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A New Method of Synthesizing Phenalen-1-one: Reduction of 3-Hydroxyphenalen-1-one Using $NaBH_4$ and Lanthanoid Chlorides

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Abstract: Phenalen-1-one was obtained in considerable yield by reducing 3-hydroxyphenalen-1-one. Most of known preparation methods are not very practical, either because their yields are very poor or because their processes have many steps. This regioselective 1,2-reduction proceeded by the action of $NaBH_4$ and various cations of rare-earth elements and metals. The yields of phenalen-1-one were examined as a function of typical lanthanoids, molar ratios of lanthanoid ions to 3-acetoxy-phenalen-1-one, and differing methods of protecting the hydroxyl group. Lanthanum chloride ($LaCl_3$) gave the greatest yield (45.3%) of phenalen-1-one at molar ratios higher than a third, probably because La^{3+} ion is a hard acid and coordinates easily to a hard solvent such as methanol. Further, it has the largest ionic radius among all lanthanoid ions.

Keywords: α-Enone, 3-hydroxyphenalen-1-one, lanthanoid salt, $NaBH_4$, phenalen-1-one, 1,2-reduction

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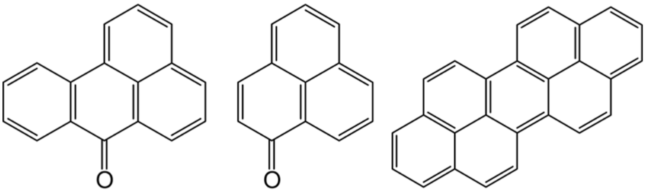


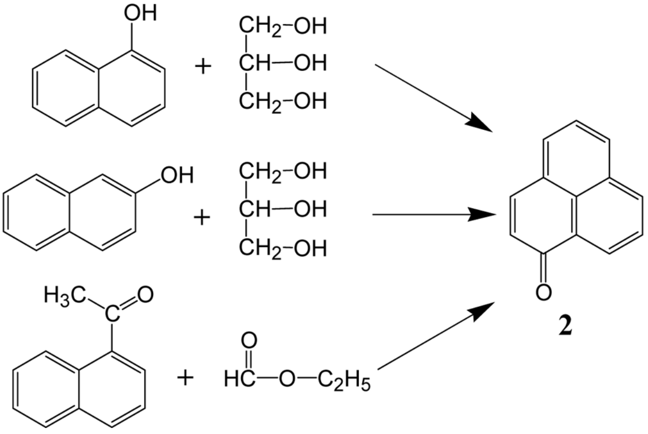
1 **2** **3**

Scheme 1. Polycyclic aromatic compound and two important intermediates.

INTRODUCTION

7*H*-Benz[*de*]anthracen-7-one (benzanthrone) (**1**) gives nanocyclic aromatic compounds by its self-condensation.[1] Some of them have been used as excellent vat dyes since the beginning of the 20th century and since 1950 have also been shown to be prototypes for organic semiconductors[2] and photoconductors.[3]

Phenalen-1-one (**2**), which is smaller by one benzene ring than **1**, as seen in Scheme 1, also affords interesting condensation products. Among them, dibenzo[*cd,lm*]perylene (peropyrene) (**3**) has a symmetric structure of approximate D_{2h} symmetry and is a significant compound that is basic in the study of these conductors. This hydrocarbon can easily be prepared from **2** by a reported method.[4] However, the synthesis of **2** is not so easy. Several methods have been already reported (Scheme 2),[5,6] but most of these methods are not very practical because of poor yields or long processes.



Scheme 2. Previously reported synthetic methods of phenalen-1-one.

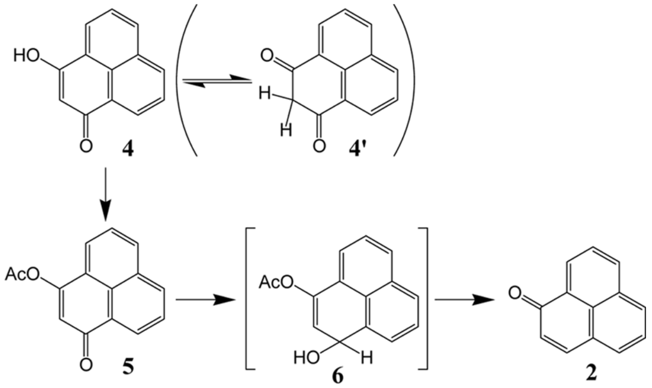
We succeeded in preparing this compound in considerable yield by reducing 3-acetoxy-phenalen-1-one (**5**), in which the OH group of 3-hydroxyphenalen-1-one (**4**) was protected, by the action of sodium borohydride ($NaBH_4$) and lanthanum chloride. As the starting material, **4** was obtained in a good yield by heating a mixture of naphthalic anhydride and diethyl malonate in the presence of zinc chloride.[7,8] This method may be considered as a convenient new method of synthesizing **2** and thus **3**.

In this article, we report the results obtained under various reaction conditions. The reaction mechanism will be also discussed.

RESULTS AND DISCUSSION

3-Hydroxyphenalen-1-one (**4**) has a tautomer, 2,3-dihydrophenalen-1,3-dione (**4′**), but it has been reported to exist predominantly as **4**.[8] To obtain phenalen-1-one (**2**) from **4**, the hydroxyl group of **4** must first be protected and then the carbonyl group of **5** [an α,β-unsaturated ketone (α-enone)] must be reduced to the allylic alcohol type (**6**). Finally, **2** is produced from **6** by dehydration and deacetylation with an acid catalyst as shown in Scheme 3.

On the other hand, it has been previously reported that such regioselective 1,2-reductions can proceed using $NaBH_4$ and metallic ions,[9,10] and so the yields of **2** under various reaction conditions were investigated in detail. Each operation was carried out in a manner similar to that described under **2** in the experimental part.



Scheme 3. New synthetic method of phenalen-1-one.

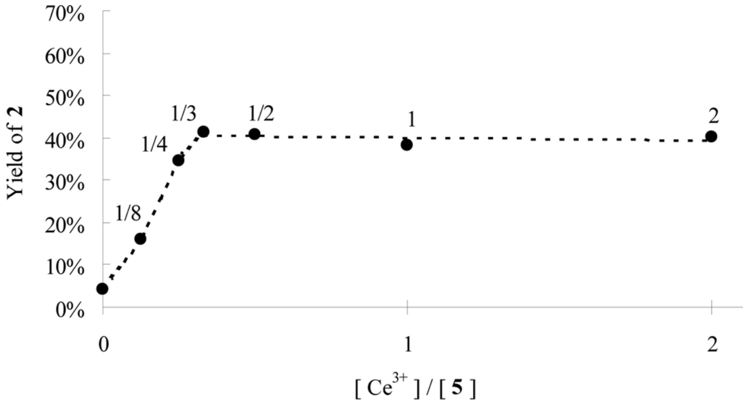


Figure 1. Effect of molar ratios of cerium ion Ce^{3+} to **5** on the yield of **2**.

Effect of Molar Ratios of $CeCl_3$ to 5

Gemal and Luche[9] reported that the reduction of α,β-unsaturated ketone (α-enone) proceeded efficiently in the presence of lanthanoid chlorides, especially cerium chloride ($CeCl_3$) at the molar ratio of Ce^{3+} ion $>$ 1:4 to substrate. When isomolar $CeCl_3$ was applied to the mixture of $NaBH_4$, methanol, and tetrahydrofuran (1:1), **2** was obtained in a yield of 38%. By-products were small amounts of **3**, 2,3-dihydrophenalen-1-one, and unknown material. As shown in Fig. 1, the yield of **2** remained around 38% even when the molar ratio of Ce^{3+} ion to **5** was varied between 2.0 and 1/3.

Effect of Other Cerium Salts

When other cerium salts were applied, the yields of **2** were very poor in the cases of sulfate, carbonate, and acetate as shown in Fig. 2. These observations may be explained as follows. The former two salts were hardly soluble, and thus their solutes were suspended in the solvent [CH_3OH–tetrahydrofuran (THF)]. Cerium acetate was soluble but the degree of ionization was low. On the other hand, the nitrate of a strong electrolyte gave a yield as great as chloride. The necessity of ionization of the added salt may be supported by the fact that yields of **2** were decreased more as the content of cerium acetate was increased by the addition of sodium acetate to the reactant solution containing cerium chloride (Fig. 3).

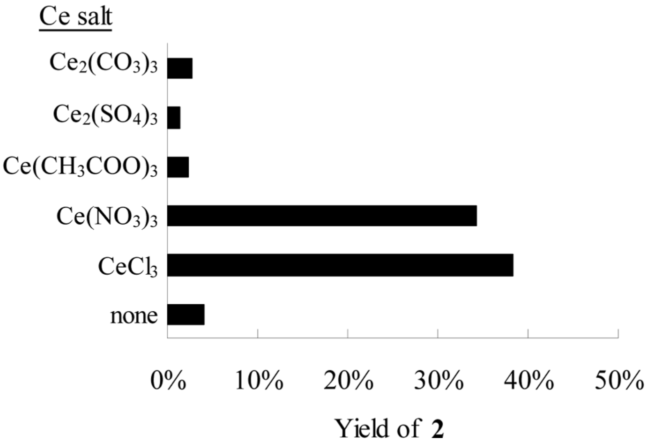


Figure 2. Effect of cerium salts on the yield of **2**.

Yields of 2 Using Various Metallic Ions

Various kinds of metal chlorides were examined, using an isomolar ratio of M^{n+} to **5**. As shown in Table 1 and Fig. 4, yields of **2** decreased as the atomic number of trivalent lanthanoid cations increased from La through Ce, Sm, and Gd to Yb. In addition, the yield of **2** decreased from La through Y to Sc as the ionic radius of similar rare-earth metallic ions decreased. It is well known that the trivalent ionic radius of lanthanoid

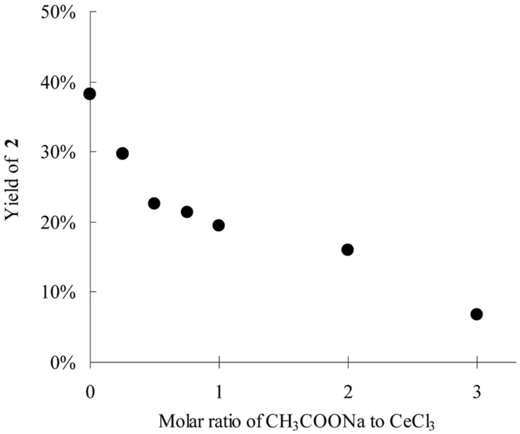


Figure 3. Effect of the ionization of Ce^{3+} ion on the yield of **2**, caused by the composition change between cerium chloride and cerium acetate.

Table 1. Yield of **2** using various metallic ions

Ions	Yield of **2**
Sc^{3+}	6.7%
Y^{3+}	26.2%
La^{3+}	45.3%
Ce^{3+}	38.2%
Sm^{3+}	25.7%
Gd^{3+}	24.6%
Ho^{3+}	27.1%
Yb^{3+}	16.2%
Ba^{2+}	Trace
Sr^{2+}	1.4%
Tl^{3+}	Trace
Al^{3+}	Trace
Mn^{2+}	Trace
Fe^{3+}	1.1%
Cu^{2+}	Trace

Note. The term “trace” signifies a yield of <1.0%.

ions decreases gradually from 1.061 Å in the case of La^{3+} down to 0.858 Å with Yb^{3+} and 0.848 Å with Lu^{3+}. It is evident from Fig. 4 that the curve has an inflection point between Gd and Ho: the yield of Ho is more than that of Gd. This feature might be interpreted by the decrease of coordination number by one between Gd and Ho in the series of lanthanoid contraction. Lanthanum ion La^{3+}, having the largest ionic radius, gave the greatest yield of **2**. Alkaline-earth metallic ions such as Ba^{2+} and Sr^{2+} have larger ionic radii than lanthanoid ions but showed

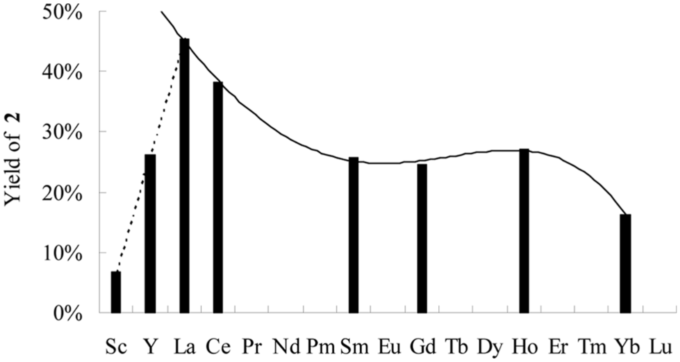
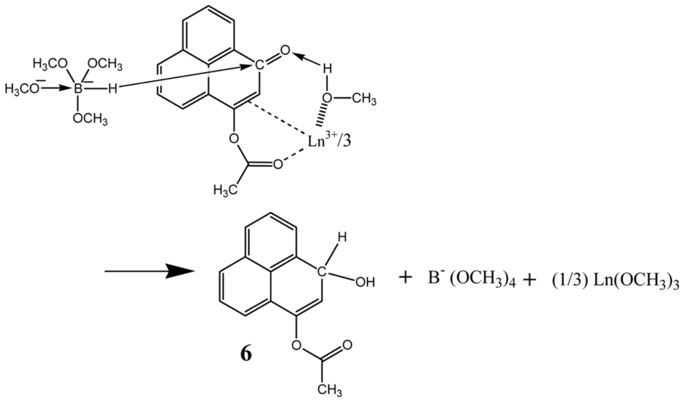


Figure 4. Effect of increasing atomic number of lanthanoid ions on the yield of **2**.



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Scheme 4. Activated complex model for the region-selective 1,2-reduction.

very poor yield of **2**. Other kinds of metallic ions such as Mn^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, and Tl^{3+}, which are bound easily to oxygen, had no effect on the regioselective reduction. Apparently it is necessary for metallic ions to be hard acids and to easily coordinate with hard solvents such as methanol. They also need to have enough space to receive such large ligands as compound **5**, as shown in Scheme 4.

Protection of Hydroxyl Group

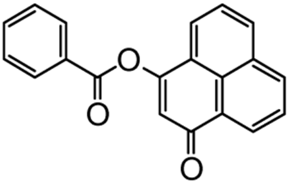
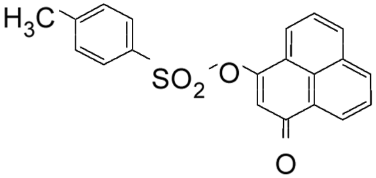
These examinations were carried out using acetoxy **4** (i.e., **5**). In addition, other ester types were also examined. Table 2 shows the yields of **2** obtained by 1 molar equivalent (equiv.) $LaCl_3$ and 2 molar equiv. $NaBH_4$ to 1 molar equiv. ester.

The maximum yield (45.3%) was obtained with acetyl protection (**5**) and lanthanum ion. The other protecting groups were so large that the complexation with lanthanum ion is probably less favorable than that of the acetyl group, and hence the yields of **2** were poor, as shown in Table 2.

Hypothetical Mechanism of Regioselective 1,2-Reduction

Compound **2** can be obtained from **4** by reduction of the carbonyl group only to the alcoholic hydroxyl group for α-enone [O(1) = C(2)–C(3) = C(4); see also Scheme 3]. A reducing agent such as sodium borohydride $NaBH_4$ may give all four types of reduced products; those of 1,2-reduction,

Table 2. Yield of **2** from ester type (R) protection of **4**

R	Yield of **2**
H **(4)**	Trace
CH_3CO (Ac) **(5)**	45.3%
 C_6H_5CO (Bzl) **(7)**	11.0%
 p-CH_3-$C_6H_4SO_2$ (Tos) **(8)**	3.9%

Note. The term "trace" signifies a yield of <1.0%.

3,4-reduction, 1,4-reduction, and complete 1,2,3,4-reduction are HO–CH–C=C, O=C–CH–CH, HO–C=C–CH, and HO–CH–CH–CH, respectively. $NaBH_4$ alone preferentially gave the starting material **4** and only 4% of **2** after the dehydration and deacetylation. It worked mainly as a deacetylation agent for **5** rather than a reductant. Regioselective 1,2-reduction might be carried out by the addition of metallic ions, especially lanthanoid ions.[9,10]

The result described previously suggests that $CeCl_3$ reacted stoichiometrically with **5** rather than catalytically. Vigorous hydrogen evolution and a large amount of precipitates, perhaps cerium trimethoxide, were observed upon addition of $NaBH_4$ to a solution of $CeCl_3$ in CH_3OH–THF. This demonstrates an important role for the Ce^{3+} ion in the CH_3OH–BH_4^- reaction. Furthermore, it also suggests that the precipitation reflects the formation of the salt $Ce(OCH_3)_3$ and that one-third molar equivalence (equiv.) of $CeCl_3$ equals one molar equiv. of proton from methanol. Thus one molar equiv. of **5** was reduced stoichiometrically together with one molar equiv. of $NaBH(OCH_3)_3$, as shown in Scheme 4.

Our assumption may be described as follows. For the first and second steps, we accept that the reaction proceeds according to the mechanism of Gemal and Luche.[9]

$$CH_3OH + Ln^{3+} \rightarrow CH_3 - O(H) - Ln^{3+}$$
$$^{-}BH_{4-n}(OCH_3)_n + CH_3OH \rightarrow {}^{-}BH_{4-p}(OCH_3)_p + H_2$$
$$n = 0, 1, 2; \quad p = n + 1$$

The reducing power of $^{-}BH_{4-n}(OCH_3)_n$ may be expected to be greatest for $^{-}BH\ (OCH_3)_3$, and 75% of H^- is evolved as hydrogen gas.[9]

The lanthanoid ion Ln^{3+} may form a bulky chelate complex composed of methanol and substrate **5**. We assume that 1,2-reduction may be induced more easily by an increased number of chelate rings. The chelate ring ligates Ln^{3+} ion with the O atom of methanol and either the π electron of C=C bond or the O atom of acetyl C=O group. This ligand is very bulky, and the central metal necessitates a large ionic radius.

In the process of 1,2-reduction, methoxide anion CH_3O^- approaches the $[CH_3O]_3B^-H$ group, and then the hydride anion H^- attacks the C atom of the C=O group, accompanying the acceptance of a proton H^+ from the methanol ligand at the O atom of the C=O group. The lanthanoid ion may form a trimethoxide salt of $Ln(OCH_3)_3$ and precipitate out of the solution.

EXPERIMENTAL

All melting points were uncorrected. Ultraviolet (UV)–visible absorption spectra were measured in toluene on a Shimadzu UV-2200 spectrophotometer. NMR spectra were recorded on a Jeol JNM A-500 spectrometer (^{1}H, 500 MHz) at room temperature. All samples were freshly prepared (ca. 5 mg) and dissolved in dimethylsulfoxide (DMSO-d_6) or $CDCl_3$ (0.5 ml). Purifications with column chromatography were carried out using silica gel and toluene.

Protection of the Hydroxyl Group in 4

Acetylation

Acetic anhydride (2.8 ml, 30 mmol) was added to a suspension of 3.90 g (20.0 mmol) of **4** in 9.7 ml of pyridine. The mixture was stirred for 1 h and added to 200 g of cold water. It was neutralized with 20% sodium hydroxide solution; the resultant precipitate was filtered off and dried. It was crystallized from benzene to give 3.58 g (yield 75.1%) of gold yellow plates of 3-acethoxyphenalen-1-one (**5**): mp 120–121°C (ref. 7, 124°C); λ_{max} (toluene) = 356 nm. EI-mass calc. for $C_{15}H_{10}O_3$: $[M]^+ =$ 238.06; found: $m/z = 238$. ^1H NMR (DMSO-d_6) δ (ppm) = 8.50 (dd, $J = 7.34$, 1.28, 1H), 8.49 (dd, $J = 8.07$, 1.28, 1H), 8.35 (dd, $J = 8.25$, 0.92, 1H), 8.15 (dd, $J = 7.24$, 1.01, 1H), 7.92 (dd, $J = 7.98$, 0.55, 1H), 7.78 (dd, $J = 8.25$, 0.92, 1H), 6.60 (s, 1H), 2.49 (s, 3H).

The synthesis was also carried out by the method reported by Eistert et al.[7] Compound **4** (9.80 g) was converted into sodium salt by sodium methoxide, and acetylation was performed by acetyl chloride. Yield 4.78 g, 43.8%.

Benzoylation

By a method similar to that described in Ref. 7, sodium salt prepared from 9.80 g of **4** was dispersed into 100 ml of ether, and to this was added 5.8 ml (50 mmol) of benzoyl chloride. The mixture was stirred for 1 h at room temperature, and the precipitate was filtered off and dried. It was crystallized from benzene to give 12.06 g (yield 83.5%) of gold yellow crystals of 3-benzoyloxyphenalen-1-one (**7**). Calc. for $C_{20}H_{12}O_3$: C, 79.99%; H, 4.03%. Found: C, 79.58%; H, 4.00%. Mp 144–146°C; λ_{max} (toluene) = 356 nm. EI–mass calc. for $C_{20}H_{12}O_3$: $[M]^+ = 300.08$. Found: $m/z = 300$. ^1H NMR (DMSO-d_6) δ (ppm) = 8.54 (dd, $J = 7.31$, 1.26, 1H), 8.52 (dd, $J = 8.09$, 1.26, 1H), 8.37 (dd, $J = 8.25$, 0.83, 1H), 8.28 (dd, $J = 8.39$, 1.33, 2H), 8.13 (dd, $J = 7.31$, 0.94, 1H), 7.95 (dd, $J = 8.05$, 0.69, 1H), 7.84 (tt, $J = 7.45$, 1.54, 1H), 7.78 (dd, $J = 8.23$, 0.87, 1H), 7.69 (t, $J = 7.61$, 2H), 6.81 (s, 1H).

Tosylation

By the method similar to that described previously, application of 9.53 g of p-tosyl chloride gave 4.67 g of 3-(p-tosyloxy)phenalen-1-one (**7**). Calc. for $C_{20}H_{14}O_4S$: C, 68.56%; H, 4.03%; S, 9.15%. Found: C, 68.53%; H, 3.94%; S, 9.12%. Orange brown crystals, mp 148–150°C; λ_{max} (toluene) = 358 nm. EI–mass calc. for $C_{20}H_{14}O_4S$: $[M]^+ = 350.06$. Found: $m/z = 350$. NMR (DMSO-d_6) δ (ppm) = 8.47 (dd, $J = 8.12$, 1.20, 1H), 8.46 (dd, $J = 7.36$, 1.31, 1H), 8.34 (dd, $J = 8.32$, 0.99, 1H), 8.01 (dd, $J = 7.38$, 0.96, 1H), 8.00 (d, $J = 8.53$, 2H), 7.90 (t, $J = 7.73$, 1H), 7.74 (dd, $J = 8.25$, 0.87, 1H), 7.51 (dd, $J = 8.60$, 0.57, 2H), 6.41 (s, 1H), 2.41 (s, 3H).

Phenalen-1-one (2)[11]

A mixture of 1.20 g (5.0 mmol) of **5**, 1.86 g (5.0 mmol) of lanthanum chloride heptahydrate, 25 ml of methanol, and 25 ml of tetrahydrofuran was stirred for 30 min at room temperature, and to this was added 0.38 g (10 mmol) of sodium tetrahydroborate $NaBH_4$ in several portions. The reaction mixture was stirred further for 1 h and evaporated to dryness. The residue was stirred in 30 g of conc. sulfuric acid for 1 h. This solution was diluted with 60 g of ice water, and after being neutralized with 20% sodium hydroxide solution, 100 ml of toluene were added several times to extract the toluene-soluble part. The toluene extract was dried with anhydrous sodium sulfate and evaporated to dryness. The residue was purified with column chromatography.

The first eluent gave a small amount (yield: 1%) of yellow leaflet crystals of **3**: mp 378–380°C [Ref. 6 374–375°C, Ref. 4 375–376°C, Ref. 12 380–385°C (decomp)]; λ_{max} (toluene) = 441, 414 nm. EI–mass calc. for $C_{26}H_{14}$: $[M]^+ = 326.11$. Found: $m/z = 326$. NMR (DMSO-d_6) δ (ppm) = 9.49 (d, $J = 9.5$, 4H), 8.56 (d, $J = 9.2$, 4H), 8.51 (d, $J = 7.5$, 4H), 8.25 (t, $J = 7.6$, 2H).

The second eluent gave a smaller amount (yield: <1%) of light-yellow plate crystals of 2,3-dihydrophenalen-1-one: mp 79–80°C (Ref. 13 80–81°C); λ_{max} (toluene) = 320 nm; NMR ($CDCl_3$) δ (ppm) = 8.18 (dd, $J = 7.2$, 1.2, 1H), 8.07 (dd, $J = 8.2$, 1.2, 1H), 7.78 (dd, $J = 7.2$, 1.7, 1H), 7.59 (dd, $J = 8.1$, 7.2, 1H), 7.48 (t, $J = 7.3$, 1H), 7.45 (dd, $J = 7.7$, 1.6, 1H), 3.43 (t, $J = 7.1$, 2H), 2.97 (t, $J = 7.2$, 2H).

The third eluent gave a small amount of yellow needle-like crystals of an unknown material: mp 299–300°C (decomp); λ_{max} (toluene) = 411, 351 nm.

The fourth eluent gave 0.204 g (yield: 45.3%) of yellow plate crystals of **2**: mp 155–156°C (Ref. 6 156°C); λ_{max} (toluene) = 382, 357 nm. EI–mass calc. for $C_{13}H_8O$: $[M]^+ = 180.06$. Found: $m/z = 180$. NMR (DMSO-d_6 at 90°C) δ (ppm) = 8.47 (d, $J = 7.3$, 1H), 8.39 (d, $J = 7.9$, 1H), 8.19 (d, $J = 7.6$, 1H), 7.96 (d, $J = 9.8$, 1H), 7.96 (d, $J = 8.0$, 1H), 7.86 (t, $J = 7.6$, 1H), 7.70 (t, $J = 7.8$, 1H), 6.65 (d, $J = 9.8$, 1H).

Results shown in Figs. 1 and 3 were obtained by the method similar to that described but using $CeCl_3$ instead of $LaCl_3$. The use of other salts and other esters gave the results shown in Fig. 2 and Table 1, and Fig. 4 and Table 2.

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