Journal of Organometallic Chemistry 724 (2013) 40–44

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Thermal reaction of cyclic alkadiene with trichlorosilane. Preparative and mechanistic aspects

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ARTICLE INFO

Article history:
Received 14 August 2012
Received in revised form
28 September 2012
Accepted 4 October 2012

Keywords:
Hydrosilylation
Thermal reaction
Cycloalkadiene
Hydrosilane
Trichlorosilane
Cycloalkenyltrichlorosilane

ABSTRACT

The thermal reactions of trichlorosilane (**1a**) with cyclic alkadienes such as cyclopentadiene (**2a**), 1,3-cyclohexadiene (**2b**), and 1,4-cyclohexadiene (**2c**) were studied at temperatures ranging from 170 °C to 250 °C. In this reaction, the hydrosilylation rate increased as the reaction temperature was raised using an equimolar ratio of **1a** to **2a**. The reaction of **2a** with **1a** at 250 °C afforded 2-cyclopentenyltrichlorosilane (**3a**) as the major hydrosilylation product within 1 h in good yield (82%). This reaction also works when dicyclopentadiene (**2a′**) was used as a reactant instead of **2a**. In a large scale preparation under the same conditions, **3a** was obtained in 82% isolated yield. It is significant to note that **2a′** can be used for the hydrosilylation, with no requirement of a cracking step under our thermal conditions. While the reaction of cyclohexadienes with **1a** under the same conditions gave a mixture of three hydrosilylation products such as 2-cyclohexenyltrichlorosilane (**3b**), 3-cyclohexenyltrichlorosilane (**3c**) and cyclohexyltrichlorosilane (**5**) in moderate yields, along with other unsaturated C6 components, such as benzene and cyclohexene. In the thermal reaction of cycloalkadienes with **1a**, the five-membered-ring diene **2a** undergoes both a hydrosilylation reaction with **1a** as well as a [4 + 2] cycloaddition reaction, leading to the hydrosilylation product **3a** in good yield. While the six-membered ring dienes, **2b** and **2c**, undergo four different types of reactions, including hydrosilylation, [4 + 2] cycloaddition, dehydrogenation, and hydrogenation in competition to give the hydrosilylation products, hexane, and benzene, respectively. The reaction rates of cyclic alkadienes under our thermal conditions increase in the following order: **2c** << **2b** < **2a**.

1. Introduction

The hydrosilylation reaction, the addition of a Si—H unit to a C—C multiple bond, is a useful reaction for the preparation of organosilicon compounds [1–11] as well as the modification of silicon wafer surfaces [12–14]. This reaction is typically induced by photoinitiation [11,12] or catalyzed by metal compounds [1–10]. Commonly, platinum derivatives such as the Speier catalyst ($H_2PtCl_6/^iPrOH$) [6] and the Karstedt catalyst [8] are used. Although these reactions have been well studied from both academic and industrial points of view, they either require expensive metals such as platinum as a catalyst or UV radiation [11,12]. Meanwhile, the simple hydrosilylation under thermal conditions, without the use of a catalyst, is rarely reported and remains a relatively unexplored area. Recently we have reported the hydrosilylation reaction of simple cyclic alkenes with trichlorosilane (**1a**) under thermal conditions that gave cycloalkylchlorosilanes in excellent yields [15]. Such cycloalkylchlorosilanes can be useful materials as modifiers for the surface of inorganic oxide particles [16] and as electron donors for the preparation of polypropylene [17]. Following this work, the reaction was extended to employ cycloalkadienes, which are more activated than simple cycloalkenes such as cyclopentadiene (**2a**), 1,3-cyclohexadiene (**2b**), and 1,4-cyclohexadiene (**2c**). In the thermal reaction with **1a**, the cyclic alkadienes undergo a competitive reaction between hydrosilylation, [4 + 2] cycloaddition [18], and especially in the case of **2b** and **2c**, hydrogenation and dehydrogenation. Herein we report the thermal reaction of cyclic alkadienes **2a**–**2c** with **1a**, at temperatures ranging from 170 °C to 250 °C, which leads to the formation of the hydrosilylated products.

2. Results and discussion

2.1. Thermal synthesis of cyclopentenylchlorosilanes

The thermal reaction of the activated cyclic diene **2a**, which is easily dimerized to dicyclopentadiene (**2a′**) at room temperature and can be effectively decomposed to form **2a** at elevated temperatures,

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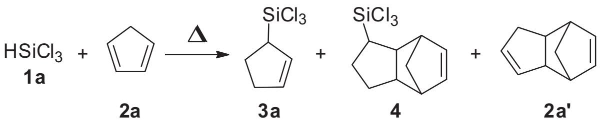
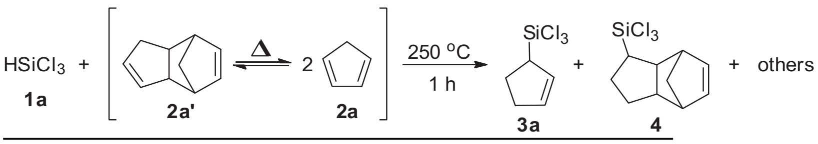
http://dx.doi.org/10.1016/j.jorganchem.2012.10.015

with **1a** was carried out at temperatures varying from the boiling point of **2a**′ (170 °C) to 270 °C without any additional catalyst. In the reaction, **2a** undergoes both the hydrosilylation reaction with **1a**, leading to formation of cyclopentenyltrichlorosilane (**3a**), and the Diels–Alder reaction ([4 + 2] cycloaddition) to form **2a**′ [18]. In addition, other [4 + 2] cycloadducts (**4**) were obtained as minor products formed from the Diels–Alder reaction of compound **3a** with **2a** (eq. (1)). These results are summarized in Table 1.

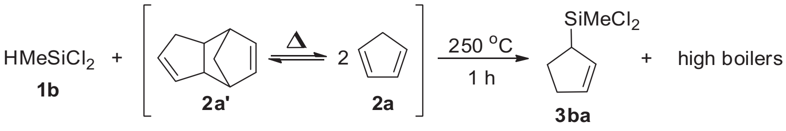


(1)

As shown in Table 1, after 8 h, the reaction of **2a** with **1a** at 170 °C gave **3a** (52%), **4** (2%), and **2a**′ (17%) in *exo*-form (entry # 1). The same reaction at 200 °C afforded **3a** in a slightly higher yield (61%) with less *exo*-**2a**′ formed (6%) (entry #2). The reaction at 230 °C required a shorter reaction time of 4 h and gave **3a** in better yield (74%) with little formation of *exo*-**2a**′ (1%) (entry # 3). The reaction at 250 °C afforded **3a** in the best yield (82%) within 1 h (entry # 4), and the same reaction at 270 °C gave a similar yield of **3a** (81%) (entry # 5). These results show that the yields of **3a** and **4** increase as the reaction temperature is raised from 170 °C to 250 °C. While the formation of *exo*-**2a**′ is observed at lower temperatures, the formation of *endo*-**2a**′ is not observed, thus suggesting that the decomposition of *endo*-**2a**′ to **2a** is much easier than that of *exo*-**2a**′ [18]. In addition to **3a**, the [4 + 2] cycloadducts **4**, which are formed by the Diels–Alder reaction of **3a** with **2a**, are obtained as byproducts (2–8%) in all reactions. These results indicate that **3a** can be produced in the highest yield from the reaction of **2a** with **1a** at 250 °C. To investigate the optimum ratio of **1a** to **2a** for synthesizing **3a**, the reaction was carried out by varying the mol ratio of **1a**/**2a** from 1.2 to 4. The reactions using a mol ratio of the 2–4 (**1a**/**2a**) afforded **3a** in 80–83% yields (entry # 4, 7 and 8), while using the 1.2 mol ratio of **1a**/**2a** resulted in the lowest observed yield (63%) (entry # 6). These results show that the formation of **3a** is favored when **1a** is used in excess compared to **2a**. From an economical point of view, it is reasonable to use the 3 mol ratio of **1a**/**2a** for the preparation of **3a** via the thermal reaction. These results suggest that the interconversion between **2a** and **2a**′ takes place reversibly under our thermal conditions and that they react with **1a** to give **3a**. Thus, a mixture of *exo*- and *endo*-**2a**′, which are cheap and commercially available on large scales, were used as starting materials instead of **2a**. The reaction of **2a**′ with **1a** at 250 °C gave **3a** in 82% yield within 1 h (eq. (2)). In a large scale preparation (**2a**′, 0.19 mol), under the same reaction conditions, **3a** was obtained in 82% isolated yield. These results indicate that the use of **2a**′ instead of **2a** works effectively at 250 °C. In the preparation of **3a**, it is significant to note that **2a**′ can be used as reactant instead of the unstable **2a**, which has the benefit of not requiring a cracking step under our thermal conditions.



(2)



(3)

Table 1
Thermal reaction of **2a** with **1a**.

Entry #	Ratio of reactants	Reaction conditions		Product yields (%)[a]		
	1a/**2a**	Temp. (°C)	Time (h)	**3a**	**4**	**2a**′ (*exo*-form)
1	3	170	8	52	2	17
2	3	200	8	61	4	6
3	3	230	4	74	5	1
4	3	250	1	82	7	–
5	3	270	1	81	8	–
6	1.2	250	1	63	7	–
7	2	250	1	80	7	–
8	4	250	1	83	7	–

[a] Yields were determined by GLC using *n*-dodecane as an internal standard.

This reaction can then be applied to methyldichlorosilane (**1b**) instead of **1a**. A 6 mol ratio reaction of **1b**/**2a**′ at 250 °C for 1 h afforded 2-cyclopentenylmethyldichloro silane (**3ba**) in relatively low yield (29%) as well as other high boilers [20] formed by [4 + 2] cycloaddition reactions (eq. (3)).

2.2. Thermal reaction of cyclohexadiene with trichlorosilane (1a)

First, the reaction of the 6-membered ring conjugated diene, such as 1,3-cyclohexadiene (**2b**), with **1a** was studied at temperatures between 170 °C and 250 °C. In this reaction, three types of hydrosilylation products were obtained, 2-cyclohexenyltrichlorosilane (**3b**), 3-cyclohexenyltrichlorosilane (**3c**), and cyclohexyltrichlorosilane (**5**), along with unsaturated hydrocarbons such as the mixture of two dimeric forms (*exo*- and *endo*-**2b**′) of **2b**, 1,4-cyclohexadiene (**2c**), cyclohexene, and benzene (eq. (4)). These results are summarized in Table 2.

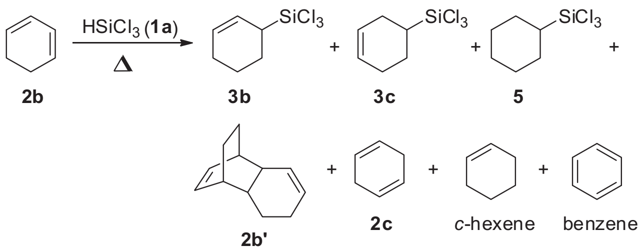


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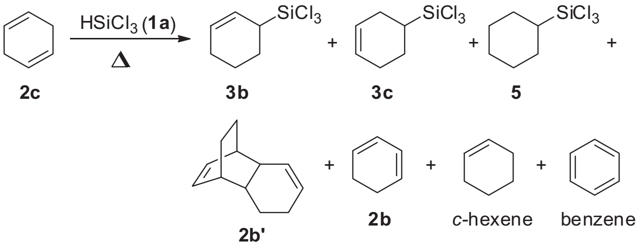
Table 2
Thermal reaction of **2b** with **1a**.

Entry #	Reactant	Reaction conditions		Product yields (%)[a]				
	2b (%)	Temp. (°C)	Time (h)	**2b′**	**2c**	Cyclohexene	Benzene	Hydrosilylation (**3b**:**3c**:**5**)
9	84	170	8	9[b]	2	2	1	5 (4:1:–)
10	22	200	8	13[b]	3	18	8	36 (30:5:1)
11	1	230	4	4	6	9	10	66 (59:6:1)
12	–	250	1	2	6	9	11	69 (64:4:1)[c]

[a] Yields were determined by GLC using *n*-dodecane as an internal standard.
[b] The 5:1 isomeric mixture of *exo*- and *endo*-**2b′**.
[c] Isolated yields.

As shown in Table 2, the thermal reaction of **2b** with **1a** proceeded slowly at 170 °C to give a 5% yield of a 4:1 mixture of the hydrosilylation products, **3b** and **3c**. Additional C6 components such as **2c** (2%), cyclohexene (2%), and benzene (1%) were observed with a 16% consumption of **2b** after 8 h (entry # 9). The same reaction at a slightly higher temperature of 200 °C gave a mixture of **3b** (30%), **3c** (5%), and **5** (1%) as the hydrosilylation products along with **2c** (3%), **2b′** (13%), cyclohexene (18%) and benzene (8%) (entry # 10). The reaction at an elevated temperature of 230 °C afforded a mixture of **3b** (59%), **3c** (6%), and **5** (1%), and other unsaturated compounds such as **2c** (6%), **2b′** (4%), cyclohexene (9%), and benzene (9%), with a 96% consumption of **2b** within 4 h (entry # 11). The reaction at 250 °C gave a 64:4:1 mixture of **3b**, **3c**, and **5** in 69% isolated yield within 1 h along with **2c** (6%), **2b′** (2%), cyclohexene (9%), and benzene (11%) (entry # 12). These results suggest that the production of the hydrosilylation compounds **3b** and **3c** from the reaction of **2b** with **1a** increase as the reaction temperature is raised. The reaction of **2b** is much more complex than that of **2a** to give a wide range of products through hydrosilylation, double bond migration, hydrogenation, dehydrogenation, and other processes. Compound **3c** can be formed by the hydrosilylations of **2c** or **2b** with **1a**, or through the double bond migration of **3b**. To test this, **2c**, which is less reactive than **2b**, was allowed to react with **1a** at various temperatures between 170 °C and 250 °C. While the products obtained from the reaction of **2c** with **1a** are the same as those obtained from the reaction of **2b** with **1a** (eq. (5)), their distribution is different and the results are summarized in Table 3.



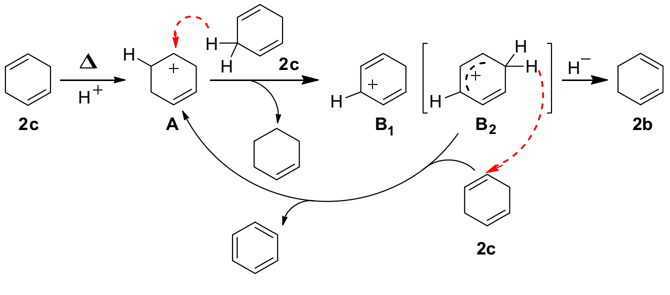
(5)

Table 3
Hydrosilylation reaction of **2c** with **1a**.

Entry #	Reactant	Reaction conditions		Product yields (%)[a]			
	2c (%)	Temp. (°C)	Time (h)	**2b**	Cyclohexene	Benzene	**3** (**3b**:**3c**:**5**)
13	92	170	8	1		6	Trace
14	75	200	8	2	–	14	5 (3:2:trace)
15	37	230	4	–	6	25	27 (15:9:3)
16	5	250	4	–	8	31	35 (19:11:5)[b]

[a] Yields were determined by GLC using *n*-dodecane as an internal standard.
[b] Isolated yields.

As shown in Table 3, the reaction of **2c** with **1a** at 170 °C afforded no appreciable amount of the hydrosilylation products, but benzene (6%) was obtained as a major product along with **2b** (1%). During this reaction, an 8% consumption of **2c** after 8 h was observed (entry # 13). The same reaction at 200 °C afforded a 5% yield of a 3:2 mixture of **3b** and **3c** as the hydrosilylation products along with **2b** (2%) and benzene (14%), with a 25% consumption of **2c** (entry # 14). The reaction at 230 °C afforded a 15:9:3 mixture of **3b**, **3c** and **5** in 27% yield, benzene (25%), and cyclohexene (6%), with a 63% consumption of **2c** within 4 h (entry # 15). The reaction at 250 °C gave a 19:11:5 mixture of **3b**, **3c** and **5** in 35% isolated yield, **2b′** (4%), benzene (31%), and cyclohexene (8%) with complete consumption of **2c** within 1 h (entry # 16). In these reactions, the mol ratio of hydrosilylation products to benzene is 5/14 at 200 °C but changes to 27/25 at 230 °C and 35/31 at 250 °C, respectively. This suggests that **2c** is less activated than **2b** and undergoes the dehydrogenation reaction predominantly, leading to the formation of benzene [19] at the lower temperature of 200 °C. However, both the hydrosilylation and dehydrogenation reactions are in competition at the high temperature of 250 °C. In these reactions, under the same conditions, the hydrosilylation products are obtained in a lower yield than when compared to the reaction of **2b** with **1a**. In the thermal reaction with **1a**, the reactivity of cycloalkadienes increases in the following order: **2c** << **2b** < **2a**. From our results a mechanism for the formation of C6 components from the reaction of **2c** (as a representative reactant) with **1a** is proposed in Scheme 1. To clarify whether the neat thermal reaction of each reactant had occurred, only **1a** or **2c** was heated up to 250 °C for 2 h, respectively. In these reactions, no products were observed by GLC. Therefore, the dehydrogenation or isomerization of **2c** (neat) can be ruled out under our reaction conditions. For a reasonable mechanism for the formation of the wide range of products, a small amount of hydrogen chloride resulting from the reaction of **1a** with moisture that is inevitably present in the reaction mixture initiates the proton generation reaction. This interacts with the π–bond of **2c** to give the carbonium intermediate **A**, which can abstract from **2c** to give new intermediate B_1 (or B_2), which is stabilized by forming the allylic carbonium and cyclohexene. The intermediate **B** can be deprotonated to provide benzene and the



Scheme 1. Mechanism for the formation of unsaturated compounds, benzene, cyclohexene, **2b** from the reactant **2c**.

intermediate **A**. Except for benzene, all the unsaturated compounds, **2b**, **2c**, and cyclohexene, can react with **1a** to yield the hydrosilylation products, **3b**, **3c** and **5**, respectively.

In conclusion, we describe a rare example of a thermal hydrosilylation of cyclic alkadienes with **1a** affording the hydrosilylated products in moderate to good yields without the use of a catalyst. Additionally, the thermal reaction of **2a** with **1a** is a one-pot synthesis affording cyclopentenylchlorosilane (**3a**) in good yield. Although these reactions require the relatively high temperature of 250 °C, they remain simple and require no catalyst. Importantly, the mixture of the two isomers of *exo*- and *endo*-dicyclopentadene (**2a**′), which are cheap and commercially available in large scales, can be used as a starting material in place of **2a**. This does not require the use of an additional thermal cracking process of **2a**′ to **2a** and its subsequent distillation. This reaction is a possible method for Si–C bond formation for the synthesis of cycloalkenylchlorosilanes, which are expected to be utilized as coupling agents for composites of inorganic oxide particles and olefin polymers within the plastics industry.

3. Experimental

3.1. General comments

All reactions and manipulations were carried out under a nitrogen atmosphere using cannula techniques. Solvents were dried according to standard procedures. Trichlorosilane, methyldichlorosilane, cyclopentene, cyclohexene, 1-hexene, and dicyclopentadiene were purchased from Aldrich Chem. Co or TCI and used without further purification. 1,3-Cyclohexadiene and 1,4-cyclohexadiene were purchased from Aldrich Chem. Co and purified by simple distillation before use. Cyclopentadiene was freshly prepared by thermal dedimerization of dicyclopentadiene before use. The reaction products were analyzed by gas–liquid chromatography (GLC) over a packed column (10% OV-101 on 80–100 mesh Chromosorb W/AW, 1/8 in. × 1.5 m) or a capillary column (SE-30, 30 m) using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector (TCD). The yields of products were calibrated with the GLC response factor. The samples for characterization were purified by a preparative GLC using a packed column (20% OV-101 on 80–100 mesh Chromosorb P/AW, 1/8 in. × 4 m) with a DS 6200 gas chromatography (Donam Instruments Inc.) equipped with a TCD. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz for ^{1}H; 75 MHz for ^{13}C) or a Varian Gemini 300 spectrometer (60 MHz for ^{29}Si) using $CDCl_3$ as a solvent. The chemical shifts are given in ppm relative to the standards as follows: $CHCl_3$ 7.25 ppm (^{1}H), $CDCl_3$ central transition 77.0 ppm (^{13}C), and external $SiMe_4$ 0.0 ppm (^{29}Si). GC/MS analyses were conducted on a HP 6890/5973 system (70 eV, EI) equipped with a capillary column (HP-1, i.d. 0.2 mm × 25 m). Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology.

3.2. General procedure for optimizing thermal hydrosilylation of cyclopentadiene (*2a*) with trichlorosilane (*1a*)

In a typical experiment reactants **1a** (12.30 g, 90.8 mmol), **2a** (2.00 g, 30.3 mmol), and *n*-dodecane (1.00 g) as an internal standard were charged into a 25-mL dried stainless tube under an atmosphere of nitrogen. After the tube was sealed with a cap, the reactions were carried out at temperatures ranging from 170 to 270 °C. The progress of the reaction was monitored by GLC. The yields of **3a** (CAS no. 14579-09-0), **4** (CAS no. 14579-12-5), and **2a**′ are based on the amount of **2a** used and were calculated using *n*-dodecane as an internal standard. The results are summarized in Table 1 (entry # 1–5). To check for the optimal molar ratio of reactants, 16.40 g (121.1 mmol), 8.20 g (60.5 mmol), and 4.90 g (36.2 mmol) of **1a** were reacted with 2.00 g (30.3 mmol) of **2a**, respectively. The results are summarized in Table 1 (entry # 6–8).

3.3. Thermal hydrosilylation of dicyclopentadiene (*2a*′) with trichlorosilane (*1a*)

Following the same procedure as described in the general procedure, the reaction of **1a** (12.30 g, 90.8 mmol) with **2a**′ (2.00 g, 15.1 mmol, 97:3 mixture of *exo*- and *endo*-) was carried out at 250 °C for 1 h. **3a** was obtained in 82% yield.

In a scaled-up preparation, a 250-mL dried stainless steel tube was charged commercial **2a**′ (25.00 g, 189.1 mmol, 97:3 mixture of *exo*- and *endo*-) and **1a** (102.50 g, 756.7 mmol) under an atmosphere of nitrogen. The reaction was carried out at 250 °C for 1 h. The excess **1a** was removed under vacuum, and 62.51 g (82%) of **3a** was isolated by vacuum distillation. And the residue was bulb-to-bulb vacuum distilled to give 4.63 g of a mixture of high boilers, which contains four isomers of [4 + 2] cycloadducts **4** (CAS no. 14579-12-5) in 7:90:1:2 ratio (GC area %).

3.4. Thermal reaction of dicyclopentadiene (*2a*′) with methyldichlorosilane (*1b*)

Following the same procedure as described in the general procedure, a 1 h reaction of a 97:3 mixture of *exo*- and *endo*-**2a**′ (2.00 g, 15.1 mmol), **1b** (10.42 g, 90.6 mmol), and *n*-dodecane (1.00 g) at 250 °C afforded 3.2 g (29%, based on the amount of **2a**′ used) of (2-cyclopentenyl)methyldichlorosilane (**3ba**, CAS no. 68559-08-0) [21] as well as other high boilers, which GC/MS analysis indicated to be polycyclic compounds formed by the self-[4 + 2] cycloaddition of **2a** [20].

3.5. Thermal reaction of 1,3-hexadiene (*2b*) with trichlorosilane (*1a*)

Following the same procedure as described in the general procedure, the reactions of **2b** (2.00 g, 25.0 mmol), **1a** (10.10 g, 74.6 mmol), and *n*-dodecane (1.00 g) as an internal standard were carried out at temperatures ranging from 170 °C to 250 °C. The yields of **3b** (CAS no. 18139-74-7), **3c** (CAS no. 10137-69-6), **5** (CAS no. 98-12-4), and **2b**′ (CAS no. 2808-38-0) are based on the amount of **2b** used and were calculated using *n*-dodecane as an internal standard. The results are summarized in Table 2 (entry # 9–12).

3.6. Thermal reaction of 1,4-hexadiene (*2c*) with trichlorosilane (*1a*)

Following the same procedure as described in the general procedure, the reactions of **2c** (2.00 g, 25.0 mmol), **1a** (10.10 g, 74.6 mmol), and *n*-dodecane (1.00 g) were carried out at various temperature between 170 °C and 250 °C. The yields of **3**, **3c**, **5**, and **2b**′ (CAS no. 2808-38-0) are based on the amount of **2c** used and were calculated using *n*-dodecane as an internal standard. The results are summarized in Table 3 (entry # 13–16).

Acknowledgments

This research was supported by the Korea Institute of Science and Technology.

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