

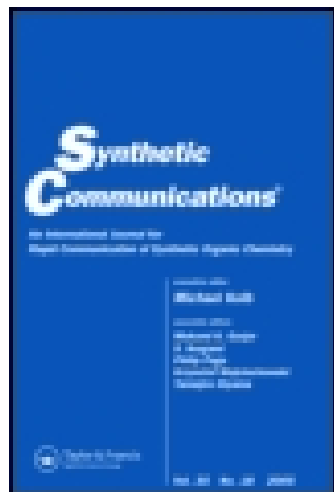
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Efficient Microwave-Assisted Synthesis of 9,9-Bis[4-(2-hydroxyethoxy)phenyl]fluorene from 9-Fluorenone and 2-Phenoxyethanol

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Abstract: 9-Fluorenone (**1**) smoothly reacts with phenoxyethanol (**2**) in the presence of Al^{3+} -montmorillonite catalyst and 3-mercaptopropionic acid as a cocatalyst under microwave irradiation at 160°C for 10 min to give 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene (**3**) in 81% yield, which was much higher than the yield of 33% obtained by conventional heating using an oil bath. A similar acceleration effect of microwave irradiation was observed in other metal-cation-exchanged montmorillonite catalysts as well.

Keywords: fluorene, microwave, montmorillonite

INTRODUCTION

Fluorene unit-containing polymers have attracted increasing interest for their intriguing properties applicable to heat-resistant, mechanically strong, and/or optoelectric materials.^[1,2] In particular, 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene (**3**) is a useful monomer for preparation of highly functional polymers with superior optical and/or mechanical properties.^[2] In a recently developed process, the fluorene derivative **3** is conveniently prepared by a Friedel–Crafts one-step reaction of 9-fluorenone (**1**) with 2-phenoxyethanol (**2**) in the presence of sulfuric acid^[3] or cation-exchanged

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montmorillonite catalysts at high temperature.^[4] The latter catalytic process is heterogeneous and has the advantage of very easy separation of catalyst, although the reaction requires rather severe conditions (170°C, 2 h). On the other hand, microwave-assisted processes are current topics in organic chemistry^[5] because of their potential to achieve highly efficient and environmentally friendly chemical processes including polymer synthesis.^[5a,b] In the course of our studies on the development of new microwave-assisted synthetic processes, we have found that microwave irradiation effectively accelerates the reaction of **1** with **2** catalyzed by metal-cation-exchanged montmorillonites in the presence of a cocatalyst, 3-mercaptopropionic acid.

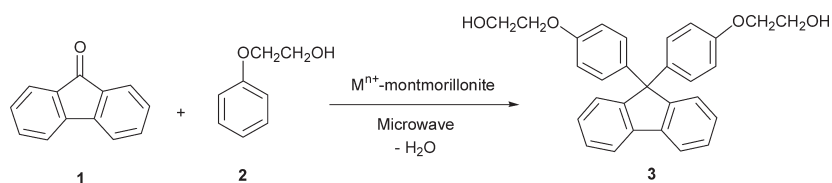
RESULTS AND DISCUSSION

Reactions of **1** with **2** in the Presence of Al³⁺-Montmorillonite

A Friedel–Crafts reaction of **1** with two molecules of **2** smoothly proceeded under temperature-controlled microwave irradiation at 2.45 GHz (max. 300 W) in the presence of Al³⁺-montmorillonite catalyst and 3-mercaptopropionic acid as a cocatalyst (Scheme 1, Table 1). After irradiation at 160°C for 10 min, the desired fluorene derivative **3** was obtained in 81% yield with 91% conversion of **1** (entry 1). Separation of montmorillonite catalyst was easily achieved by centrifugation of the reaction mixture. In another reaction under the same reaction conditions, **3** could be isolated in 70% yield by silica-gel column chromatography. With remarkable contrast, conventional heating using an oil bath instead of a microwave instrument under the same reaction temperature and time resulted in a much lower yield of **3** (33%, entry 2), showing that microwave irradiation accelerates the reaction very efficiently.

The microwave-promoted reaction took place without 3-mercaptopropionic acid as a cocatalyst. However, the reaction became much slower, decreasing the yield of **3** from 81% to 32% (entry 3). Although the reaction mechanism has not been clearly elucidated yet, the cocatalyst would participate in the reaction pathway that involves addition of the cocatalyst to **1**, giving a reactive thionium intermediate as suggested previously (Scheme 2).^[3]

The degree of absorption of microwave energy for a particular material has been assumed to depend on the dielectric loss factor in the complex



Scheme 1.

Table 1. Reaction of **1** with **2** affording **3**^a

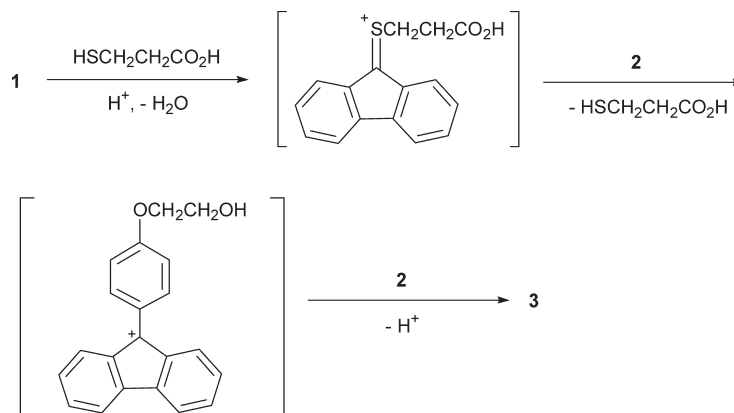
Entry	Catalyst (g)	Cocatalyst ^b (mmol)	Heating method ^c	Conversion of 1 ^d (%)	Yield of 3 ^d (%)
1	Al ³⁺ -montmorillonite (0.20)	MP (0.016)	MW	91	81
2	Al ³⁺ -montmorillonite (0.20)	MP (0.016)	OB	37	33
3	Al ³⁺ -montmorillonite (0.20)	None	MW	41	32
4	Al ³⁺ -montmorillonite (0.10)	MP (0.008)	MW	61	52
5	Al ³⁺ -montmorillonite (0.10)	MP (0.008)	OB	36	28
6	Ti ³⁺ -montmorillonite (0.10)	MP (0.008)	MW	39	35
7	Ti ³⁺ -montmorillonite (0.10)	MP (0.008)	OB	30	25
8	Ti ⁴⁺ -montmorillonite (0.10)	MP (0.008)	MW	56	46
9	Ti ⁴⁺ -montmorillonite (0.10)	MP (0.008)	OB	30	24
10	Zr ⁴⁺ -montmorillonite (0.10)	MP (0.008)	MW	38	30
11	Zr ⁴⁺ -montmorillonite (0.10)	MP (0.008)	OB	17	11
12	Ga ³⁺ -montmorillonite (0.10)	MP (0.008)	MW	38	33
13	Ga ³⁺ -montmorillonite (0.10)	MP (0.008)	OB	25	20
14	In ³⁺ -montmorillonite (0.10)	MP (0.008)	MW	17	13
15	In ³⁺ -montmorillonite (0.10)	MP (0.008)	OB	13	6
16	Sn ⁴⁺ -montmorillonite (0.10)	MP (0.008)	MW	35	31
17	Al ³⁺ -montmorillonite (0.10)	None	MW	32	24
18	Al ³⁺ -montmorillonite (0.10)	None	OB	21	16
19	Ti ³⁺ -montmorillonite (0.10)	None	MW	29	22
20	Ti ³⁺ -montmorillonite (0.10)	None	OB	19	10
21	Ti ⁴⁺ -montmorillonite (0.10)	None	MW	24	18
22	Ti ⁴⁺ -montmorillonite (0.10)	None	OB	16	7
23	Zr ⁴⁺ -montmorillonite (0.10)	None	MW	28	19
24	Zr ⁴⁺ -montmorillonite (0.10)	None	OB	15	11
25	Fe ³⁺ -montmorillonite (0.10)	None	MW	17	11
26	Fe ³⁺ -montmorillonite (0.10)	None	OB	12	6
27	Ga ³⁺ -montmorillonite (0.10)	None	MW	30	23
28	Ga ³⁺ -montmorillonite (0.10)	None	OB	17	8
29	In ³⁺ -montmorillonite (0.10)	None	MW	20	12
30	In ³⁺ -montmorillonite (0.10)	None	OB	5	4
31	Montmorillonite K10 (0.10)	None	MW	16	13
32	Montmorillonite KSF (0.10)	None	MW	8	5
33	Silica (mesoporous, MCM-41 type) (0.10)	None	MW	3	2

^aReaction conditions: **1**, 0.80 mmol; **2**, 8.0 mmol; catalyst, 0.20 g for entries 1–3 or 0.10 g for entries 4–33; cocatalyst, 0.016 mmol for entries 1 and 2 or 0.008 mmol for entries 4–16; 160°C, 10 min.

^bMP: 3-mercaptopropionic acid.

^cMW: microwave; OB: oil bath.

^dConversions and yields were estimated by HPLC.



Scheme 2.

dielectric constant of the material.^[6] Measurement of the complex dielectric constant of hydroxyl-group-containing **2** at 2.45 GHz showed that the value of the dielectric loss factor was 1.83, which was comparable with those of other alcohols such as 1-butanol (1.98) and 2-butanol (1.77). These values are medium for the dielectric loss factors of normal liquid organic compounds, enabling sufficient interaction of these alcoholic compounds with microwaves. Accordingly, **2** can absorb an appropriate amount of microwave energy and become a suitable starting material in the present microwave-assisted reaction.

Reactions of **1** with **2** in the Presence of Other Catalysts

Besides Al^{3+} -montmorillonite, other metal-cation-exchanged montmorillonite catalysts were also effective in the present reaction. For instance, metal cations such as Ti^{3+} , Ti^{4+} , Zr^{4+} , Ga^{3+} , and Sn^{4+} exhibited moderately high catalytic activities among the catalysts examined; the yields of **3** were 35, 46, 30, 33, and 31%, respectively (Table 1, entries 6, 8, 10, 12, and 16). However, their catalytic activities were not as high as those of Al^{3+} -montmorillonite (52%, entry 4). Previously, Ti^{4+} -montmorillonite was reported to show higher catalytic activity than Al^{3+} -montmorillonite.^[4] Slight differences in preparation conditions of the catalysts and/or in catalytic reaction conditions such as the presence of the cocatalyst, the ratio of **1/2**, and/or temperature may affect the catalyst activities, although further studies are required to elucidate the origin of the difference in catalytic activity.

In the montmorillonite catalyst system containing Ti^{3+} , Ti^{4+} , Zr^{4+} , Ga^{3+} , or Ir^{3+} , microwave irradiation gave **3** in higher yields than conventional heating by oil bath as observed in Al^{3+} -montmorillonite catalyst. The results in the

presence and absence of 3-mercaptopropionic acid cocatalyst are summarized in Table 1 (entries 4–15 and entries 17–24 and 27–30, respectively) and Fig. 1. In each catalytic system, microwave heating gave 1.3–3.9 times higher yield than oil-bath heating. This indicates microwave irradiation is effective irrespective of the kind of metal cation of the montmorillonite catalyst.

Commercially available montmorillonite K10 and montmorillonite KSF were also active, although the efficiency was not so high; the yields of **3** were 13% and 5%, respectively (entries 31 and 32). A mesoporous silica gel with MCM-41 type was much less effective than metal-cation-exchanged montmorillonite catalysts, giving **3** in only 2% yield (entry 33).

In summary, a Friedel–Crafts reaction using 9-fluorenone and 2-phenoxyethanol has been found to proceed efficiently by combination of cation-exchanged montmorillonite catalysts with microwave irradiation. In particular, employment of Al^{3+} cation and a cocatalyst of 3-mercaptopropionic acid is effective in the present microwave-assisted reaction. Further investigation on the synthetic applications of the montmorillonite catalysts and microwaves is under way.

EXPERIMENTAL

Reagents and Instruments

9-Fluorenone (**1**) was purchased and used as it was. Phenoxyethanol (**2**) was used after drying with molecular sieve 4Å. Metal-cation-exchanged

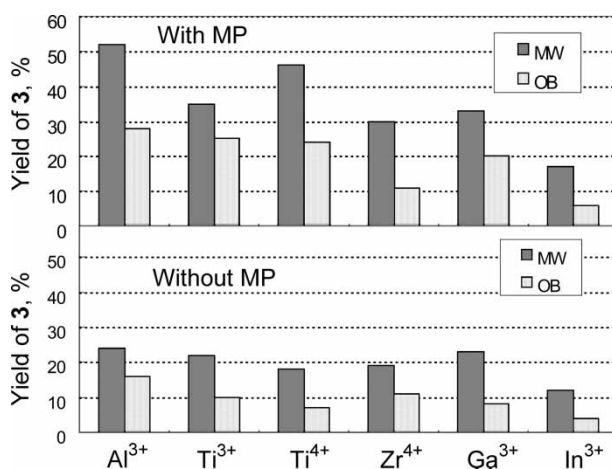


Figure 1. Comparison of the reactions by microwave irradiation (MW) with those by an oil bath (OB) using metal-cation-exchanged montmorillonite catalysts; with 3-mercaptopropionic acid (MP) cocatalyst (top, entries 4–15 in Table 1) and without MP (bottom, entries 17–24 and 27–30 in Table 1).

montmorillonite catalysts were prepared by a general method of treating commercially available Na⁺-montmorillonite (Kunimine Industries Co., Ltd., Kunipia F; cation exchange ability 115 mgeq., surface area 56 m²/g) with excess amounts of suitable cation salts such as metal nitrates or chlorides.^[4,7] A most active catalyst, Al³⁺-montmorillonite, had a surface area of 141 m²/g. Montmorillonite K10, montmorillonite KSF, and mesoporous silica of type MCM-41 were purchased (Sigma-Aldrich, Ltd.) and used as they were.

Microwave-irradiation experiments were carried out using a CEM Discover instrument for closed Pyrex[®] glass tubes (10 mL) with Teflon[®]-coated septa. Centrifugation was performed by a Porta centrifuge. The reaction mixtures were analyzed by a high performance liquid chromatography (HPLC) system equipped with two high-pressure pumps (Jasco PU-980), a solvent mixing module (Jasco HG-980-31), a HPLC column [Shiseido CAPCELL PAK C18 MG (4.6 mmϕ × 250 mm)], and a UV detector (Jasco UV-970) using an eluent of MeCN/H₂O (55/45) at a flow rate of 1 mL/min. Complex dielectric constants of alcoholic compounds were measured with a system of Kanto Electronic Application and Development Inc. comprising a vector network analyzer (Agilent 8720ES) and a 2.45-GHz cylindrical cavity of TM₀₂₀ mode using Teflon[®]-type sample tubes. Surface areas of montmorillonite catalysts were analyzed by the Brunauer-Emmett-Teller (BET) method using a Fisons Sorptomatic 1990 instrument. ¹H and ¹³C NMR spectra of **3** and its authentic sample were measured by a Jeol JNM-LA600 instrument using chloroform-*d* solvent.

Microwave-Assisted Catalytic Reactions

A typical reaction procedure is as follows. A mixture of **1** (144 mg, 0.80 mmol), **2** (1.0 mL, 8.0 mmol), Al³⁺-montmorillonite (0.20 g), and 3-mercaptopropionic acid (1.4 μL, 0.016 mmol) and a Teflon[®]-coated magnetic bar were sealed in a glass tube. The glass tube was heated at 160°C for 10 min under temperature-controlled microwave irradiation (max. 300 W) and magnetic stirring. The reaction mixture was centrifuged (ca. 3000 rpm) to separate the montmorillonite catalyst solid. The supernatant solution was analyzed by HPLC using an internal standard (*p*-xyloquinone), showing the formation of **3** in 81% yield with 91% conversion of **1**.

In another reaction under the same conditions, the reaction mixture was centrifuged, and the supernatant was separated. The residual solid was washed with methanol (1 mL × 3), and the methanol solution was combined with the supernatant. Concentration of the combined solution followed by column chromatography (silica gel, hexane/ethyl acetate = 3/2) gave **3** in 70% yield (245 mg, 0.56 mmol). The identification of **3** was made by comparison of the ¹H and ¹³C NMR spectra and the HPLC retention time of **3** with those of an authentic sample (Tokyo Chemical Industry Co., Ltd.).

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