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PARTIAL OXIDATION OF ALIPHATIC SIDE CHAINS WITH CERIUM (IV)

Ludwik Syper
Department of Chemistry,
Technical University, Wrocław, Poland

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The ready availibity of aromatic compounds with a methyl substituent makes it desirable to have convenient synthetic routes from such compounds to corresponding aldehydes. The transformation from hydrocarbons to aldehydes may be accomplished directly by various oxidizing agents,but known methods are limited to the preparation of specific aldehydes. Many compounds with the methyl group joined to an aromatic nucleus cannot be converted succesfully into the corresponding aldehydes by direct methods.

In an attempt to develop a simple method of partial oxidation of the aromatic side chains, we have investigated the reaction of these compounds with cerium (IV) in acidic media. Although cerium (IV) is a powerful oxidizing agent, and is a widely used oxidant in analytical chemistry, little attention has been given to its use as an oxidant of organic compounds. Only very recently Trahanovsky and Young (1) have made interesting observation that cerium (IV) oxidizes benzyl alcohols to the corresponding aldehydes. Cerium (IV) is a particular interest as an oxidant because, unlike most other oxidants, it appears capable to effect only one-electron change.Moreover, we have expected a similarity between cerium (IV) and electrophilic reagents in its reaction with aromatic compounds, because of its large positive charge.

In our experiments we have found that cerium (IV) ion is very specific oxidant towards aromatic hydrocarbons, and oxidizes readily methyl group to aldehyde group in acidic media. The aldehyde group is never further oxidized. The reaction proceeds selectively, e.g. only one methyl group is oxidized easily to carbonyl group. The oxidation of more than one methyl group may also be achieved, but requires much more drastic conditions.

This communication deals with our experiments in benzene series. Our results are summarized in Table 1. The procedure for this reaction is as follows: To the stirred solution of organic compound (1 mM) in appropriate acid (5 ml) a solution of ceric ammonium nitrate (4 mM) in the same acid (10 ml) was added dropwise,at constant temperature,at such rate that reaction mixture was only pale yellow. When the reaction was over, the mixture was colorless. In the case of acetyltoluidines and methyl ethers of cresols the course of oxidation could not be observed, because the reaction mixture was colored. Then, the solution was cooled to room temperature,diluted with water and extracted three times with ether. Extract was dried ($MgSO_4$) and tested for aldehydes by thin-layer chromatography. From thin-layer chromatogram we have obtained informations about purity and identity of the aldehydes.In case of aldehydes listed in Table 1 only one spot was visible, when chromatogram was

TABLE 1

Aldehydes and Ketones Obtained by Oxidation of Aromatic Side Chains with Cerium (IV)

Starting compound	Reaction Conditions			Reaction Product	Yield
	Acid	Temp. °C	Time min.		
$C_6H_5CH_3$	$HClO_4$ 6N	40	80	C_6H_5CHO	92%
	HNO_3 3,5N	80	90		
o-$C_6H_4(CH_3)_2$	CH_3CO_2H 50%	100	105	o-$H_3CC_6H_4CHO$	quant.
	HCO_2H 45%	80	135		quant.
	HNO_3 3,5N	60	70		quant.
m-$C_6H_4(CH_3)_2$	CH_3CO_2H 50%	100	95	m-$H_3CC_6H_4CHO$	quant.
	HCO_2H 45%	80	135		quant.
	HNO_3 3,5N	60	75		quant.
p-$C_6H_4(CH_3)_2$	CH_3CO_2H 50%	90	90	p-$H_3CC_6H_4CHO$	quant.
	HCO_2H 45%	80	100		quant.
	HNO_3 3,5N	60	75		quant.
1,3,5-$C_6H_3(CH_3)_3$	CH_3CO_2H 50%	80	120	1,3,5-$(H_3C)_2C_6H_3CHO$	quant.
	HCO_2H 45%	60	150		quant.
o-$ClC_6H_4CH_3$	$HClO_4$ 6N	60	70	o-ClC_6H_4CHO	74%
m-$ClC_6H_4CH_3$	$HClO_4$ 6N	60	65	m-ClC_6H_4CHO	60%

TABLE 1

(Continued)

Starting compound	Reaction Conditions			Reaction Product	Yield
	Acid	Temp. °C	Time min.		
o-$O_2NC_6H_4CH_3$	$HClO_4$ 6N	80	80	o-$O_2NC_6H_4CHO$	43%
m-$O_2NC_6H_4CH_3$	HNO_3 3,5N	90	4,5hs.	m-$O_2NC_6H_4CHO$	50%
p-$O_2NC_6H_4CH_3$	$HClO_4$ 6N	80	120	p-$O_2NC_6H_4CHO$	47%
o-$AcNHC_6H_4CH_3$	CH_3CO_2H 90%	20	7hs.	o-$AcNHC_6H_4CHO$	93%
p-$AcNHC_6H_4CH_3$	CH_3CO_2H 90%	20	7hs.	p-$AcNHC_6H_4CHO$	94%
o-$H_3COC_6H_4CH_3$	CH_3CO_2H 90%	10	9,5hs.	o-$H_3COC_6H_4CHO$	63%
p-$H_3COC_6H_4CH_3$	CH_3CO_2H 90%	10	7hs.	p-$H_3COC_6H_4CHO$	quant.
m-$PhSO_2OC_6H_4CH_3$	HNO_3 6N	90	150	m-$PhSO_2OC_6H_4CHO$	quant.
p-$PhSO_2OC_6H_4CH_3$	HNO_3 6N	90	120	p-$PhSO_2OC_6H_4CHO$	quant.
$C_6H_5CH_2CH_3$	HNO_3 3,5N	70	90	$C_6H_5COCH_3$	77%
$(C_6H_5)_2CH_2$	HNO_3 3,5N	90	75	$(C_6H_5)_2CO$	76%
Indane	HNO_3 3,5N	30	90	1-Indanone	78%
Tetraline	HNO_3 3,5N	30	90	1-Tetralone	76%

sprayed with a solution of 2,4-dinitrophenylhydrazine. Upon removal of the ether by distillation, the residue containing the aldehyde was diluted with ethyl alcohol, and aldehyde was converted into the 2,4-dinitrophenylhydrazone, which was filtered off, dried and weighed. The yields of the aldehydes were calculated from amounts of 2,4-dinitrophenylhydrazones. Further support for identity of the aldehydes was obtained from melting points and nitrogen content of 2,4-dinitrophenylhydrazones. For melting point and nitrogen determination,2,4-dinitrophenylhydrazones were crystallized from appropriate solvents.

In the case of nitro-and chlorotoluenes the aldehydes were accompanied by appreciable amount of not oxidized substrate. It is well known, that ketones readily react with cerium(IV) (2 - 6) , however upon oxidation ethylbenzene, indane and tetraline we obtained corresponding aromatic 1-ketones. These ketones were not chromatographically pure, when tested as above. Pure product could be obtained,however, when 2,4-dinitrophenylhydrazone of acetophenone was crystallized once from glacial acetic acid. Other two 2,4-dinitrophenylhydrazones requiered two crystallization until correct melting points were obtained. When p-cymene was oxidized under mild conditions, e.g. in acetic or formic acid, chromatography indicated the presence of two carbonyl compounds in the reaction mixture. One of these, which was a major product was isolated as 2,4-dinitrophenylhydrazone and identified as p-methylacetophenone.Oxidation of p-cymene in perchloric or nitric acid gave the mixture containing at least four carbonyl compounds. The reaction of unsubstituted methylnaphtalenes with cerium (IV) gave only high colored substances, and no aldehydes were isolated.

It cannot be said much about the mechanism of the described reaction, but it is probable that first step is electron transfer from aromatic ring to cerium (IV) ion. Reactions of this kind are well known in inorganic chemistry.

Currently we are applying our reaction to the preparation of aldehydes, which cannot be obtained by known methods, especially in heterocycle series.

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