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# Hard Acid and Soft Nucleophile System. VII.$^{1)}$ A Convenient Reduction of Functionalized Polyarenes to Parent Polyarenes

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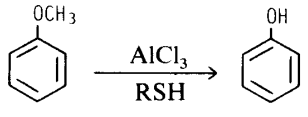
Oxygen functions and halogens at the *peri*-carbon atom in polyarenes were reductively removed with the $AlCl_3$–EtSH reagent system to afford the parent polyarenes in high yield. The reaction consists of two steps of reactions involving displacement of a functionality with an alkylthio group followed by reductive removal of the introduced alkylthio moiety. A radical cation induced mechanism for the latter process is proposed on the basis of several observations.

**Keywords**——hard acid; soft nucleophile; aromatic sulfide; ethanethiol; aluminum chloride; naphthalene; phenanthrene; anthracene; radical cation; reductive displacement

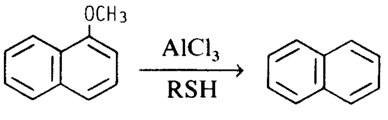
Reported methods for reductive deoxygenation of oxygenated polyarenes can be roughly divided into two classes, one of which involves direct reduction of the substrate. However, it usually requires drastic conditions such as heating at 550 °C with zinc powder$^{2)}$ or refluxing in acetic acid with hydroiodic acid.$^{3)}$ Another method consists of reduction after derivatization of an oxygen function into a group more amenable to reductive conditions. Such derivatives include 2,4-dinitrophenyl ethers,$^{4)}$ thiols *via* *S*-aryldimethylthiocarbamate,$^{5)}$ methanesulfonates,$^{6)}$ *O*-aryl-*N*,*N*-dialkylisoureas,$^{7)}$ potassium aryl sulfates,$^{8)}$ and diethylphosphates.$^{9)}$ Obviously, multistep operations are necessary for the latter methods. Here, we describe a new reagent system involving $AlCl_3$–EtSH which has overcome those shortcomings. This reagent system can be utilized for the reductive displacement of halogen and sulfur functions as well.

We have developed several combination systems of a hard acid and a soft nucleophile, which are practically useful for the cleavage of various carbon–oxygen bonds,$^{10)}$ of activated carbon–carbon double bonds,$^{11)}$ of a certain type of carbon–carbon single bond,$^{12)}$ and of aromatic carbon–halogen bonds,$^{13)}$ for reductive displacement of a nitro group with hydrogen,$^{12)}$ and for preparation of alkylthiopolyarenes.$^{1)}$ Among the combination systems reported, an $AlCl_3$ and thiol system has been shown to be a powerful agent for demethylation of methyl ethers of aliphatic alcohols and phenols, which proceeds through an activated $S_N2$ mechanism.$^{14)}$ Thus, anisole afforded an excellent yield of phenol, resulting from the cleavage of an alkyl carbon–oxygen bond (Eq. (1)).$^{10)}$ On the other hand, aromatic carbon–oxygen bond cleavage occurred when 1-methoxynaphthalene reacted with this system (Eq. (2)). To understand this unusual reaction and hopefully to extend the scope of this reaction, a number of substrates were treated with this system. The results are listed in Table I.

As ethanethiol was most effective among the thiols tested (runs 1—3), the $AlCl_3$–EtSH system was chosen for subsequent experiments. Relative reactivity among the basic skeletons increases in the order of naphthalene < phenanthrene < anthracene. Hydroxyl, methoxyl, ethoxyl, and phenoxyl groups were easily replaced by hydrogen with this system. 9-Anthrol did not afford the desired product because complexation of $AlCl_3$ removed the substrate from the reaction medium as a solid material (run 16). Reductive removal of halogen took place in



(1)



(2)

Table I. Reduction of Functionalized Polyarenes

$$\text{Ar}-\text{Y}\xrightarrow[\text{in CH}_2\text{Cl}_2,\ \text{N}_2]{\text{AlCl}_3-\text{RSH (5 mol eq)}}\text{Ar}-\text{H}$$

| Run | Substrate | | Thiol | $AlCl_3$ (mol eq) | Temp. (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|---|
| | Ar | Y | | | | | |
| 1 | 1-Naphthyl | OMe | PhSH | 1.5 | r.t | 24 | 72[a] |
| 2 | 1-Naphthyl | OMe | Iso-PrSH | 2.5 | r.t | 72 | 80[a] |
| 3 | 1-Naphthyl | OMe | EtSH | 2.5 | r.t | 4.5 | 87[b] |
| 4 | 1-Naphthyl | OEt | EtSH | 2.5 | r.t | 5 | 83[a] |
| 5 | 1-Naphthyl | OPh | EtSH | 2.5 | r.t | 4 | 88[a] |
| 6 | 1-Naphthyl | OH | EtSH | 2.5 | r.t | 5 | 76[a] |
| 7 | 1-Naphthyl | F | EtSH | 2.5 | r.t | 7 | 87[a] |
| 8 | 1-Naphthyl | Cl | EtSH | 2.5 | r.t | 7 | 57[a] |
| 9 | 1-Naphthyl | Br | EtSH | 2.5 | r.t | 8 | 67[a] |
| 10 | 9-Phenathryl | OMe | EtSH | 2.5 | r.t | 2 | 100[a] |
| 11 | 9-Phenathryl | OEt | EtSH | 2.5 | r.t | 2.5 | 96[a] |
| 12 | 9-Phenathryl | OH | EtSH | 2.5 | r.t | 6 | 82[a] |
| 13 | 9-Phenathryl | Br | EtSH | 1.5 | r.t | 6 | 97[b] |
| 14 | 9-Anthryl | OMe | EtSH | 2.5 | 0 | 0.5 | 84[c] |
| 15 | 9-Anthryl | OEt | EtSH | 2.5 | 0 | 0.5 | 85[c] |
| 16 | 9-Anthryl | OH[d] | EtSH | 2.5 | 0 | 0.5 | 0 |
| 17 | 9-Anthryl | Br | EtSH | 2.5 | 0 | 0.5 | 79[c] |

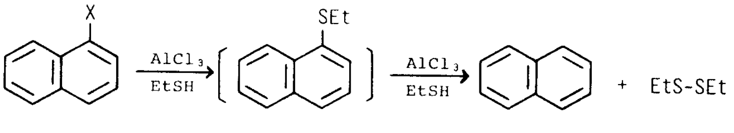
[a] Yields were estimated on the basis of NMR spectra of the mixture of parent aromatics and diethyldisulfide, which could not be separated by $SiO_2$ column chromatography, unless otherwise stated.

[b] The disulfide was removed by a treatment of the mixture with $NaClO_4$.

[c] Isolated yield.

[d] 9-Anthrone was used as an 9-anthrol equivalent.

some cases (runs 7—9, 13, 17). It is worthy of note that defluorination of 1-fluoronaphthalene proceeded in high product yield (run 7). 2-Substituted naphthalenes did not afford naphthalene but gave 2-ethylthionaphthalene.[1] This fact and the results in Table I suggest that the reductive displacement is selective at the *peri*-carbon atoms in polyarenes.



(3)

This defunctionalization involves a sulfide as an intermediate which can be trapped under milder reaction conditions.[1] Thus, the overall sequence of this one-pot reaction actually consists of displacement of a given function by sulfide followed by reductive removal of the alkylthio moiety (Eq. (3)). As the mechanism for the first step has been discussed in detail,[1] our attention will be focused on the latter step. In order to identify general features of this desulfurization reaction, three alkylthiopolyarenes were treated under various conditions; the results are listed in Table II. An inspection of Table II reveals the following facts.

1. Ethanethiol is indispensable (run 1).
2. $AlCl_3$ acts as a catalyst (runs 2 and 3).
3. The reaction rate is remarkably lowered without dichloromethane as a cosolvent (runs 4 and 5).
4. A strong Brønsted acid can be used in place of $AlCl_3$ (run 6).
5. A bulkier alkyl group in the thiol seems to retard the rate (compare run 4 with 7.)
6. 9-Ethylthiophenanthrene is more reactive than 1-ethylthionaphthalene under comparable conditions (runs 4 and 9).
7. This reductive displacement is specific at the *peri*-carbon atoms in polyarenes.
8. Thiols cannot be replaced by diethylsulfide as a soft nucleophile (run 10).

Substantial amounts of disulfides were obtained in every case where the reaction proceeded to afford the parent polyarenes. As this reaction is catalyzed by both a strong Lewis acid and a strong Brønstead acid, the ionic mechanism shown in Chart 1 may be considered to be a likely one at first glance.

TABLE II. Reduction of Alkylthiopolyarenes with Hard Acid–Soft Nucleophile

$$\mathrm{Ar-SR}\xrightarrow[\text{in } \mathrm{CH_2Cl_2,\ N_2}, \text{ at room temp.}]{\text{Acid}-\text{Nucleophile (5 eq)}}\mathrm{Ar-H}$$

| Run | Substrate | | Acid (mol eq) | Nucleophile | Time[a] (h) | Yield[b] (%) | Recovery of substrate |
|---|---|---|---|---|---|---|---|
| | Ar | R | | | | | |
| 1 | 1-Naphthyl | Et | $AlCl_3$ (2.4) | Non | 2 | 0 | 92 |
| 2 | 1-Naphthyl | Et | $AlCl_3$ (0.4) | EtSH | 48 | 82 | — |
| 3 | 1-Naphthyl | Et | $AlCl_3$ (0.8) | EtSH | 9 | 82 | — |
| 4 | 1-Naphthyl | Et | $AlCl_3$ (1.5) | EtSH | 5.5 | 89 | — |
| 5 | 1-Naphthyl | Et | $AlCl_3$ (1.5)[c] | EtSH | 48 | 86 | — |
| 6 | 1-Naphthyl | Et | $CF_3SO_3H$ (1.5) | EtSH | 11 | 84 | — |
| 7 | 1-Naphthyl | Iso-Pr | $AlCl_3$ (1.5) | EtSH | 10 | 91[d] | — |
| 8 | 2-Naphthyl | Et | $AlCl_3$ (1.5) | EtSH | 24 | 1 | 65 |
| 9 | 9-Phenathryl | Et | $AlCl_3$ (1.5) | EtSH | 2.5 | 100 | — |
| 10 | 9-Phenathryl | Et | $AlCl_3$ (1.5) | Et–S–Et | 5 | 0 | 93 |

*a*) The time required for complete disappearance of the starting material was checked by TLC.

*b*) Yields were estimated on the basis of NMR spectra of the mixture of parent aromatics and diethyldisulfide, which could not be separated by $SiO_2$ column chromatography.

*c*) The reaction was carried out in ethanethiol (2.4 ml) without $CH_2Cl_2$.

*d*) Diethyldisulfide (49%) and ethylisopropyldisulfide (19%) were observed in the NMR spectrum.

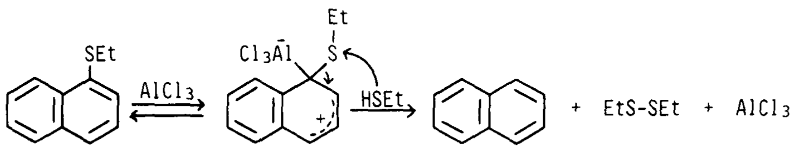
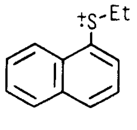
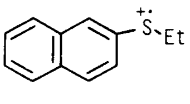


Chart 1

However, the remarkable change in the rate depending upon the solvent and the ineffectiveness of diethylsulfide as a nucleophile cannot be well explained by the ionic mechanism. Moreover, the most probable position in 1-ethylthionaphthalene to be attacked by an acid should be C(4) rather than the *ipso*-carbon. It has been reported that $AlCl_3$ can act as a one-electron oxidant, the oxidation potential of which corresponds to a first ionization potential of *ca.* 8 eV.[15)] Alkyl aryl sulfides are known to have first ionization potential below 8 eV.[16)] These facts suggest the intervention of a radical cation. Addition of $AlCl_3$ to a solution of 1-ethylthionaphthalene in anhydrous dichloromethane furnished a purple green solution. Formation of a stable radical cation **1a**[17)] in the solution was proved by the electron spin resonance (ESR) spectrum ($g=2.0071$). Naphthalene was obtained in 92% yield 6 h after the addition of EtSH to this solution. It can, therefore, reasonably be concluded that the radical cation **1a** is an intermediate species in this reductive process. The same radical species **1a** was detected when triflic acid was used in place of $AlCl_3$.



**1a**



**2**

Surprisingly, a stable radical species ($g=2.0072$) was detected by ESR when 2-ethylthionaphthalene was treated with $AlCl_3$ under the same conditions as for 1-ethylthionaphthalene. However, the coupling pattern of the signal was at variance with that of the cation radical **2**. The intensity of the signal gradually increased and was sustained even after 150 h. These facts indicated that the radical species observed by ESR did not originate from 2-ethylthionaphthalene itself but from a degradation product.

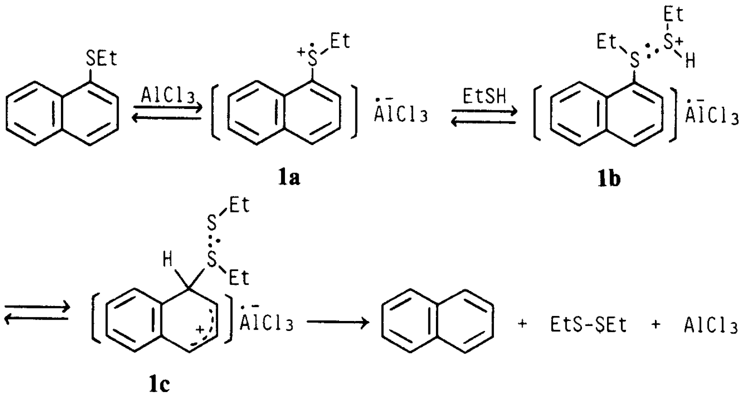
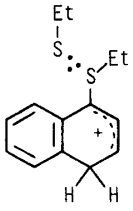
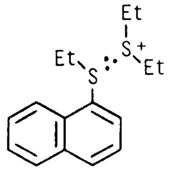


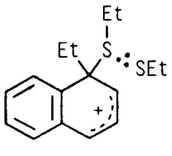
Chart 2



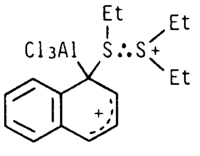
**3**



**4**



**5**



**6**

The sulfur radical cation has been reported to show a strong tendency to stabilize by coordination with a free electron pair from another sulfur atom, which forms a sulfur–sulfur bond involving three electrons.[18,19)] Thus, the radical cation **1a** coordinates with EtSH in the reaction media to provide the three-electron bonded species **1b**. Prototropy from **1b** may afford the cationic species **1c**, in which unfavorable steric interaction between the bulky substituent at C(1) and the hydrogen atom at the *peri*-carbon is eliminated because of rehybridization of orbitals in C(1) from $sp^2$ to $sp^3$. The same reasoning excludes an alternative species **3** resulting from the prototropy to C(4), because C(1) in **3** still possesses $sp^2$ hydridized orbitals. Transfer of the electron pair in the C–S bond in **1c** into the ring assisted by one-electron transfer from $\mathrm{\bar{A}lCl_3}$ to **1c** gives rise to naphthalene as shown in Chart 2. The overall mechanism can reasonably explain all of the observations including the points which cannot be explained by the ionic mechanism shown in Chart 1. The sulfur radical cations have been reported to have long lifetimes in aprotic solvents. In particular, dichloromethane is the most suitable solvent for one-electron oxidation of sulfides using $AlCl_3$,[20] which explains a dramatic change in rate between runs 4 and 5 in Table II. In the three electron-bonded species **4**, which is expected to be produced in the reaction medium when diethylsulfide is used in place of EtSH, rearrangement of the ethyl group affording **5** is highly inaccessible compared with the process **1b** to **1c**. The alternative candidate **6** for further transformations is also unlikely because it has an unstable dicationic structure. Thus, the reaction may be blocked in the step **1b** to **1c**, when EtSH is replaced by diethylsulfide. Although the possibility of the ionic mechanism shown in Chart 1 cannot be completely excluded, available data support the radical cation mechanism.

In conclusion, the $AlCl_3$–EtSH system can convert polyarenes possessing various functional groups at the *peri*-carbon atom into the parent polyarenes. The practical utility of this procedure arises from the mild conditions, one-pot reaction, and high yield. The reductive displacement under acidic conditions and chemoselectivity at the *peri*-carbon atom in polyarenes are characteristic features of this reaction.

## Experimental

**Materials**——$\alpha$-Phenoxynaphthalene was prepared by the Ullmann reaction.[21] 1-Ethylthionaphthalene, 1-isopropylthionaphthalene, 2-ethylthionaphthalene, and 9-ethylthiophenanthrene were prepared from the corresponding methoxyl derivatives and the corresponding alkanethiol.[1] Other materials were commercially available.

**General Procedure for Reduction of Functionalized Polyarenes into Parent Polyarenes**——The functionalized polyarene (1 mmol) was added to a stirred solution of $AlCl_3$ (purified by sublimation) in thiol (purified by distillation with $CaH_2$) and 2 ml of dichloromethane (purified by distillation with $CaH_2$) under the conditions described in Table I. The reaction was monitored by thin-layer chromatography ((TLC), $AlCl_3$ was quenched with methanol in a capillary). The reaction mixture was poured into water to which dilute HCl was added, and the mixture was extracted with dichloromethane. The organic layer was shaken with brine, dried by ($Na_2SO_4$), filtered, and then evaporated to leave a crude material, which was purified by chromatography over a silica gel column. This chromatography provided pure anthracene, but the mixtures of naphthalene or phenanthrene and the corresponding disulfide were not separated. On runs 3 and 13 in Table I, the mixture was added to a solution of sodium periodate (2.5 mmol) in 20 ml of methanol–water (1 : 1). After being stirred for 2 h at room temperature, the reaction mixture was poured into water and extracted with dichloromethane. The usual work-up of the organic layer gave a crude product which was chromatographed on an $SiO_2$ column to give pure naphthalene and phenanthrene, respectively. All polyarenes were identified by comparison of nuclear magnetic resonance (NMR) spectra and gas-liquid chromatography (GLC) with those of corresponding authentic samples (commercially available). The yields of polyarenes on runs 1—12 in Table I (except for run 3) were estimated on the basis of integration of the NMR spectra (JEOL JNM-FX 100 or JEOL JNM-PMX 60 spectrometers).

**General Procedure for Reduction of Alkylpolyarenyl Sulfides**——A substrate (1 mmol) was added to a stirred solution of a hard acid ($AlCl_3$, purified by sublimation; triflic acid, purified by distillation) in a soft nucleophile (*ca.* 5 mol eq; thiols or diethylsulfide was purified by distillation) and dichloromethane (2 ml; shaken with water to remove a trace of methanol followed by distillation with $CaH_2$) at 0 °C under nitrogen. Then, the reaction mixture was stirred at room temperature. After the reaction time described in Table II, the reaction mixture was treated as usual to give crude products, which were chromatographed over a silica gel column to afford a mixture of parent polyarene and the corresponding disulfide. The yields of parent polyarenes (shown in Table II) were estimated on the basis of the integration of the NMR spectra of the mixtures.

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