

A CONVENIENT REDUCTION OF FUNCTIONALIZED POLYCYCLIC AROMATICS INTO PARENT HYDROCARBONS

Manabu Node, Kiyoharu Nishide, Keiichiro Ohta, and Eiichi Fujita*

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu, 611 Japan

Summary: Polycyclic aromatics with various functional group (e.g. OH, OR, SR, and halogen) were easily defunctionalized by aluminum chloride and ethanethiol to give parent aromatics in high yields under mild conditions. This reaction proceeds through sulfide as the intermediate, hence it is also useful for the synthesis of sulfides of polycyclic aromatics.

We have reported that the combination system of a hard acid and a soft nucleophile is an excellent reagent for cleavage of various carbon-oxygen bonds.¹ In the course of our investigation on the deprotection of alkyl ethers of phenols with the aluminum chloride and ethanethiol system, alkyl polyarenyl ethers were found to be subject to unexpected reductive cleavage of phenolic carbon-oxygen bond.² For instance, 1-methoxynaphthalene was treated with aluminum chloride (2.5 mol equiv.) and ethanethiol (ca. 5 mol equiv.) at room temperature for 4.5 h to afford naphthalene in 86.8% yield. Then, several 1-substituted naphthalenes, 9-substituted anthracenes, and 9-substituted phenanthrenes shown in Table I were treated as well. As the result, not only alkoxy groups but phenoxy, hydroxy, alkylthio and halo groups were also defunctionalized effectively to give the parent aromatics in high yields (see Table I).

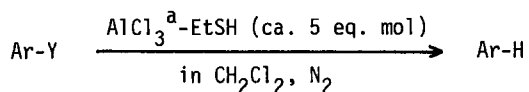
The most reactive substrate among polycyclic aromatics was anthracene derivatives (see entries 13~15); phenanthrene derivatives gave the highest yields of the products (see entries 9~12). Reactive substrates in the naphthalene series were only 1-naphthyl derivatives (see entries 1~8).

In order to confirm the intermediate in the defunctionalization reaction, we tried the product analysis at the initial stage. For this purpose, the milder reaction conditions (the less amount of aluminum chloride and the lower temperature) than those in the reactions shown in Table I were used. The result is summarized in Table II. The sulfides were yielded expectedly in the reactions of entries 1 to 5 in the Table II. However, the reaction of 9-bromoanthracene was too fast to trap its sulfide, when aluminum chloride was used as Lewis

acid. Hence, zinc chloride, a weaker Lewis acid, was used in this case (entry 6). From the results shown in entries 1-6 in Table II and the fact that the sulfides were reduced to the corresponding polycyclic aromatics (see entries 5, 6, and 11 in Table I), it was established that sulfide was an intermediate of this defunctionalization.

The reduction of the intermediate sulfide **1** into parent hydrocarbon was assumed to proceed through the steps shown in the Scheme 1, in which the defunctionalization of 1-naphthalene

Table I Defunctionalization of Polycyclic Aromatics



Entry	Substrate		Conditions			Yield ^b of ArH (%)
	Ar	Y	mol eq. of AlCl ₃	Temp.	Time (h)	
1	1-naphthyl	OMe	2.5	r.t.	4.5	86.8
2	"	OEt	2.5	r.t.	5	82.7
3	"	OPh	2.5	r.t.	4	88.2
4	"	OH	2.5	r.t.	5	76.3
5	"	SEt	1.5	r.t.	5.5	89.2
6	"	S	1.5	r.t.	10	90.9
7	"	F	2.5	r.t.	7	87.3
8	"	Br	2.5	r.t.	8	66.9
9	9-phenanthryl	OMe	2.5	r.t.	2	99.7
10	"	OEt	2.5	r.t.	2.5	95.5
11	"	SEt	1.5	r.t.	2.5	100
12	"	Br	1.5	r.t.	6	96.5
13	9-anthryl	OMe	2.4	0°C	0.5	83.6 ^c
14	"	OEt	2.6	0°C	0.5	84.5 ^c
15	"	Br	2.5	0°C	0.5	78.6 ^c

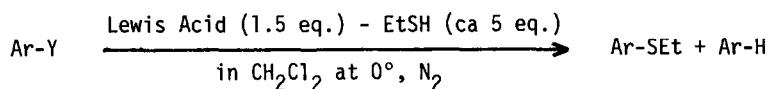
a Purified reagent by sublimation was used.

b Yields are estimated on the basis of NMR spectra of the mixture of reduced aromatics and diethyldisulfide, which could not be separated by SiO₂ column chromatography, unless otherwise stated. The disulfide could be removed by treatment of the mixture with NaIO₄.

c Isolated yield.

derivative is shown, on the basis of the following facts: (1) formation of diethyl disulfide was observed in all defunctionalization reaction, but none of the disulfide was observed at the initial sulfide preparation stage; (2) the final product of the reactions with 2-naphthyl

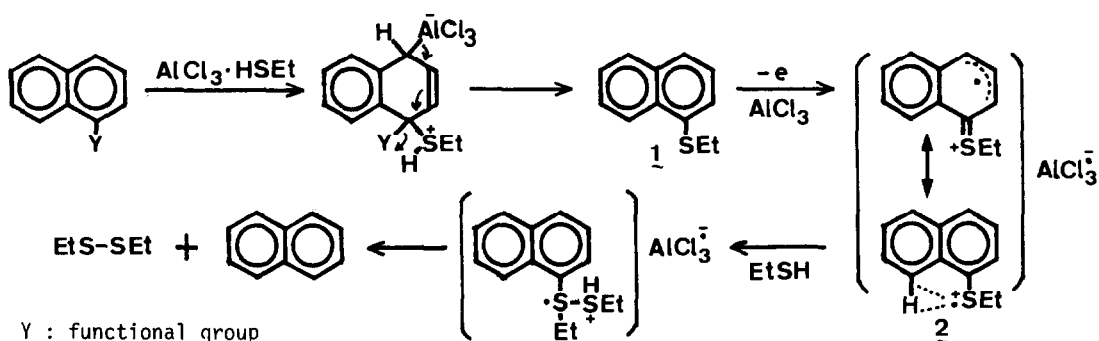
Table II Preparation of Ethyl Polycyclic Aromatic Sulfides



Entry	Substrate		Conditions		Yield ^a of Products	
	Ar	Y	Lewis Acid	Time	Ar-SEt ^b (%)	Ar-H (%)
1	1-naphthyl	OMe	AlCl ₃	40 min	92.0	—
2	"	OPh	"	"	92.0	—
3	"	OH	"	1 h	86.2	—
4	"	F	"	"	79.2	—
5	9-phenanthryl	Br	"	30 min	48.5	50.8
6	9-anthryl	Br	ZnCl ₂	2 h	47.1	14.4
7	2-naphthyl	OEt	AlCl ₃	25 min	93.6	—
8	"	OH	"	20 min	93.4	—
9	"	Br	"	10 h	84.8	—

a Isolated yield. b The ethyl thio substituent is located in the same position as that of the Y group in the substrate.

Scheme 1 The Possible Mechanism of the Defunctionalization with AlCl₃-EtSH



derivatives was ethyl 2-naphthyl sulfide (entries 7-9 in Table II); its reduction into parent hydrocarbon occurred scarcely; (3) it has been well known that aluminum chloride acts as one electron oxidizing agent³ except for action as a Lewis acid.

The ease of one electron transfer from sulfide 1 must be attributed to the radical cation 2 stabilized highly by a hydrogen atom or a σ -bond at the peri-position of naphthalene. Thus, ethyl 1-naphthyl sulfide was subject to reduction to give naphthalene. On the other hand, ethyl 2-naphthyl sulfide cannot form such a stabilized radical cation as 2, hence the further reduction from sulfide may not occur.

This method offers distinct advantages over recently described reductive defunctionalization procedures.⁴ Our reaction gives a high yield of the product under mild conditions and has a wide utility for several functional groups on polycyclic aromatics. The result shown in Table II provides another utility of the Lewis acid and thiol system for preparation of alkyl polyarenyl sulfides.

References and Notes

- 1) M. Node, H. Hori, and E. Fujita, *J. C. S. Perkin I*, 2237 (1976); M. Node, K. Nishide, M. Sai, and E. Fujita, *Tetrahedron Letters*, 5211 (1978); M. Node, K. Nishide, M. Sai, K. Ichikawa, K. Fuji, and E. Fujita, *Chemistry Letters*, 97 (1979); K. Fuji, K. Ichikawa, M. Node, and E. Fujita, *J. Org. Chem.*, 44, 1661 (1979); M. Node, K. Nishide, K. Fuji, and E. Fujita, *J. Org. Chem.*, 45, 4275 (1980); K. Fuji, T. Kawabata, and E. Fujita, *Chem. Pharm. Bull.*, 28, 3662 (1980); M. Node, K. Nishide, M. Sai, K. Fuji and E. Fujita, *J. Org. Chem.*, 46, 1991 (1981); M. Node, K. Nishide, M. Ochiai, K. Fuji, and E. Fujita, *J. Org. Chem.*, in press.
- 2) In the use of Lewis acid and sulfide system, alkyl polyarenyl ether causes the normal C-O bond cleavage to give the corresponding phenol.
- 3) For example: H. Bock and W. Kaim, *J. Am. Chem. Soc.*, 102, 4429 (1980).
- 4) Ar-Br \rightarrow Ar-H: Cf. e.g. R. G. R. Bacon and S. C. Rennison, *J. Chem. Soc. (c)*, 308 (1969); B. Loubinoux, R. Vanderesse, and P. Caubere, *Tetrahedron Letters*, 3951 (1977).
Ar-OR \rightarrow Ar-H: W. H. Pirkle and J. L. Zabriskie, *J. Org. Chem.*, 29, 3124 (1964); M. Konieczny and R. G. Harvey, *J. Org. Chem.*, 44, 4813 (1979).

(Received in Japan 6 November 1981)