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SELECTIVE ORTHO-WALLACH REARRANGEMENT OF 1:1 COMPLEX OF AZOXYBENZENES WITH $SbCl_5$[1]

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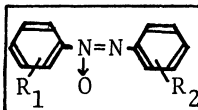
Treatment of azoxybenzenes with $SbCl_5$ gave crystalline 1:1 complexes, which on heating underwent selective ortho-Wallach rearrangement to yield exclusively o-hydroxyazobenzenes.

The Wallach rearrangement of azoxybenzenes using an acid catalyst[2] is known to give hydroxyazobenzenes, in which para-hydroxylation is largely predominant over ortho-hydroxylation, except the case of p,p'-disubstituted azoxybenzenes.[3] The formation of p-hydroxyazobenzenes has been rationalized by a mechanism involving a dicationic intermediate which is formed from a monoprotonated azoxybenzene by further protonation and subsequent dehydration,[3,4] while o-hydroxyazobenzenes are considered to be formed by an intramolecular mechanism.[5,6] We reported here a new finding that a 1:1 complex of azoxybenzenes with $SbCl_5$, on thermolysis, gives rise to selective production of the corresponding o-hydroxyazobenzenes.

When equimolar solutions of azoxybenzene and $SbCl_5$ in carbon tetrachloride were mixed, a 1:1 complex immediately deposited as orange crystals in 95.5 % yield. The compound gave satisfactory elemental analysis. The complex was very hygroscopic and on hydrolysis gave the starting azoxybenzene. Results on the thermal reaction of complexes of various azoxybenzenes with $SbCl_5$ in nitrobenzene, giving o-hydroxyazobenzenes as the main product, were shown in Table, which includes the o/p product ratios in the usual Wallach rearrangement conditions (80—90 % sulfuric acid). Thus, the present reaction provided a novel synthetic method for preparing o-hydroxyazobenzenes. Although the mechanism of this Wallach rearrangement remains to be clarified, the predominant formation of o-hydroxyazobenzenes without azobenzenes suggests that the intramolecular attack of the O-Sb group is involved.

Treatment of azoxybenzene with other Lewis acids, such as $FeCl_3$, $AlCl_3$, and CuCl, in carbon tetrachloride gave no precipitation and the isolation of the complexes in

Table Selective ortho-Wallach rearrangement of 1:1 Complex of Azoxybenzenes with $SbCl_5$

 R_1 R_2		m.p.[a] (°C)	Reaction Condition		Alkali soluble products (%)			o/p Ratio[b]
			Temp. (°C)	Time (hr)	o-Hydroxy-azobenzenes	p-Hydroxyazo-benzenes	Polymer	
H	H	107—107.5	86—88	5.0	63.5	1.6	24.8	98:2(13:87)
o-CH_3	o-CH_3	134—134.5	190—195	0.5	12.5	Not detected	12.5	100:0(0:100)
m-CH_3	m-CH_3	111—112	103[c]	20.0	16.4[d]	4.5	4.4	78:22(9:91)
H	p-CH_3	107—108	92	5.0	72.8[e]	Not detected	27.2	100:0(21:79)
p-Cl	H	40.5—41	103[c]	20.0	0.7[f]	Not detected	9.6	100:0(17:83)
p-NO_2	H	[g]	200	5.0	7.1[h]	2.5	5.8	74:26(7:93)

[a] Melting point was measured in a capillary and uncorrected. [b] In parentheses, the o/p ratio in the Wallach rearrangement of each azoxybenzenes using 80—90 % sulfuric acid is given. [c] Nitromethane was used as the solvent for thermolysis. [d] 2-Hydroxy-5,3'-dimethylazobenzene. [e] 2-Hydroxy-4-methylazobenzene. [f] 2-Hydroxy-4'-chloroazobenzene. [g] Measurement of melting point was difficult because of its highly hygroscopic character. [h] 2-Hydroxy-4'-nitroazobenzene.

pure form was unsuccessful. However, on refluxing an equimolar mixture of azoxybenzene and $FeCl_3$[7] in nitrobenzene for 5 hr, 8.2 % of o-hydroxyazobenzene and 3.1 % of azobenzene were obtained. α-Pyridone was obtained in 80 % yield by the thermolysis of the isolated 1:1 complex of pyridine N-oxide with $SbCl_5$ in nitromethane.

References and Notes

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