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Application of Lanthanoids to Organic Chemistry. Direct Alkoxylation of Anthracene[†]

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Direct alkoxylation of anthracene with some lower alcohols and ethylene glycol monoalkyl ethers, or monoacetate were carried out in the presence of cerium(IV)tetrakis(trifluoro acetate), and expected alkoxylated anthracene derivatives were obtained.

Considerable attention has been focused on the usefulness of lanthanoid compounds in synthetic chemistry.1) The author has developed a practical method of halogenation of some aromatic compounds with CAN.2) It should be emphasized that in this reaction a halide anion is employed as a reagent for net aromatic substitution. Although there are several examples for the reaction of this type among biological systems (e.g. halogenation with chloroperoxidase3)), it is quite common to use a positive halogen in artificial halogenation of aromatic ring.

The procedure was further extended to substitution of aromatic hydrogen by an alkoxyl group directly. Here again, there is no equivalent example for direct alkoxylation of aromatic compounds except for an electrochemical procedure.4) Now, the author wishes to report a preliminary result of this brand-new alkoxylation.

Cerium(IV) tetrakis(trifluoroacetate) (CTFA), which has less nucleophilic ligand than ammonium hexanitratocerate(IV) (CAN) has, is better reagent than CAN for the present purpose.5)

Ho and his coworkers reported that anthracene was oxidized into anthraquinone in the presence of CAN in tetrahydrofurane.6) The author investigated

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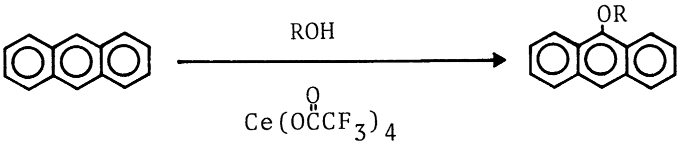
[†] This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

the reaction in methanol, and obtained the same results. However, when CTFA was used as a cerium salt in place of CAN, the yield of anthraquinone was lowered dramatically, and alkoxyanthracene was yielded.



The following procedure is typical: into a suspension of 4.0 mmol of anthracene in 30 ml alcohol was added a solution of 8.0 mmol of CTFA in 90 ml of alcohol. The mixture was stirred for prescribed time interval at 25 °C or 80 °C under nitrogen atmosphere, in the dark to avoid the decomposition of CTFA. After normal work-up, the isolated product was identified by usual methods. Some representative results are listed in Tables 1, 2, and 3. Several minor products were detected in VPC in addtion to the ether and anthraquinone, but their structures were not identified.

Table 1 shows the results from alkoxylation of anthracene with normal alcohols (C_1-C_6). In all cases, the alkoxylation takes place at meso-position of anthracene selectively. The yield of alkoxylated anthracene is reduced with increase in the length of alkyl chain, while the amount of anthraquinone, a side product increases. Trahanovsky et al. reported that oxidation with ceric ion

Table 1. Alkoxylation of Anthracene with n-Alcohols[a)]

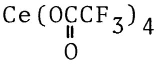
ROH	Temp °C	Time h	Recov.[b)] %	Yield/%[b,c)] ArOR	 Anthraquinone
CH_3OH	25	72	11	75	5
C_2H_5OH	25	72	37	36	4
C_3H_7OH	25	72	16	50	6
C_4H_9OH	80	17	40	33	15
$C_5H_{11}OH$	80	17	55	15	29
$C_5H_{11}OH$[d)]	80	17	50	11	24
$C_6H_{13}OH$	80	17	60	16	22
$C_6H_{13}OH$[d)]	80	17	52	10	24

a) The experiments were carried out in 1/40 scale of that described in the text. b) Conversions and yields were determined by VPC. c) Yields are based on anthracene used. d) DMF (ROH: 2.0 mmol).

Table 2. Alkoxylation of Anthracene with Isomeric Butanols[a)]

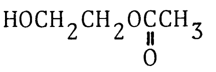
BuOH (mmol)	Solvent	Recov./%	Yield/%[b,c)] ArOBu	Anthraquinone
$CH_3(CH_2)_3OH$	——[d)]	40	33	15
$CH_3(CH_2)_3OH$[e)]	——[d)]	40	31	13
$CH_3(CH_2)_3OH$ (2.0)	DMF	47	15	14
$CH_3(CH_2)_3OH$ (2.0)[f)]	DMF	53	16	24
$(CH_3)_2CHCH_2OH$	——[d)]	48	5	30
$(CH_3)_2CHCH_2OH$ (2.0)	DMF	48	13	16
$C_2H_5CH(OH)CH_3$	——[d)]	57	5	11
$C_2H_5CH(OH)CH_3$	DMF	45	8	19
$(CH_3)_3COH$	DMF	41	trace	16

a) The experiments were carried out in 1/40 scale of that described in the text. Temp: 80 °C. Time: 17 h. b) Conversions and yields were determined by VPC. c) Yields are based on anthracene used. d) The excess alcohol was used as a solvent. e) Temp: 117 °C.

f)  $Ce(O\underset{\overset{\|}{O}}{C}CF_3)_4$: 0.3 mmol.

of an alkanol with a δ-hydrogen such as pentanol, produces tetrahydrofurane derivatives.[7)] Analogous process seemed to be competiting with alkoxylation in the case of long-chain alcohols, in the present reaction.

Table 3. Alkoxylation of Anthracene with Ethylene Glycol Monoalkyl Ether[a)]

ROH	CTFA (mmol)	Recov./%[b)]	Yield/%[b,c)] ArOR	Anthraquinone
$HOCH_2CH_2OCH_3$	0.2	26	58	8
$HOCH_2CH_2OCH_3$	0.4	2	54	26
$HOCH_2CH_2OC_2H_5$	0.2	11	65	17
$HOCH_2CH_2OCH(CH_3)_2$	0.4	16	45	32
 $HOCH_2CH_2O\underset{\overset{\|}{O}}{C}CH_3$	0.4	43	30	18

a) The experiments were carried out in 1/40 scale of that described in the text. Temp: 80 °C. Time: 24 h. b) Conversions and yields were determined by VPC. c) Yields are based on anthracene used.

In order to investigate the effect of branching of alkyl chain, similar reactions were studied using butanol isomers (Table 2). As degree of branching of carbon chain increases, reactivities of the alcohols decreases, and tertiary butanol exerted no reactivity in the present reaction. Perhaps, such results might be attributed partly to the steric effect for the attack of the alcohol on anthracene.

Table 3 shows that ethylene glycol monoalkyl ethers and monoacetate are able to alkoxylate anthracene, respectively. In every case, the reaction proceeds smoothly and corresponding anthracene derivatives were obtained in 45-65% yields. However, when ethylene glycol, cyanohydrin, and halohydrins were used as reagents, satisfactory results were not obtained.

Another noteworthy fact is that the use of CTFA which is prepared freshly or stored carefully to avoid light and moisture, is favorable for the reaction.

Further extention on the scope and the study on the mechanism of this reaction, are in progress.

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