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SYNTHESIS OF AZOXYBENZENE-$SbCl_5$ COMPLEXES AND THEIR SELECTIVE ORTHO-WALLACH REARRANGEMENT

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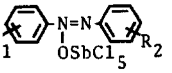
Abstract—When an equimolar solution of various azoxybenzenes and $SbCl_5$ in carbon tetrachloride were mixed, a 1:1 complex immediately deposited as orange crystals in high yield. The thermal reaction of these complexes in inert solvents gives *o*-hydroxy-azobenzene selectively. On the contrary, other Lewis acids such as $TiCl_4$, $AlCl_3$, $FeCl_3$ and $ZnBr_2$ failed to give an isolatable complex with azoxybenzene, and their direct thermal reaction with azoxybenzene resulted in deoxygenation to yield azobenzene as a main product.

The Wallach rearrangement of azoxybenzenes using proton acids as catalyst giving rise to hydroxyazobenzenes, the *para*-isomer being predominant over *o*-isomer. In addition, azobenzene is a minor deoxygenation product. The Lewis acid-catalyzed reactions of azoxybenzenes are always associated with deoxygenation in the course of the reaction.[1–4] For example, treatment of azoxybenzene with acetyl chloride in the presence of $AlCl_3$ gives *p*-chloroazobenzene. Hence, we considered it possible that azoxybenzene could form, like aromatic N-oxides,[5–7] a complex with Lewis acids in which the oxygen-Lewis acid moiety acts as a good leaving group. In our attempts to isolate such a complex, we found that azoxybenzenes give crystalline 1:1 complexes with $SbCl_5$ and that the complexes on thermolysis undergo selective ortho-Wallach rearrangement to yield *o*-hydroxyazobenzenes.[8] This paper deals with the details of these findings and the reaction of azoxybenzene with other Lewis acids.

RESULTS AND DISCUSSION

Mixing of equimolar solutions of various azoxybenzenes (**1**) and $SbCl_5$ in carbon tetrachloride immediately deposited orange crystals in essentially quantitative yield. The crystals had a sharp mp and their elemental analysis showed them to be 1:1

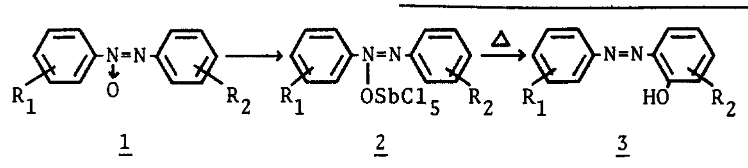
Table 1. 1:1 Complexes of Azoxybenzenes with $SbCl_5$

		Yield (%)	mp (°C)	Elemental analysis, Found(Calcd.) %			IR (cm^{-1})	UV $\lambda_{max.}^{CHCl_3}$, nm(ε)
				C	H	N		
H	H	93.5	107-107.5	27.62(28.03)	2.20(2.11)	5.57(5.63)	1614,1470	240(8800) 322(10900)
H	2-CH_3	97.3	109-110.0	29.37(30.61)	2.26(2.38)	5.41(5.49)[a)]	1620,1475	242(10500) 325(7800)
2-CH_3	2-CH_3	98.0	134-134.5	31.52(32.05)	2.62(2.70)	5.25(5.33)[b)]	1620,1450, 1340	244(9100) 311(6000)
3-CH_3	3-CH_3	97.5	111-112.0	31.10(32.05)	2.83(2.70)	5.22(5.33)	1620,1450, 1090, 915	243(9100) 325(7800)
H	4-CH_3	98.6	107-108.0	29.81(30.61)	2.56(2.38)	5.57(5.49)	1600,1460, 1300,1170	241(7300) 324(12000)
4-CH_3	H	96.6	110-111.0	29.31(30.61)	2.36(2.38)	5.13(5.49)	1600,1465, 1430,1260	243(920) 327(11200)
4-Cl	H	93.4	40-40.5	27.76(27.10)	2.23(1.83)	5.35(5.26)	1620,1470, 1400,1280	242(8400) 261(7900) 328(13000)
4-Br	H	94.4	56-59.0	24.59(25.02)	2.11(1.56)	4.79(4.85)	1605,1330, 1110	240(9000) 270(10300) 327(15800)
4-NO_2	H	91.0	c)		c)		1590,1530, 1430	256(25800) 290(7000)

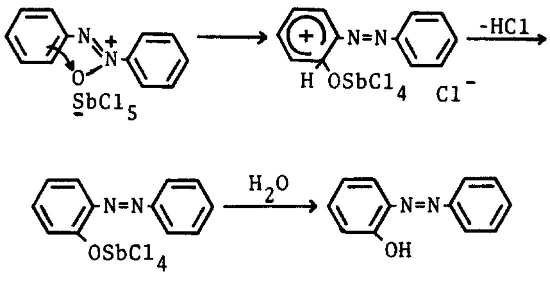
a) Cl: Found, 34.83 %; Calcd., 34.90 %. b) Cl: Found, 34.11 %; Calcd., 34.00 %.

c) Measurement of melting point and elemental analysis were unsatisfactory because of its highly hygroscopic character.

complexes (Table 1). The complexes were highly hygroscopic and hydrolysis gave the starting azoxybenzenes in essentially quantitatively yield. Table 1 lists the IR and UV spectal data which show a characteristic IR band around 1600 cm^{-1} and a strong UV maximum around 320 nm tailing to visible spectal regions. The IR band of the starting azoxybenzenes at 890–845 cm^{-1} due to N-O stretching disappears completely or is weakened in the IR spectra of the complexes. The azoxybenzene-$SbCl_5$ complexes are assumed to have an ionic structure (**2**) by analogy with the ionic or highly polarized structure of acyl halides with antimony pentahalide ($RCO^+SbX_6^-$ or $RCOX^{+\delta}SbX_5^{-\delta}$; X = F or Cl).[9a,9b] Thermolysis of the azoxybenzene-$SbCl_5$ complexes followed by hydrolysis was found to give the corresponding *o*-hydroxyazobenzenes (**3**) as the main product. The formation of the corresponding *p*-hydroxyazobenzenes was only minor process and no deoxygenation into azobenzenes was observed. The other pathway leading to tarry products occurred to a considerable extent in the thermolysis. The product distribution with respect to **3** and tarry products was highly temperature-dependent. In the case of the complex of azoxybenzene itself, the yield of tarry products increased with increasing temperature at the expense of **3**, and the maximum yield of **3** was obtained at about 85° (Fig. 1).



This selective *ortho*-Wallach rearrangement appears to proceed via an ionic intramolecular attack of the O-Sb group as shown in Scheme 1. In accordance with this ionic mechanism, styrene added to the reaction system with the azoxybenzene-$SbCl_5$ complex did not undergo radical polymerization.



Scheme 1

Attempts to extend the complex formation from azoxybenzene with other Lewis acids such as $TiCl_4$, $AlCl_3$, $FeCl_3$ and $ZnBr_2$ followed by the thermal *ortho*-Wallach rearrangement were unsuccessful. For example, in the reaction with azoxybenzene $FeCl_3$ deposited a viscous solid from which the expected complex could not be isolated in a crystalline state. Therefore, direct thermal reaction of azoxybenzene with these Lewis acids was carried out in nitromethane (Table 3). The major reaction was deoxygenation to give azobenzene with the concominant formation of tarry products, while the formation of *o*-hydroxyazobenzene was only a minor path. When the Lewis acids

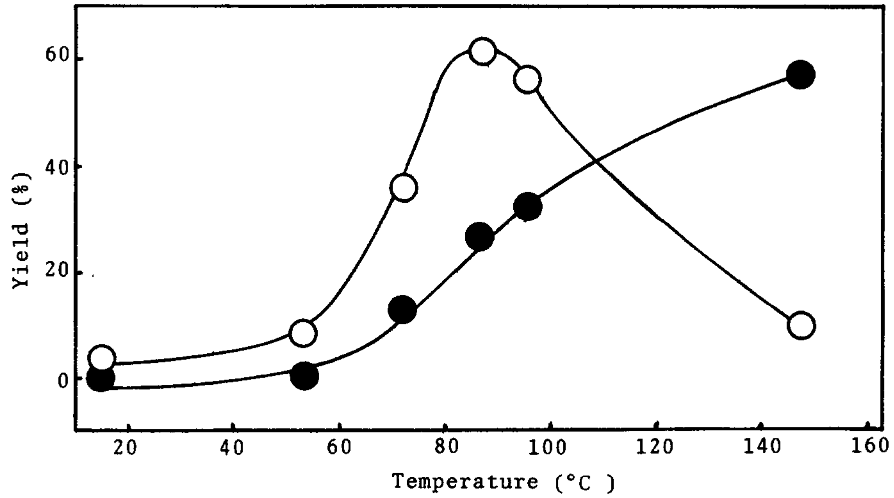
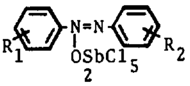
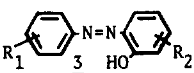
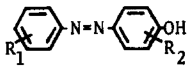


Fig. 1. Temperature dependance in selective ortho-Wallach rearrangement of 1:1 complex of azoxybenzene with $SbCl_5$.

Reaction conditions—

Starting material; 0.7–0.8 g (1.19–1.36 mmol);
Solvent; Nitrobenzene;
Reaction time; 5 hr except 18 hr at 20°C and 2 hr at 145°C;
○, *o*-Hydroxyazobenzene;
●, Tarry products.

Table 2. Selective ortho-Wallach rearrangement of 1:1 complexes of Azoxybenzenes with $SbCl_5$

		Reaction conditions			Reaction products (%)			
 2		Solvents	Temp. (°C)	Time (hr)	 3		Tarr	Recovered starting (%) materials
H	H	$C_6H_5NO_2$	86-87	5.0	63.5[10]	1.6[11]	24.0	3.5
H	2-CH_3	CH_3NO_2	81-83	3.0	34.0[a)]	2.1[13]	8.5	46.4
2-CH_3	2-CH_3	$C_6H_5NO_2$	199-200	0.5	12.5[13]	trace	12.6	59.3
3-CH_3	3-CH_3	CH_3NO_2	101.3	20.0	16.3[16]	4.5[16]	12.3	43.2
H	4-CH_3	$C_6H_5NO_2$	92.0	5.0	72.8[17]	trace	27.0	Not detected
4-CH_3	H	$C_6H_5NO_2$	163-165	3.0	32.4[18]	trace	22.1	27.4
4-Cl	H	$C_6H_5NO_2$	180-181	2.0	11.6[19]	Not detected	16.6	48.7
4-Br	.H	$C_6H_5NO_2$	154-155	3.0	46.7[19]	Not detected	3.0	43.0
4-NO_2	H	$C_6H_5NO_2$	200	5.0	7.1[20]	Not detected	5.8	68.5

a) The product was identified to be 2-hydroxy- 6 -methylazobenzene because it is not agreed with an authentic sample of 2-hydoxy-2'-methylazobenzene.[12]

Table 3. Thermal reaction of azoxybenzene with Lewis acids

Lewis acids	Amounts of azoxybenzene g (mmol)	Solvent[a)]	Reaction time (hr)	Reaction products (%) o-Hydroxy-azobenzene	p-Hydroxy-azobenzene	Azobenzene	Tarry products (%)	Reccoverd azoxybenzene (%)
$ZnBr_2$	1.00(5.05)	CH_3NO_2	3.5	trace	trace	1.5	18.0	80.0
$FeCl_3$	1.62(8.20)	CH_3NO_2	5.0	8.2	trace	31.1	1.0	32.9
$AlCl_3$	1.21(6.10)	CH_3NO_2	4.0	3.4	0.9	61.9	6.2	17.9
$TiCl_4$	1.16(5.86)	CH_3NO_2	3.0	0.9	Not detected	49.9	46.5	trace

a) Reaction condition: at reflux temperature

such as $TiCl_4$, $AlCl_3$ and $FeCl_3$ were used in excess of azoxybenzene, *p*-chloroazobenzene was formed with decreased yield of azobenzene. The difference between $SbCl_5$ and the other Lewis acids in the reaction with azoxybenzene should await further investigation.

EXPERIMENTAL

Materials. Azoxybenzene[21] was prepared by boiling a MeOH soln containing nitrobenzene and NaOH. 2,2'- and 3,3'-Dimethylazoxybenzene were prepared by allowing a mixture of Zn dust, a sat NH_4Cl aq, MeOH and the corresponding nitrobenzenes to stand.[22] α- and β-*p*-Methylazoxybenzene,[23] β-*p*-chloro-[24] and β-*p*-nitroazoxybenzene[25] were obtained by oxidized with hydrogen peroxide, α- and β-*p*-methylazoyperoxide in acetic acid. After *p*-methyl-azobenzene was oxidized with hydrogen peroxide, α- and β-*p*-methylazoxybenzenes were separated by fractional recrystallization from EtOH.[23] β-*p*-Bromoazoxybenzene[26] was obtained by fractional recrystallization from benzene-petroleum ether from a mixture of α- and β-*p*-bromoazoxybenzenes obtained by hydrogen peroxide oxidation of *p*-bromoazobenzene.

Preparation of 1:1-*complex of azoxybenzene with* $SbCl_5$ (Table 1). Reddish orange crystals were deposited immediately by mixing solns of azoxybenzene (5 g; 2.52×10^{-2} mol) and $SbCl_5$ (7.6 g; 2.52×10^{-2} mol) in CCl_4 (10 ml each). The mixture was allowed to stand overnight and the crystals were collected by filtration in an atmosphere of dry N_2. The crystals were thoroughly washed with CCl_4, then with petroleum ether. The yield was 12.0 g (95.5 %). The complexes of azoxybenzene derivatives were prepared by the same procedure. Chloroform was used as a solvent only in the case of β-*p*-nitroazoxybenzene because of its less solubility in CCl_4, and the complex of this compound was obtained by removal of the solvent under reduced pressure. The mp of complexes were measured in a sealed capillary tube.

Thermal reaction of 1:-*complex of azoxybenzene with* $SbCl_5$ (Table 2). A soln of the complex (0.8 g; 1.36×10^{-3} mol) in 10 ml nitromethane was heated at 85° for 5 hr, in a 100 ml flask equipped with a $CaCl_2$ tube and then the mixture was poured into water. A white ppt of Sb_2O_5 was filtered off and washed with water and benzene. The combined organic layer was separated and extracted with 3 % NaOH aq. The alkaline soln was acidified with HCl and extracted with benzene. The extract was dried and concentrated. The residue was chromatographed on a silica gel column (7–8 g) eluting with benzene to remove tarry products.

The eluate containing azoxybenzene was washed with dil HCl and water successively, dried and evaporated. Thus, 0.228 g (63.5 %) of *o*-hydroxyazobenzene, 5.8 mg (1.6 %) of *p*-hydroxyazobenzene and 86 mg (24 wt %) of tarry products were obtained and 12.6 mg (3.5 %) of azoxybenzene was recovered. The other azoxybenzenes–$SbCl_5$ complexes were treated by a similar procedure. *o*-Hydroxyazobenzenes were identified by comparison of mp and IR spectra of the authentic samples, which were prepared by diazo-coupling of the corresponding phenols and diazonium salts.[27] *o*-Hydroxyazobenzenes were also characterized by forming a characteristic copper salt with cupric acetate in aqueous EtOH solutions.[28, 29]

Thermal reaction of azoxybenzene with Lewis acids (Table 3). A soln of equimolar amounts (5.05–8.20 mmol) of azoxybenzene and a Lewis acid in 10 ml nitromethane was heated under reflux. After removal of the solvent, the mixture was worked up as above. A soln of 1.16 g (5.86 mmol) and 5.44 g (29.3 mmol) of $TiCl_4$ in 10 ml nitromethane was treated similarly. From the r mixture, 0.43 g (40.1 %) of azobenzene and 0.38 g (37.2 %) of *p*-chloroazobenzene were obtained. The latter product was identical with an authentic sample.

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