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HYDROXYLATION OF ANISOLES BY PHOTOOXYGENATION IN THE PRESENCE OF LEWIS ACIDS[1)]

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Irradiation of anisoles in the presence of oxygen and a Lewis acid gave hydroxyanisoles where BF_3 caused only ortho-hydroxylation and $AlCl_3$ did ortho- and para-hydroxylation.

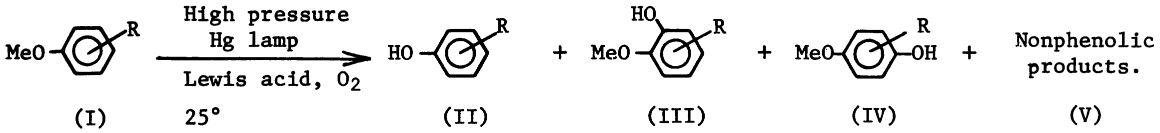
As a part of studies on electron transfer reactions of alkoxybenzenes with Lewis acids[2)], photochemical reaction of the well known Lewis acid complexes of anisoles were investigated. Anisoles reacted with oxygen by the action of light in the presence of Lewis acids to give monohydroxyanisoles besides nonphenolic products. Using BF_3 as Lewis acid, hydroxylation takes place only at ortho-position of anisoles and $AlCl_3$ gives rise to ortho- and para-hydroxylation. Neither meta-hydroxy- nor dihydroxy-anisoles were detected in each case of Lewis acids. The present results provide a new hydroxylation reaction of anisoles.

When anisoles bubbled with oxygen in benzene were irradiated by means of a high pressure mecrury lamp in the presence of Lewis acid, the solution, after 5 min. irradiation, turned to purple, then darkened gradually during 5 hr. The purple solution gave single broad e.s.r. signal but almost no appreciable product was detected in this solution. After 5-48 hr. irradiation, phenolic compounds produced were separated by extraction with 10% NaOH and isolated by preparative t.l.c. Nonphenolic products (V) remained after distilling off the recovered anisoles in the organic layer consisted of a complicated mixture, of which the main part was presumed by n.m.r. to be a mixture of polymerized quinones containing methoxy groups. The results are listed in Table 1.
The reaction rate increased with time (Exp. No. 2-4) but almost no change of the product pattern was recognized indicating that nonphenolic products (V) are not formed by degradation of hydroxyanisoles. Among the methylanisoles the ortho-derivative has the highest reactivity, and the highest ratio of hydroxylation to demethylation of methoxy group is seen for the para-derivative. The variation of ratio of Lewis acid to anisoles used did not much affect on the reaction course.. There is an evidence for the existence of an oxygen-anisole complex[3)] and other ether-oxygen complexes,[4)] and photochemical reactions of the latter to give esters are known.[5)] The present hydroxylation, however, requires all light, oxygen, and a Lewis acid. Although no evidence was available to elucidate the mechanism of this hydroxylation, the exclusive ortho-hydroxylation of anisoles with BF_3 can be rationalized by assuming a cyclic complex with anisole, BF_3, and oxygen as a transition state or an intermediatee in this reaction, in which BF_3 participates for the preferential attack of oxygen at the ortho position. A different presumable mechanism involving oxidation of aromatic boron compound intermediately formed[6)] may be ruled out because no reaction took place under nitrogen atmosphere to recover anisoles quantitatively.

It would be appropriate to take into account an intermolecular reaction to interpret ortho- and para-hydroxylation with $AlCl_3$.

As yields of the hydroxylated products in the present reactions are very poor, effects of Brønsted acids in connection with increasing the yield in the hydroxylation are burther under investigations.

Table 1

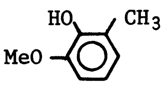


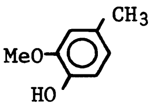
Exp. No.	(I)	Lewis acid	Lewis acid/Anisole (molar ratio)	Reaction period (hr)	Conversion rate (%)	Product (%)[b] (II)	(III)	(IV)	(V)[c]
1	R=H	BF_3[a]	0.3	48	4	trace	18	-	80
2	R=H	$AlCl_3$	1.0	55	2.7	7.9	11.0	1.5	77
3	R=H	$AlCl_3$	1.0	15	3.5	6.1	10.4	2.3	70
4	R=H	$AlCl_3$	1.0	22	5.1	8.2	9.4	2.4	73
5	R=o-Me	BF_3	0.8	48	10	9	6	-	78
6	R=m-Me	BF_3	0.8	48	6	1.8	3.6[d]	-	86
7	R=p-Me	BF_3	0.8	48	4	0.7	5.3	-	66

(a) Similar results were obtained with using BF_3 etherate complex or BF_3 itself.

(b) Hydroxyanisoles were identified with authentic samples. (i.r. and n.m.r.). The yield was determined by g.l.c. and calculated based on the converted anisoles for (II), (III), and (IV).

(c) Weight %

(d) 

2.4%, 

1.2%

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