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that the reaction of anthracene and acyl chloride in the presence of chlorotrimethylsilane as the additive in LiClO4/THF, produces the cyclized products, in which magnesium anthracenes might not be involved in their process. In contrast, electrochemical reduction is also a powerful tool for organic transformations.16–18 It has, in fact, been recognized that Mg electrodes in LiClO4/THF show a high-reducing power for various organic molecules.19–25 In the course of our research on electrochemical reduction using Mg electrodes, we have found that the electrochemical reduction of the solution of anthracenes and esters, in the presence of chlorotrimethylsilane as the additive in LiClO4/THF, produces the cyclized products, in which magnesium anthracenes might be generated in situ and react with the esters (Scheme 1 (5)). Herein, we wish to describe in detail the current reactions involving reaction optimization, the scope and limitations of anthracenes and esters, and the investigation of the reaction mechanism.

1. Introduction

Magnetence anthracenes and their related intermediates have been of interest thus far because they have exhibited interesting reaction behavior, as well as useful synthetic potentials.1–8 The chemistry of this field has been extensively studied since the important discovery of magnesium anthracenes by Ransden in 1965.3,6 The reactions of magnesium anthracenes and esters, as the electrophile, are of particular interest (Scheme 1). For example, Janke and Bogdanović discovered that magnesium anthracene can react with ethyl acetate to give the acetylated product (Scheme 1 (1)),1 whereas a similar reaction using dimethyl substituted magnesium anthracene with ethyl acetate produced the cyclized product (Scheme 1 (2)).8 This might have been due to the steric repulsion of the dimethyl groups that were substituted for the magnesium anthracene, which might have resulted in the formation of intermolecular carbon–carbon bonds, followed by intramolecular cyclization. Regarding the acylation for anthracene, Nishiguchi and Maekawa (2007) reported that the reaction of anthracene and acyl chloride in the presence of Mg metal in DMF produced the double-acylated compounds (Scheme 1 (3)).7 Additionally, the use of succinyl dichloride showed the formation of the cyclized diketone compounds (Scheme 1 (4)).9 In both cases, Mg metal seems to have served as the donor of electrons and the reductant. These researchers assumed that magnesium anthracenes might not be involved in their process. In contrast, electrochemical reduction is also a powerful tool for organic transformations.16–18 It has, in fact, been recognized that Mg electrodes in LiClO4/THF show a high-reducing power for various organic molecules.19–25 In the course of our research on electrochemical reduction using Mg electrodes, we have found that the electrochemical reduction of the solution of anthracenes and esters, in the presence of chlorotrimethylsilane as the additive in LiClO4/THF, produces the cyclized products, in which magnesium anthracenes might be generated in situ and react with the esters (Scheme 1 (5)). Herein, we wish to describe in detail the current reactions involving reaction optimization, the scope and limitations of anthracenes and esters, and the investigation of the reaction mechanism.

2. Experimental

2.1 General remarks

1H and 13C NMR spectra were measured using a Varian MERCURY 300 (1H, 300 MHz; 13C, 75 MHz) and a JEOL JNM-ECX 400 (1H, 400 MHz; 13C, 100 MHz). Unless otherwise noted, CDC13 was used as the solvent. The NMR value of 1H NMR in the case of CDC13 is reported based on 7.26 or 0.00 ppm from the tetramethylsilane as an internal standard. The NMR value of 13C NMR in the case of CDC13 is reported based on 77.0 ppm. High-resolution mass spectra (HRMS) were measured using a Thermo Fisher Scientific Exactive Plus and a JEOI JMS-SX102A. In some cases, an AMR DART ion source was also used with the Thermo Fisher Scientific Exactive Plus. Merck pre-coated silica gel F254 plates (thickness 0.25 mm) were used for the TLC analysis. A silica gel column (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100 μm) was used for the flash chromatography using an air pump. A Japan Analytical Industry LC-9201, LC-9110 NEXT, or LC-9210 NEXT, equipped with JAIGEL-1H and JAIGEL-2H, was used for the preparative GPC separation, and CHCl3 was used as an eluent. If necessary, preparative GPC separation was conducted to obtain the purified compounds. All reactions were conducted in a N2 atmosphere.

2.2 Materials

Dry solvents of THF (tetrahydrofuran) and DMF (N,N-dimethylformamide), Me2SiCl (chlorotrimethylsilane), t-BuMe2SiCl (tert-butylidimethylchlorosilane), Et3SiCl (chlorotriethylsilane), BF3·OEt2 (boron trifluoride diethyl etherate), AlCl3 (aluminium chloride), LiClO4 (lithium perchlorate), anthracene (1a), 9-methylanthracene (1b), methyl butanoate (2a), propyl acetate (2c), and ethyl acetate (2f) were obtained from commercial suppliers. The MS 5A (molecular sieve 5A) was obtained from a commercial supplier, and was activated before use.

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Methyl heptanoate (2b). Heptanoic acid (1.51 g, 11.6 mmol) and 98% H$_2$SO$_4$ (0.5 mL) were dissolved in MeOH (20 mL), and the solution was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NaHCO$_3$ (50 mL). The aqueous phase was extracted by CH$_2$Cl$_2$ (100 mL), saturated aqueous NaHCO$_3$ (100 mL), and brine (100 mL). The organic extract was dried by Na$_2$SO$_4$, filtered and concentrated. The crude material was purified by flash chromatography (hexane:EtOAc, 10:1) to obtain methyl heptanoate (2b, 1.33 g, 8.2 mmol, 80% yield), which was identified by comparison of the reported spectroscopic data, although the reported data was based on the mixture of isomers. Because we recognize the insufficient data, we also report spectroscopic data. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.03 (t, $J$ = 7.2 Hz, 3H), 1.25 (sextet, $J$ = 7.0 Hz, 2H), 2.52 (t, $J$ = 7.2 Hz, 2H), 7.00–7.06 (m, 4H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 13.5, 18.3, 36.0, 115.9 (d, $J$ = 23.5 Hz), 122.9 (d, $J$ = 8.0 Hz), 146.5 (d, $J$ = 2.9 Hz), 160.0 (d, $J$ = 242.7 Hz), 172.1 ppm; HRMS (ESI) calculated for C$_7$H$_{14}$O (M+H)$: 112.1010$, found 112.1013.

Phenyl butanoate (2d). Phenol (1.03 g, 10.9 mmol) and butyryl chloride (3.36 g, 31.5 mmol) were dissolved in CH$_2$Cl$_2$ (50 mL) at 0°C, and then pyridine (1.5 mL) was added to the solution. The reaction temperature was increased from 0°C to room temperature, and stirring was continued overnight. The reaction was quenched with saturated aqueous Na$_2$S$_2$O$_3$ (150 mL). The aqueous phase was extracted by CHCl$_3$ (100 mL), and the organic phase was washed with aqueous 1 M HCl (100 mL). The organic extract was dried by Mg$_2$SO$_4$, filtered and concentrated. The crude material was purified by flash chromatography (hexane:EtOAc, 10:1) to obtain phenyl butanoate (2d, 1.33 g, 8.1 mmol, 74% yield), which was identified by comparison of the reported spectroscopic data.

4-Fluorophenyl butanoate (2e). 4-Fluorophenol (1.14 g, 10.9 mmol) and butyryl chloride (3.36 g, 31.5 mmol) were dissolved in CH$_2$Cl$_2$ (50 mL) at 0°C, and then pyridine (1.5 mL) was added to the solution. The reaction temperature was increased from 0°C to room temperature, and stirring was continued overnight. The reaction was quenched with H$_2$O (100 mL). The aqueous phase was extracted by CH$_2$Cl$_2$ (100 mL), and the organic phase was washed with aqueous 1 M HCl (100 mL), saturated aqueous NaHCO$_3$ (100 mL), and brine (100 mL). The organic extract was dried by Na$_2$SO$_4$, filtered and concentrated. The crude material was purified by flash chromatography (hexane:EtOAc, 10:1) to obtain 4-fluorophenyl butanoate (2e, 1.50 g, 8.2 mmol, 80% yield), which was identified by comparison of the reported spectroscopic data, although the reported data was based on the mixture of isomers. Because we recognize the insufficient data, we also report spectroscopic data. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.00 (m, 4H), 7.22 (d, $J$ = 8.0 Hz, 2H), 7.32 (d, $J$ = 8.0 Hz, 2H), ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 125.0, 127.8, 128.7, 135.9, 158.6 ppm; HRMS (ESI) calculated for C$_{10}$H$_{13}$F (M+H)$: 154.1040$, found 154.1045.

9,10-Dimethylanthracene (1c). Anthracene (5.01 g, 28.1 mmol) was dissolved in CHCl$_3$ (100 mL). Then, the solution of Br$_2$ (3.6 mL, $d$ = 3.1 g/mL, approximately 11.2 g, 70.1 mmol) in CHCl$_3$ (50 mL) was added dropwise at room temperature, and the reaction mixture was stirred at the same temperature overnight. The reaction was quenched with saturated aqueous Na$_2$S$_2$O$_3$ (150 mL). The aqueous phase was extracted by CHCl$_3$ (100 mL), and the organic phase was washed with saturated aqueous Na$_2$S$_2$O$_3$ (100 mL $\times$ 2) and brine (100 mL). The organic extract was dried by MgSO$_4$, filtered and concentrated to give 9,10-dibromoanthracene (5.65 g, 70.1 mmol, 61% yield) as the high-purity material, which was identified by comparison of the reported spectroscopic data.28

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9,10-Dibromoanthracene (1.05 g, 3.1 mmol) was dissolved in THF (20 mL), and the solution was cooled at −78°C. n-BuLi (1.6 M in hexane, 2.2 mL, approximately 3.5 mmol) was slowly added to the solution at the same temperature, and the mixture was stirred for 1.5 h. After MeI (1.2 mL, $d$ = 2.28 g/mL, approximately 2.74 g, 19.3 mmol) was added to the reaction mixture, the reaction temperature was gradually increased from −78°C to room temperature.
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ature, and the mixture was stirred overnight. The reaction was quenched with saturated aqueous NH₄Cl (20 mL). The aqueous phase was extracted by CH₂Cl₂ (50 mL x 2), and the combined organic phase was washed with H₂O (100 mL). The organic extract was dried by MgSO₄, filtered, and then 9-bromo-10-methylnanthracene (792.4 mg, approximately 2.9 mmol, approximately 94% yield) was obtained as the crude material, which was identified by comparison of the reported spectroscopic data.25 The crude material obtained here was used in the next step without further purification.

9-Bromo-10-methylnanthracene (761.2 mg, approximately 2.8 mmol) was dissolved in THF (20 mL), and the solution was cooled to −78°C. n-BuLi (1.6 M in hexane, 2.2 mL, approximately 3.5 mmol) was slowly added to the solution at the same temperature and stirred for 1 h. After MeI (1.2 mL, 2.28 g/mL, approximately 2.74 g, 19.3 mmol) was added to the reaction mixture, the reaction temperature was gradually increased from −78°C to room temperature, and the mixture was stirred overnight. The reaction was quenched with saturated aqueous NH₄Cl (20 mL). The aqueous phase was extracted by CH₂Cl₂ (50 mL x 2), and the combined organic phase was washed with H₂O (100 mL). The organic extract was dried by MgSO₄, filtered and concentrated. The crude material obtained here was used in the next step without further purification.

Typical procedure of electrochemical reduction of anthracene with esters (Table 1, entry 14)

Electrochemical reduction was conducted using a 30 mL three-necked round flask, equipped with two Mg electrodes. The size of each Mg electrode was 1 x 1 x 4 cm. LiClO₄ (532.8 mg, 5.01 mmol) was dissolved in dry THF (10.0 mL) in the presence of the activated MS 5A (752.1 mg). Anthracene (1a, 134.0 mg, 0.752 mmol), methyl butanoate (2a, 30.9 mg, 0.303 mmol), and TMSCl (5 eq based on 2a, 0.19 mL, d = 0.86 g/mL, approximately 163.4 mg, 1.50 mmol) were added to the solution. An electric current was passed at 25 mA until the 4 F charge was consumed; the anode and cathode were switched alternately every 15 s. After the electrolysis, H₂O (10 mL) was added to the solution for quenching the reaction, then cefiletation was conducted. After the addition of H₂O (50 mL), the organic phase was extracted by Et₂O (50 mL x 3). The combined organic phase was washed with brine (50 mL), followed by drying over MgSO₄. After the filtration and the removal of the organic solvent, the crude material was purified by flash chromatography (hexane:EtoAc, 5:1) to produce 11-propyl-9,10-dihydro-9,10-methanoanthracen-11-ol (3aa, 16.1 mg, 0.0643 mmol, 21% yield). 1H NMR (300 MHz, CDCl₃) δ 0.79 (t, J = 6.6 Hz, 3H), 1.35–1.50 (m, 4H), 2.64 (s, 1H), 4.10 (s, 2H), 6.96–7.10 (m, 4H), 7.20–7.27 (m, 2H), 7.34–7.40 (m, 2H) ppm; 13C NMR (75 MHz, CDCl₃) δ 14.5, 18.0, 34.6, 60.1, 107.1, 122.3, 124.5, 125.5, 126.1, 146.7, 146.8 ppm; HRMS (ESI) calculated for C₁₈H₁₆ONa ([M + Na]⁺): 273.1250, found 273.1249.

9-Methyl-9,10-dihydro-9,10-methanoanthracen-11-ol (3bc).

1H NMR (300 MHz, CDCl₃) δ 0.78 (t, J = 6.9 Hz, 3H), 1.10–1.40 (m, 4H), 1.65 (s, 3H), 2.37 (d, J = 2.1 Hz, 1H), 4.18 (s, 1H), 6.94–7.15 (m, 5H), 7.18–7.26 (m, 2H), 7.32–7.38 (m, 1H) ppm; 13C NMR (75 MHz, CDCl₃) δ 7.1–7.4, 14.6, 17.1, 31.4, 60.4, 107.9, 119.1, 121.9, 122.1, 124.0, 125.3, 125.5, 125.8, 126.1, 146.6, 148.9, 149.6 ppm; HRMS (ESI) (calculated for C₁₉H₁₇ONa ([M + Na]⁺): 287.1406, found 287.1405.

10,11-Dimethyl-11-propyl-9,10-dihydro-9,10-methanoanthracen-11-ol (3cd). 1H NMR (400 MHz, CDCl₃) δ 0.75 (t, J = 7 Hz, 3H), 1.22–1.30 (m, 2H), 1.35–1.47 (m, 2H), 1.71 (s, 6H), 2.21 (s, 1H), 7.00–7.08 (m, 4H), 7.09–7.15 (m, 2H), 7.18–7.24 (m, 2H) ppm; 13C NMR (100 MHz, CDCl₃) δ 8.3, 13.1, 17.4, 32.2, 60.6, 107.5, 119.9, 121.7, 125.3, 125.8, 149.2, 149.5 ppm; HRMS (ESI) (calculated for C₂₀H₂₂ONa ([M + Na]⁺): 310.1563, found 310.1564.

2.4 X-ray crystal structure determinations of 3aa

The measurement of compound 3aa was made on a Rigaku XtaLAB-PRO MM007-PILATUS-200 diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7071 Å). The diffraction data were collected at 100(2) K by the ω scan mode. The data were collected and processed using the CrysAlisPro (Rigaku Oxford Diffraction). The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SHELXTL 2018/2) and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically (SHELXL 2018/3). All the hydrogen atoms were refined using the AFIX command. All calculations were performed using Crystal Structure (ver. 4.3). Crystal data and detailed structure determinations are summarized in Table S1. Selected bond lengths and bond angles are listed in Table S2. CCDC No: 1974257.

3. Results and Discussion

To achieve the intermolecular reaction followed by the intramolecular cyclization using electrochemistry, we investigated the reaction optimization (Table 1). The typical procedure was as follows. The electrochemical reaction was conducted in the
Table 1. Reaction optimization.

| Entry | Solvent | Additive     | Current (X mA) | T (°C) | 3aa (%) | 4aa (%) |
|-------|---------|--------------|----------------|--------|---------|---------|
| 1     | THF     | Me3SiCl      | 5              | r.t.   | <5      | n.d.  |
| 2     | THF     | Me3SiCl      | 10             | r.t.   | <4      | <7     |
| 3     | THF     | Me3SiCl      | 25             | r.t.   | <5      | n.d.  |
| 4     | THF     | Me3SiCl      | 50             | r.t.   | 6       | n.d.  |
| 5     | THF     | Me3SiCl      | 25             | −20    | <3      | n.d.  |
| 6     | THF     | Me3SiCl      | 25             | 0      | 13      | n.d.  |
| 7     | THF     | Me3SiCl      | 25             | 40     | <4      | n.d.  |
| 8*    | THF     | tBuMe2SiCl   | 25             | r.t.   | <3      | n.d.* |
| 9     | THF     | Et3SiCl      | 25             | r.t.   | n.d.   | n.d.  |
| 10    | THF     | BuMe2SiCl    | 25             | n.d.   | n.d.   | n.d.* |
| 11    | THF     | BF3·OEt2     | 25             | r.t.   | 6       | —      |
| 12    | THF     | AlCl3        | 25             | r.t.   | trace   | —      |
| 13    | DMF     | Me3SiCl      | 25             | r.t.   | n.d.   | n.d.  |
| 14+   | THF     | Me3SiCl      | 25             | r.t.   | 21      | n.d.  |

*Typical procedure: the electrochemical reduction was conducted in the undivided cell equipped with Mg electrodes. The solution of 0.5 M LiClO4/THF (10 mL) containing anthracene (1a, 1 mmol), ester 2a (1 mmol), and chlorotrimethylsilane (5 eq based on 2a, 5 mmol) was electrochemically reduced in the presence of MS 5A (750 mg) using 25 mA. The alternating time of the electrodes was 15 s, and 4 F/mol based on 1a passed at 0°C (entry 6).

*Isolated yields.

*Pt electrodes were used in the anode and cathode.

*E = OSiBuMe2.

*E = OSiEt3.

*Anthracene (1a, 0.75 mmol), ester 2a (0.3 mmol), and chlorotrimethylsilane (5 eq based on 2a, 1.5 mmol) were used in 0.5 M LiClO4/THF (10 mL). The electricity of 4 F/mol based on 1a passed with 25 mA. The alternating time of electrodes was 15 s.

undivided cell, which was equipped with two Mg electrodes. Anthracene (1a, 1 mmol) and methyl butanoate (2a, 1 mmol), in the presence of an additive such as Me3SiCl, tBuMe2SiCl, Et3SiCl, BF3·OEt2, or AlCl3, were dissolved in 0.5 M LiClO4/THF (10 mL). The current was passed to the solution at T°C using 4 F/mol based on 1a passed at 0°C (entry 6). The use of Pt electrodes instead of Mg electrodes was not effective (entry 8). The change of tBuMe2SiCl, Et3SiCl, BF3·OEt2, AlCl3 or DMF from the condition of entry 3 did not give improved results (entries 9–13). However, in the case of the condition such as anthracene (1a, 0.75 mmol, 2.5 eq based on 2a), and tBuMe2SiCl, the product yield was not sufficient, the conditions of entry 14 were decided to be the optimized parameters. In most cases in Table 1, 1-(9,10-dihydroanthracen-9-yl) butan-1-one (5) (vide infra, Scheme 2) was confirmed as the by-product. In entry 14 of Table 1, 5 was isolated at <25% yield. The chemical structure of product 3aa was confirmed by 1H NMR, 13C NMR, and HRMS. Moreover, X-ray analysis of 3aa also supported the cyclized structure, as shown in Fig. 1.

Next, we tested the scope and limitations of the current cyclization reactions using various esters (Table 2). For example, the reaction of anthracene (1a) and methyl heptanoate (2b) gave the corresponding 3ab at 15% yield (entry 1). Moreover, propyl acetate (2c) was found to be a good electrophile to afford 3ac at 42% yield (entry 2). As for the phenoxide ion and 4-fluorophenoxide ion as the leaving group, the corresponding esters, such as phenyl butanoate (2d) and 4-fluorophenyl butanoate (2e), were used as the electrophiles. In both cases, the cyclized products of 3aa were obtained at moderate yields (entries 3 and 4). The reactions using anthracene derivatives, such as 9-methylanthracene (1b) and 9,10-dimethylanthracene (1c) bearing methyl and dimethyl substituents, were also examined. The reaction of 1b and 2d produced the corresponding 3bd at 41% yield (entry 5). The reaction of 1c and 2d gave the 3ed at 15% yield (entry 6). Additionally, the reaction of 1e and 2f formed the 3ef at 51% yield (entry 7). Thus, it was found that the cyclized products could be formed at moderate yields in some cases.
To clear the current reaction, we examined some control experiments (Scheme 2). For example, the current reaction using 1a and 2a in the absence of Me3SiCl under the same conditions gave the corresponding ketone compound 5 at 16% yield (Scheme 2(a)). A trace amount of 3aa was confirmed. Likewise, the same reaction using 2d gave the corresponding ketone compound 5 at 27% yield (Scheme 2(b)). In this case, no cyclized product of 3aa was confirmed. The use of metal Mg powder as the electron donor, instead of electrochemistry without LiClO4 and with LiClO4 in THF, did not give the desired compounds, and anthracene (1a) was recovered at 94% and quantitative yields, respectively (Scheme 2(c) and (d)). Thus, it seems to be critical for the current reaction to use electrochemical reduction, equipped with Mg electrodes in the presence of Me3SiCl for the desired transformation.

The plausible reaction mechanism has been described in Scheme 3 using 1a and 2a. The above results indicate that an additive such as Me3SiCl can play an important role in the current reactions. The electrochemical reduction condition using Mg electrodes might form a magnesium anthracene intermediate A. In this step, there seemed to be two possibilities for the formation of magnesium anthracene intermediate A or its equivalent. One was electrochemical reduction of anthracene by the Mg electrode, which was coupled with eluted Mg2+ to form A. Another possibility to be considered was the reduction of anthracene by active magnesium metal, which was formed on the surface of the Mg electrode. In the next step, magnesium anthracene or its equivalent could be reacted with esters 2a to give the adduct B, which might have produced the corresponding ketone C, releasing MeO⁻. The activated carbonyl group using Me3SiCl underwent the intramolecular attack by the anionic carbon in C to afford the cyclized 4aa. Under the electrochemical reaction or workup procedure, the cleavage of the oxygen–silicon bond, of a part of the product 4aa, seemed to give 3aa.

4. Conclusions

We have found that the electrochemical reduction condition of anthracenes and esters in LiClO4/THF in the presence of chlorotrimethylsilane using Mg electrodes gives the corresponding cyclized products. In some cases, the products were obtained in moderate yields. The success of the current reactions was due to the use of chlorotrimethylsilane as the additive, which might have activated the in situ formed carbonyl compounds and might have
enabled the subsequent intramolecular attack. The mechanism of the current reactions is interesting, and the tandem reaction, involving the intermolecular followed by the intramolecular carbon–carbon bond formation, has been assumed. Further synthetic investigations have been studied in our laboratory.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00012.
Acknowledgments

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