, J=7.7 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 146.8, 140.8, 139.8, 129.5, 128.3, 127.0, 126.6, 124.6, 119.8, 49.7, 40.1. **7b**: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 7.29—7.07 (m, 12H), 4.20 (t, 1H, J=7.4 Hz), 3.06 (d, 2H, J=7.4 Hz), 2.44 (s, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 146.9, 140.8, 129.3, 129.1, 128.9, 128.7, 127.0, 126.6, 124.8, 119.7, 48.7, 39.6, 21.1.

The registry numbers are as follows: diphenylmethanol (**1a**) 91-01-0, (4-methylphenyl)(phenyl)methanol (**1b**) 1517-63-1, (2-naphtyl)(phenyl)methanol (**1c**) 35060-38-9, (phenyl)(4-pyridyl)methanol (**1d**) 33974-27-5, diphenylmethane (**2a**) 101-81-5, (4-methylphenyl)(phenyl)methane (**2b**) 620-83-7, (2-naphtyl)(phenyl)methane (**2c**) 613-59-2, (phenyl)(4-pyridyl)methane (**2d**) 2116-65-6, (2-methylphenyl)(phenyl)methane (**2e**) 713-36-0, (3-methylphenyl)(phenyl)methane (**2f**) 620-47-3, di(4-methylphenyl)methane (**2g**) 4957-14-6, fluorene (**2h**) 86-73-7, indan (**2i**) 496-11-7, 4-methylbiphenyl (**2j**) 644-08-6, 2-methylfluorene (**2k**) 1430-97-3, *N*,*N*-dimethyl-2-aminofluorene (**2l**) 13261-62-6, benzophenone (**3a**) 119-61-9, (4-methylphenyl) phenyl ketone (**3b**) 643-65-2, (2-naphthyl) phenyl ketone (**3c**) 644-13-3, phenyl (4-pyridyl) ketone (**3d**) 14548-46-0, (2-methylphenyl) phenyl ketone (**3e**) 131-58-8, (3-methylphenyl) phenyl ketone (**3f**) 643-65-2, di(4-methylphenyl) ketone (**3g**) 611-97-2, fluorenone (**3h**) 486-25-9, indanone (**3i**) 83-33-0, 4-biphenylcarboxaldehyde (**3j**) 3218-36-8, isopropyl diphenylmethyl ether (**4a**) 5670-79-1, 9-methylfluorene (**5a**) 2523-37-7, 2,9-dimethylfluorene (**5b**) 1430-97-3, 2-amino-*N*,*N*,9-trimethylfluorene (**5c**) 727415-21-6, 9-benzylfluorene (**7a**) 1572-46-9, 9-(4-methylbenzyl)fluorene (**7b**) 745809-62-5.

Results and Discussion

Reaction of Diarylmethanols in Alcohol Medium under Supercritical Conditions We first examined the reactivity of diarylmethanols (**1**) in several alcohols under supercritical conditions (Eq. 2, Table 1). When **1a** was treated with methanol at 400 °C for 5 h, the direct reduction was smoothly performed to give the corresponding alkane **2a** as a single product in 79% yield (entry 1). It was interesting to note that ketone **3a** was not observed at all, as compared with the reaction of **1a** in supercritical water.[12] In ethanol, the reduction of **1a** also proceeded to give **2a** in 83% yield (entry 2). The best result was obtained when the reaction was carried out using 2-propanol (entry 3). On the other hand, the reduction of **1a** in *tert*-butanol proceeded with great difficulty; ketone (**3a**) was obtained as the main product (35%) along with **2a** (27%) (entry 4). These facts suggested that the hydrogen at the α-position of the alcohol medium plays an important role in the reduction of **1**. This reduction also smoothly proceeded in the case of the substrate bearing 4-methyl (**1b**), 2-naphtyl (**1c**), and 4-pyridyl (**1d**) groups (entries 5, 6, and 7, respectively).



(2)

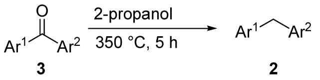
Reaction of Diaryl Ketones in 2-Propanol under Supercritical Conditions As the reduction of diarylmethanol (**1**) to diarylalkane (**2**) quite smoothly proceeded without the formation of diaryl ketone (**3**) in 2-propanol under supercritical conditions, we next studied the reactivity of diaryl ketone (**3**) in 2-propanol at high temperatures.[14] When ketone **3a** was reacted with 2-propanol at 350 °C for 5 h, alkane **2a** was obtained as a single product in good yield (Eq. 3 and Table 2, entry 1). The influence of temperature on this reduction was then investigated. The reduction of **1a** did not proceed at 250 °C, and the unchanged **3a** was recovered in quantitative yield (entry 2). Although the reduction of **1a** proceeded at 300 °C, the product selectivity was not observed; alcohol **1a**

Table 1. Reduction of **1** to **2** in Several Alcohols at 400 °C

Entry	1	Ar^1	Ar^2	Alcohol	Yield of **2** (%)$^{a)}$
1	**1a**	C_6H_5	C_6H_5	MeOH	79
2	**1a**	C_6H_5	C_6H_5	EtOH	83
3	**1a**	C_6H_5	C_6H_5	*i*-PrOH	95
4	**1a**	C_6H_5	C_6H_5	*t*-BuOH	27$^{b)}$
5	**1b**	C_6H_5	4-MeC_6H_4	*i*-PrOH	91
6	**1c**	C_6H_5	2-naphtyl	*i*-PrOH	87
7	**1d**	C_6H_5	4-pyridyl	*i*-PrOH	90

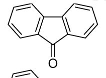
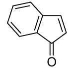
a) Isolated yield. *b*) Ketone **3a** was obtained in 35% yield.

and alkane **2a** were obtained in 28% and 34% yields, respectively (entry 3). The alcohol medium also affected the product yield and selectivity, and the results in other alcohols were as follows: methanol (**1a**, 6% yield, **2a**, 12% yield), ethanol (**1a**, 74% yield, **2a**, trace), *tert*-butanol (**1a**, 0% yield, **2a**, 0% yield). This direct reduction using supercritical 2-propanol was effective for other diaryl ketones (**3**). A similar treatment of diaryl ketones (**3b**—**i**) with 2-propanol gave the corresponding diarylmethanes (**2**) in moderate to good yields (entries 4—11). In addition, aryl aldehyde (**3j**) was found to give the desirable alkane **2j** in 85% yield after a longer reaction time (entry 12).



(3)

Table 2. Reduction of **3** to **2** in 2-Propanol at 350 °C

Entry	3	Ar^1	Ar^2	Yield of **2** (%)$^{a)}$
1	**3a**	C_6H_5	C_6H_5	96
2$^{b)}$	**3a**	C_6H_5	C_6H_5	0$^{c)}$
3$^{d)}$	**3a**	C_6H_5	C_6H_5	34$^{e,f)}$
4	**3e**	C_6H_5	2-MeC_6H_5	91
5	**3f**	C_6H_5	3-MeC_6H_4	95
6	**3b**	C_6H_5	4-MeC_6H_4	92
7	**3g**	4-MeC_6H_4	4-MeC_6H_4	93
8	**3c**	C_6H_5	2-naphtyl	90
9	**3d**	C_6H_5	4-pyridyl	89
10	**3h**			85
11	**3i**			50
12$^{g)}$	**3j**	4-PhC_6H_4	H	85

a) Isolated yield. *b)* At 250 °C. *c)* Unchanged **3a** was recovered in quantitative yield. *d)* At 300 °C. *e)* **1a** was obtained in 28% yield. *f)* A trace amount of **4a** was detected by ^{1}H-NMR. *g)* For 10 h.

Based on these results, the formation of an alkane **2** can be verified to proceed through the pathway shown in Chart 1: ketone **3** was initially transformed into alcohol **1** by MPV-reduction using supercritical 2-propanol,[15—18] and the subsequent ether **4** was formed from **1** and excess 2-propanol, and alkene **2** was produced by disproportionation of ether **4**. Indeed, a trace amount of isopropyl diphenyl ether (**4a**) was detected by ^{1}H-NMR in the reaction of **2a** using 2-propanol at 300 °C, and a similar treatment of ether **4a** with 2-propanol gave alkane **2a** in almost quantitative yield.

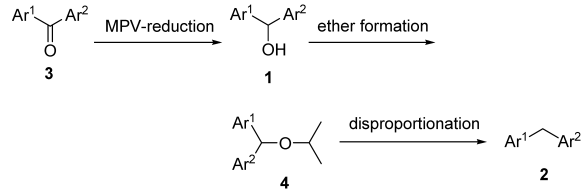
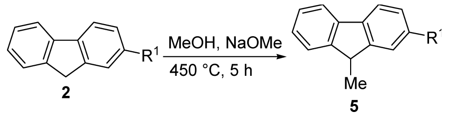


Chart 1

Reaction of Fluorenes in Supercritical Methanol During the course of our study on the reactivity of diarylmethane derivatives in an alcohol medium, we found that diarylmethanols (**1**) and diaryl ketones (**3**) were transformed into the corresponding diarylalkanes (**2**) using an alcohol having α-hydrogen. We also found that several diarylalkanes (**2**) were inert in high-temperature alcohol medium. In the treatment of fluorenes with methanol, however, we observed the specific reaction of fluorene with methanol (Eq. 4).



(4)

Table 3. Reaction of **2** Using Methanol in the Presence of NaOMe at 450 °C

Entry	2	R^1	Yield of **5** (%)$^{a)}$
1$^{b)}$	**2h**	H	42
2$^{b,c)}$	**2h**	H	0
3$^{b,d)}$	**2h**	H	14
4	**2h**	H	98
5$^{e)}$	**2h**	H	76
6	**2k**	CH_3	90
7$^{f)}$	**2l**	$N(CH_3)_2$	57

a) Isolated yield. *b)* In the absence of NaOMe. *c)* At 350 °C. *d)* At 400 °C. *e)* CD_3OD and $NaOCD_3$ was used. *f)* For 2 h.

When fluorene **2h** was conducted with methanol at 450 °C for 5 h, surprisingly, 9-methylfluorene (**5a**) was obtained in 42% yield along with the unchanged **2h** (Table 3, entry 1). The reaction temperature affected the yield of **5a**: the methylation of **2h** took place only at slightly below 450 °C (entries 2, 3). The addition of sodium methoxide improved the product yield to give **5a** in 98% yield (entry 4). The methyl group at the 9-position was found to be from the methanol; when **2h** was treated with deuterated methanol in the presence of sodium deuteroxide, fluorene (**5a**) bearing the deuterated methyl group at the 9-position was obtained in 76% yield (entry 5). Other fluorene derivatives (**2k**, **2l**) were transformed into the corresponding 9-methyl product (**5b**, **5c**) in 90% and 57% yields, respectively (entries 6, 7). This methylation is specific for fluorene derivatives, since other arylalkanes, such as diphenylmethane, triphenylmethane, 9,10-dihydroanthracene, and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene, did not react at all.

Although the detailed pathway is not clear in this specific reaction, the methylation of fluorenes seemed to be triggered by the nucleophilic addition of the fluorene anion with formaldehyde which was produced by disproportionation of methanol as shown in Chart 2: fluorene **2h** would react with formaldehyde produced by disproportionation of methanol to generate alcohol **6a**, which was transformed to 9-methyl product **5a** by subsequent ether formation and disproportionation.

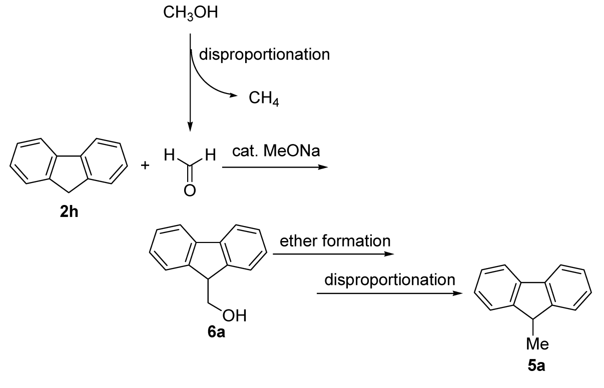
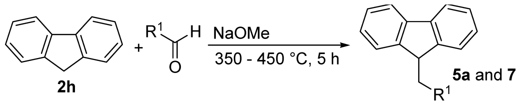


Chart 2

Indeed, 9-methyl product **5a** was obtained in 82% yield in the treatment of **2h** with formaldehyde in the presence of sodium methoxide at 450 °C for 5 h. (Eq. 5, and Table 4, entry 1). Furthermore, similar reactions of **2h** were observed using benzaldehyde derivatives instead of formaldehyde to give **7a** and **7b**, respectively (Table 4, entries 2 and 3).



(5)

Table 4. Reaction of **2h** with Aldehydes in the Presence of NaOMe

Entry	R^1	Product yield (%)[a]
1[b,c]	H	82
2[d]	C_6H_5	43
3[d]	$4\text{-}MeC_6H_5$	20

a) Isolated yield. *b*) An aqueous solution of formaldehyde (37w%) was used. *c*) At 450 °C. *d*) At 350 °C.

Conclusion

We found that the reduction of diarylmethanols (**1**) to diarylalkanes (**2**) proceeded in high-temperature alcohol medium, and the best result was obtained using 2-propanol at 400 °C. Furthermore, we revealed that diaryl ketones (**3**) were reduced to diarylalkanes (**2**) as well, and these reductions proceeded via the MPV-reduction and disproportionation. In addition, we determined the specific reaction of fluorenes (**2h**, **2k**, **2l**) with methanol and an aldehydes at high temperature.

References and Notes

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