Medium-sized cyclophanes — Part 85: Benzylation by 8-(bromomethyl)[2.2]metacyclophanes. Through-space electronic interactions of [2.2]metacyclophane benzyl cations

Tomoe Shimizu, Kan Tanaka, Arjun Paudel, and Takehiko Yamato

Abstract: $TiCl_4$-mediated Friedel–Crafts benzylation of benzene with 8-(bromomethyl)[2.2]metacyclophanes to afford 8-benzyl[2.2]metacyclophanes is described. Substituent effect through space on the rate of the benzylation of benzene with a bromomethyl group attached on the opposite aromatic ring was first found in this investigation. Interestingly, the introduction of the substituents at the internal position 16 tends to promote the present benzylation reaction rate 1.8–3.8 times. It was found that the benzyl cation intermediate was stabilized by the the direct through-space cation–π interaction among the opposite benzene ring in the benzylation of [2.2]metacyclophane systems.

Key words: cyclophanes, Friedel–Crafts benzylation, benzyl cation intermediate, through-space electronic interaction.

Résumé : On décrit la réaction de benzylation du benzène par le 8-bromométhyl)[2,2]métacyclophanes par la méthode de Friedel–Crafts catalysée par le $TiCl_4$. Dans ce travail, on a mis en évidence pour la première fois, un effet de substituant qui se fait sentir à travers l'espace sur la vitesse de benzylation du benzène en raison d'un groupe bromométhyle attachée sur le noyau aromatique opposé. Il est intéressant de noter que l'introduction de substituants à la position interne 16 tendent à accélérer les vitesses de réaction de benzylation par des facteurs allant de 1,8 à 3,8. On a trouvé que le cation benzylique intermédiaire est stabilisé par une interaction cation-π directe à travers l'espace du noyau benzénique opposé dans la benzylation de systèmes [2,2]métacyclophanes.

Mots-clés : cyclophanes, benzylation suivant Friedel–Crafts, cation benzylique intermédiaire, interaction électronique à travers l'espace.

Introduction

The geometry of the [2.2]metacyclophane ([2.2]MCP) skeleton is known in detail from an X-ray structural analysis.[2,3] The crystal consists of discrete molecules, each of which has a center of symmetry. The two halves of the molecule form a stepped system. It is interesting to note that the benzene rings are not planar, but have a boat conformation, with the result that the molecule evidently avoids the steric interaction of the central carbon atoms C(8) and C(16) and of the attached hydrogen atoms. The X-ray structural analysis of 8,16-dimethyl[2.2]MCP (**2**) confirms the increased strain in molecule **2** as compared with that in the parent hydrocarbon **1** (Fig.1).[4–16]

Although substituents at positions 8 and 16 in the [2.2]MCP system seem to have interesting chemical natures since they are covered by the opposite aromatic ring, there are few investigations concerning these problems.[17,18] Owing to electronic interaction between two benzene rings, the proximity of 8- and 16-positions, and the considerable strain energy, [2.2]MCP is prone to giving transannular reaction products.[19–21] These are mostly explained by the initial formation of a cyclodehydrogenation reaction product, 4,5,9,10-tetrahydropyrene. It has been isolated under the electrophilic,[22–25] radical,[26] and photolytic reaction conditions,[27] together with other transformation products derived from tetrahydropyrene. Sato and co-workers[28,29] reported another type of iodine-induced reaction of [2.2]MCP, which gives 1,2,3,3a,4,5-hexahydropyrene. On the other hand, we have reported[30,31] the iodine-induced transannular cyclization of 8-methoxy[2.2]MCPs to give 4,5,9,10-tetrahydropyrenes with remarkable ease and with high selectivity. This novel transannular reaction might be attributed to the presence of the methoxy group at the 8-position, which increases the π-electron density of the benzene ring. Thus, these transannular reactions were ascribed to the through-space electronic interaction through the intra-annular 8,16-positions. As mentioned above, although two through-space electronic interactions, (*i*) interaction through the intra-annular 8- and 16-positions and (*ii*) direct through-space cation–π interaction, are possi-

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Scheme 1.

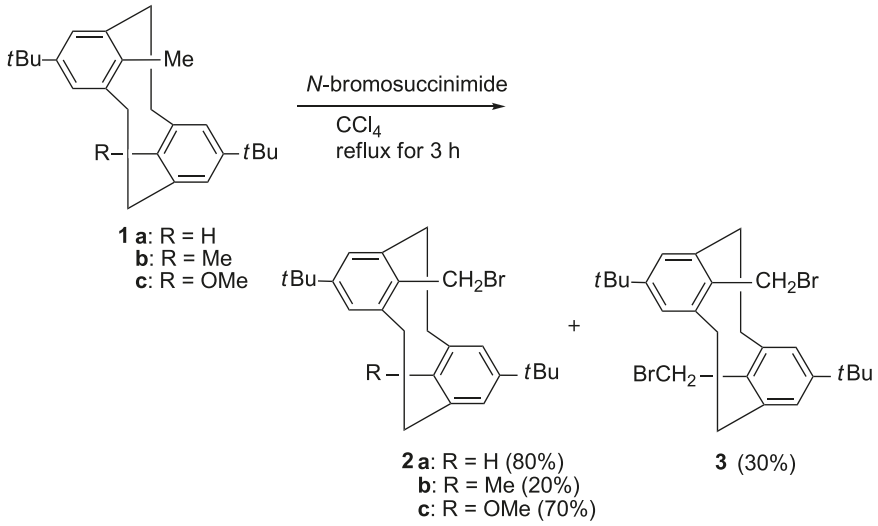
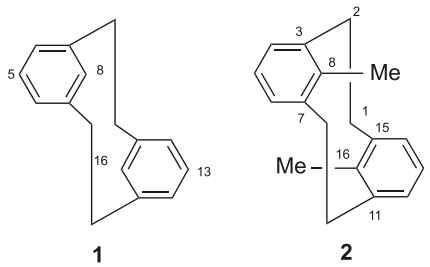
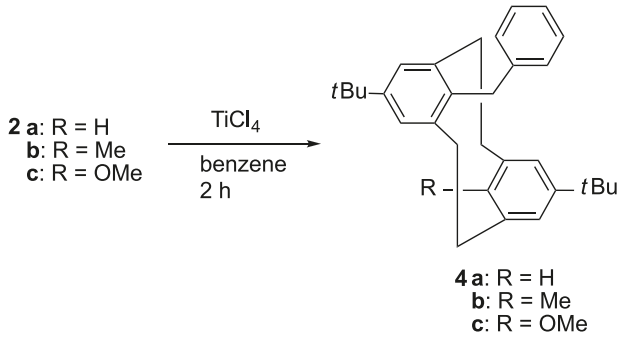


Fig. 1. Structure and numbering of [2.2]MCPs.



Scheme 2.



ble in the [2.2]MCP systems, the more favored interaction is not clear so far. Therefore, it is quite interesting to investigate the through-space electronic interaction on the rate of the benzylation of bromomethyl groups attached on the opposite aromatic ring in the [2.2]MCP systems. We wish to report the benzylation of benzene using cations derived from 8-(bromomethyl)[2.2]MCPs.

Results and discussion

The preparative route of 8-(bromomethyl)[2.2]MCPs (**2a**–**2c**) is shown in Scheme 1. Bromination of **1a** and **1c**[32–34] with *N*-bromosucccinimide (NBS) in the presence of benzoyl peroxide under CCl_4 reflux for 3 h afforded the desired 8-(bromomethyl)[2.2]MCPs (**2a** and **2c**) in good yield. However, in the case of **1b**, 8,16-bis(bromomethyl)[2.2]MCP (**3**) was also obtained in 30% yield along with the recovery of the starting compound **1b** in 20% yield in spite of 1.2 equiv of NBS used. Isolation of the desired pure **2b** was unsuccessful. We have instead prepared 8-(bromomethyl)-16-methyl[2.2]MCP (**2b**) following our previously reported procedure.[35,36]

The $TiCl_4$-mediated benzylation of benzene with 8-(bromomethyl)-5,13-di-*tert*-butyl[2.2]MCPs (**2**) was carried out under various conditions of Scheme 2. The results are compiled in Table 1.

The $TiCl_4$-mediated benzylation of benzene with compound **2a** at room temperature (25 °C) for 2 h led to benzylation reaction affording the desired 8-benzyl[2.2]MCP (**4a**) in 29% yield along with the recovery of the starting compound **2a** in 71% yield. The present benzylation reaction was carried out at 50 °C under the same reaction conditions as above to increase the yield of 8-benzyl[2.2]MCP (**4a**) to 36%. Interestingly, in similar benzylation of benzene with 16-methyl and 16-methoxy derivatives, much higher yields of the benzylation products **4b** and **4c** resulted in 52% and 85% yields, respectively. The data in Table 1 clearly show that the substituents at the 16-position affected the yield of the benzylation product of the 8-bromomethyl group in the opposite aromatic ring and that electron-donating groups, such as methyl and methoxy functions, increased the yield of the benzylation product because of its high electron-donating ability like normal aromatic benzylation.[37] Thus, such sub-

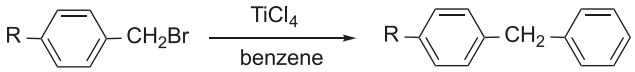
Table 1. $TiCl_4$-mediated benzylation of benzene with **2**.

Run	Reaction temperature (°C)	Product yield (%)[a]	Recovery
1	25	**4a** (29)	**2a** (71)
2	50	**4a** (36) [25]	**2a** (64)
3	50	**4b** (52) [40]	**2b** (48)
4	25	**4c** (62) [51]	**2c** (28)
5	50	**4c** (85) [76]	**2c** (15)

Note: [Benzene]/**2** = 30 (mol/mol), [$TiCl_4$]/**2** = 1.5 (mol/mol).

[a]The yields were determined by GLC analysis. Isolated yields are shown in square brackets.

Scheme 3.



	relative rate
R = H	1.0
R = Me	4.8
R = OMe	16.2

Table 2. Pseudo-first-order plots and rate constants on benzylation of benzene with **2**.

Compounds	R	$k \times 10^5$ (sec^{-1})	Relative rate
2a	H	6.21 (±0.21)	1.0
2b	Me	10.99 (±1.65)	1.8
2c	OMe	23.72 (±1.14)	3.8

stituent effect through space on the rate of the benzylation of bromomethyl group attached on the opposite aromatic ring was first found in this investigation.

The structures of **4a**–**4c** were determined on the basis of their elemental analyses and spectral data. The ^{1}H NMR spectrum of **4a** in $CDCl_3$ shows a singlet at δ 2.15 ppm for the methylene protons of the benzyl group at 8-position, which is in a strongly shielded region of the opposite meta-bridged benzene ring, and δ 3.71 ppm for the internal aromatic proton at 16-position. Similar findings were observed in compounds **4b** and **4c**.

To study the present through-space electronic interactions in more detail, we have attempted to evaluate the rate of the benzylation of benzene with 8-(bromomethyl)[2.2]MCP (**2**) in the presence of $TiCl_4$. Pseudo-first-order plots on benzylation of benzene with **2a**–**2c** are shown in Fig. 2.

The $TiCl_4$-mediated benzylation rate constant of 8-(bromomethyl)[2.2]MCP **2a** with benzene is 6.21×10^5 s^{-1} (Table 2). It was also found that the introduction of substituents at the internal position 16 tends to promote the present benzylation reaction rate 1.8–3.8 times. Thus, the rate of benzylation of internally substituted 8-(bromomethyl)[2.2]MCPs **2b** and **2c** are much larger than that of internally unsubstituted 8-(bromomethyl)[2.2]MCP **2a**, which is attributable to the electron-donating nature of 16-substituents, such as methyl and methoxy group. Although similar findings were also reported in the $TiCl_4$-catalyzed benzylation of benzene with 4-substituted benzyl bromide,[38] much smaller substituents effects on the benzylation were observed in the present [2.2]MCP systems than those of the reported benzylations of benzene with 4-substituted benzyl bromide (Scheme 3). This is ascribed to the smaller influence of the nature of a substituent on the remote aromatic ring by a direct through-space cation–π interaction than that in 4-substituted benzyl bromide.

Considering the molecular model, it is concluded that the conformation of the benzyl cation intermediates in [2.2]MCPs should also be strongly affected by the size of the substituents at position 16.

As shown in Fig. 3, the interaction between the benzyl cation and the opposite benzene ring might be much more favorable for the 16-substituted [2.2]MCP **A** than the unsubstituted one **B**. Thus, the steric repulsion of 16-substituents,

Fig. 2. Pseudo-first-order plots on benzylation of benzene with **2a**–**2c**.

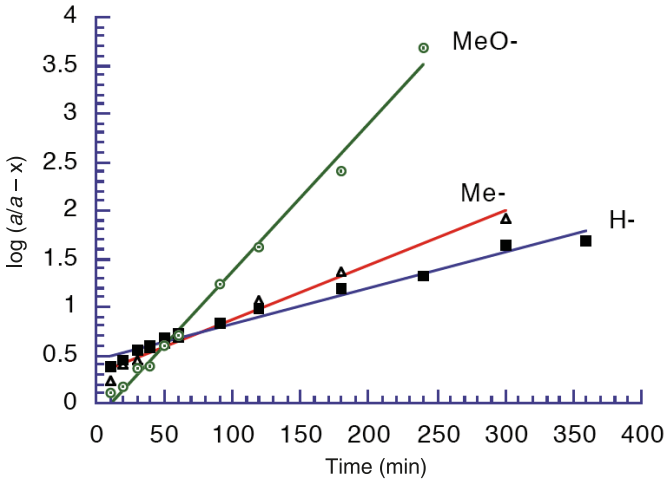
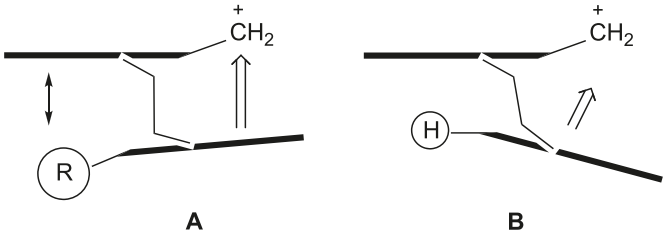


Fig. 3. Proposed through-space electronic interactions of [2.2]MCP benzyl cation.



such as methyl and methoxy groups for the opposite benzene ring could shorten the distance between the benzyl cation and the opposite benzene ring, whereas the H–π interaction could make this distance longer. The stabilization by the direct through-space cation–π interaction is possible in the benzyl cations derived from 8-(bromomethyl)[2.2]MCPs. This result strongly suggests that the benzyl cation intermediate could be stabilized by the through-space electronic interaction among the opposite benzene ring as shown in Fig. 3. As previously mentioned, although two through-space electronic interactions, (*i*) interaction through the intraannular 8,16-posisions and (*ii*) direct through-space cation–π interaction, are possible in the [2.2]MCP systems, the latter interaction might be more favorable in the present systems.

Conclusions

We have demonstrated the $TiCl_4$-mediated Friedel–Crafts benzylation of benzene with 8-(bromomethyl)[2.2]MCPs **2** to afford the corresponding 8-benzyl[2.2]MCPs **4**. The benzyl cation intermediate stabilized by the through-space electronic interaction from the opposite benzene ring was first demonstrated in the benzylation of [2.2]MCP systems. Further studies on the chemical properties of the benzylation products are now in progress.

Experimental

All melting points were uncorrected. ^{1}H NMR spectra were recorded on a Nippon Denshi JEOL FT-300 spectrometer. Chemical shifts are reported as δ values (ppm) relative

to internal Me_4Si. Mass spectra were obtained on a Nippon Denshi JIR-AQ2OM mass spectrometer at an ionization energy of 70 eV using a direct-inlet system through GLC; *m/z* values reported include the parent ion peak. Infrared (IR) spectra were obtained on a Nippon Denshi JIR-AQ2OM spectrophotometer as KBr disks. Elemental analyses were performed by Yanaco MT-5. GLC analyses were performed by Shimadzu gas chromatograph, GC-14A; silicone OV-1, 2 m; programmed temperature rise, 12 °C min^{-1}; carrier gas nitrogen, 25 mL min^{-1}.

Materials

Preparation of 5,13-di-*tert*-butyl-8-substituted 16-methyl[2.2]metacyclophane (**1a**–**1c**)[32–34] and 5,13-di-*tert*-butyl-8-(bromomethyl)-16-methyl[2.2]metacyclophane (**2b**)[35,36] were previously described.

Bromination of 8-methyl[2.2]metacyclophanes (1) with *N*-bromosuccinimide

Typical procedure

After a mixture of 5,13-di-*tert*-butyl-8-methoxy-16-methyl[2.2]metacyclophane (**1c**; 500 mg, 1.4 mmol), *N*-bromosuccinimide (300 mg, 1.7 mmol), and benzoyl peroxide (50 mg, 0.21 mmol) in carbon tetrachloride (150 mL) had been refluxed for 3 h, the formed precipitates were filtered off. The filtrate was washed with 10% sodium hydroxide and water. The organic layer was dried over sodium sulfate and evaporated in vacuo to leave a colourless solid, which was recrystallized from *n*-hexane to give 5,13-di-*tert*-butyl-8-(bromomethyl)-16-methoxy[2.2]metacyclophane (**2c**; 435 mg, 70%) as colorless prisms, mp 239–240 °C. IR (KBr, cm^{-1}) ν_{max}: 3040, 2960, 1600, 1475, 1450, 1220, 1200, 1100, 1020, 880, 805, 780, 750. ^{1}H NMR ($CDCl_3$) δ: 1.26 (s, 18H, *t*-Bu), 2.85 (s, 3H, O*Me*), 2.68–3.02 (m, 8H, CH_2), 3.08 (s, 2H, CH_2), 7.04 (s, 2H, Ar-*H*), 7.06 (s, 2H, Ar-*H*). MS *m/z* (%): 442, 444 (M^+). Anal. calcd. for $C_{26}H_{35}BrO$ (443.47): C 70.42, H 7.96; found: C 70.13, H 7.84.

Bromination of **1a** and **1b** with *N*-bromosuccinimide was carried out using the same procedure as described above to afford **2a** and **2b** in 80% and 20% yields, respectively. However, in the case of **1b**, 8,16-bis(bromomethyl)[2.2]MCP (**3**) was also obtained in 30% yield along with the recovery of the starting compound **1b** in 20% yield in spite of 1.2 equiv of *N*-bromosuccinimide used.

*8-(Bromomethyl)-5,13-di-*tert*-butyl[2.2]metacyclophane (2a)*

Colorless prisms (from *n*-hexane), mp 132–133 °C. IR (KBr, cm^{-1}) ν_{max}: 3100, 2900, 1600, 1485, 1400, 1370, 1230, 1190, 1100, 1010, 950, 920, 890, 860, 820, 760, 730, 720, 660. ^{1}H NMR ($CDCl_3$) δ: 1.29 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 2.40–3.16 (m, 8H, CH_2), 2.83 (s, 2H, CH_2), 3.68 (broad s, 1H, Ar-*H*), 6.92–7.20 (m, 4H, Ar-*H*). MS *m/z* (%): 412, 414 (M^+). Anal. calcd. for $C_{25}H_{33}Br$ (413.45): C 72.63, H 8.05; found: C 72.41, H 7.76.

*5,13-Di-*tert*-butyl-8-(bromomethyl)-16-methyl[2.2]metacyclophane (2b)*

Colorless prisms (from *n*-hexane), mp 272–275 °C. IR (KBr, cm^{-1}) ν_{max}: 3020, 2940, 1580, 1445, 1350, 1270, 1215, 1180, 990, 730. ^{1}H NMR ($CDCl_3$) δ: 0.58 (s, 3H, *Me*), 1.28 (s, 18H, *t*-Bu), 2.76–3.02 (m, 8H, CH_2), 3.07 (s, 2H, CH_2), 7.06 (s, 2H, Ar-*H*), 7.12 (s, 2H, Ar-*H*). MS *m/z* (%): 426, 428 (M^+). Anal. calcd. for $C_{26}H_{35}Br$ (427.47): C 73.05, H 8.25; found: C 72.93, H 8.21.

5,13-Di-tert-butyl-8,16-bis(bromomethyl)[2.2]metacyclophane (3)

Colorless prisms (from benzene), mp > 300 °C. IR (KBr, cm^{-1}) ν_{max}: 3040, 2960, 1585, 1475, 1360, 1225, 1220, 1190, 890, 760, 665. ^{1}H NMR ($CDCl_3$) δ: 1.33 (18H, s, *t*-Bu), 2.75–3.11 (m, 8H, CH_2), 3.04 (s, 4H, CH_2), 7.16 (s, 4H, Ar-*H*). MS *m/z* (%): 504, 506, 508 (M^+). Anal. calcd. for $C_{26}H_{34}Br_2$ (506.37): C 61.67, H 6.77; found: C 61.52, H 6.72.

Benzylation of benzene with 8-(bromomethyl)-5,13-di-*tert*-butyl-16-substituted [2.2]metacyclophane (2)

Typical procedure

To a solution of 5,13-di-*tert*-butyl-8-(bromomethyl)-16-methyl[2.2]metacyclophane (**2b**; 428 mg, 1.0 mmol) in benzene (2.67 mL, 30 mmol) was added $TiCl_4$ (0.16 mL, 1.5 mmol) at 0 °C. The reaction temperature was raised to room temperature by removing the ice bath. After the reaction mixture had been stirred at 50 °C for 2 h, it was poured into ice water and extracted with benzene. The extract was dried over anhydrous sodium sulfate and concentrated. The residue was subjected to silica-gel (Wako, C-300; 100 g) column chromatography using as eluent *n*-hexane–benzene (1:1) to give 8-benzyl-5,13-di-*tert*-butyl-16-methyl[2.2]metacyclophane (**4b**; 170 mg, 40%) as colorless prisms (from *n*-hexane), mp 167–168 °C. ^{1}H NMR ($CDCl_3$) δ: 0.62 (s, 3H, *Me*), 1.27 (s, 9H, *t*-Bu), 1.35 (s, 9H, *t*-Bu), 2.39 (s, 2H, CH_2), 2.68–3.00 (m, 8H, CH_2), 6.36–6.52 (m, 2H, Ar-*H*), 6.88–7.04 (m, 3H, Ar-*H*), 7.13 (s, 2H, Ar-*H*), 7.18 (s, 2H, Ar-*H*). MS *m/z* (%): 424 (M^+). Anal. calcd. for $C_{32}H_{40}$ (424.68): C 90.51, H 9.49; found: C 90.31, H 9.58.

Benzylation of benzene with **2a** and **2c** was carried out using the same procedure as described above and product yields are compiled in Table 1.

*8-Benzyl-5,13-di-*tert*-butyl[2.2]metacyclophane (4a)*

Colorless prisms (from *n*-hexane), mp 195 °C. IR (KBr, cm^{-1}) ν_{max}: 2964, 2864, 1594, 1478, 1477, 1454, 1359, 1275, 731. ^{1}H NMR ($CDCl_3$) δ: 1.36 (s, 18H, *t*-Bu), 2.15 (s, 2H, CH_2), 2.17–3.07 (m, 8H, CH_2), 3.71 (s, 1H, Ar-H_{16}), 6.60–7.09 (m, 5H, Ar-*H*), 7.07 (s, 2H, Ar-*H*), 7.19 (s, 2H, Ar-*H*). MS *m/z* (%): 410 (M^+). Anal. calcd. for $C_{31}H_{38}$ (410.65): C 90.67, H 9.33; found: C 90.57, H 9.35.

*8-Benzyl-5,13-di-*tert*-butyl-16-methoxy[2.2]metacyclophane (4c)*

Colorless prisms (from *n*-hexane), mp 132 °C. IR (KBr, cm^{-1}) ν_{max}: 2960, 2864, 1600, 1478, 1459, 1361, 1208, 1024, 727. ^{1}H NMR ($CDCl_3$) δ: 1.32 (s, 9H, *t*-Bu), 1.37 (s, 9H, *t*-Bu), 2.35 (s, 2H, CH_2), 2.69–2.84 (m, 8H, CH_2), 2.90 (s, 3H, O*Me*), 6.52–7.03 (m, 5H, Ar-*H*), 7.06 (s, 2H, Ar-*H*), 7.17 (s, 2H, Ar-*H*). MS *m/z* (%): 440 (M^+). Anal. calcd. for $C_{32}H_{40}O$ (440.68): C 87.22, H 9.15; found: C 87.33, H 9.74.

The reaction rate determination for the benzylation of benzene with 2 in the presence of $TiCl_4$

Typical procedure

To a solution of 5,13-di-*tert*-butyl-8-bromomethyl-16-methyl[2.2]metacyclophane (**2b**; 100 mg, 0.2 mmol) in benzene (4.2 g, 54 mmol) was added a solution of $TiCl_4$ in CS_2 (0.10 mL, 0.14 mmol), which was prepared by dissolving $TiCl_4$ (2.4 mL, 21.08 mmol) in CS_2 (12.6 mL), by syringe at 25 °C. The reaction was monitored by ^1H NMR. The reaction rate was determined by the following equations:

$$[1] \quad \mathrm{MCP{-}CH_2Br} + \text{benzene} \xrightarrow{\mathrm{TiCl_4}} \mathrm{MCP{-}CH_2C_6H_5}$$

$$[2] \quad \frac{\mathrm{d[MCP{-}CH_2Br]}}{\mathrm{d}t} = k[\mathrm{MCP{-}CH_2C_6H_5}]$$

$$[3] \quad \ln \frac{[\mathrm{MCP{-}CH_2Br}]_0}{[\mathrm{MCP{-}CH_2Br}] - [\mathrm{MCP{-}CH_2C_6H_5}]} = k\mathrm{t}$$

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