BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3759—3760 (1975)

Reaction of *N*-Aroyl-*N*-arylhydroxylamines with *o*-Nitrobenzenesulfenyl Chloride

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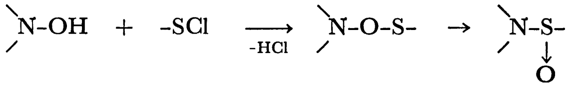
(Received April 8, 1975)

Synopsis. Reactions of *N*-aroyl-*N*-arylhydroxylamines with *o*-nitrobenzenesulfenyl chloride were found to afford the corresponding *N*-aroylarylamines and *S*-(*o*-nitrophenyl) *o*-nitrobenzenethiosulfonate in good yields, respectively. Both the product distributions and the effect of substituents on the amount of reduction product suggest these reactions to proceed *via* homolytic cleavage of the N–O bond.

The rearrangement of allylic sulfenates to the corresponding sulfoxides with no allylic shift has been known to proceed *via* the homolytic scission of C–O bonds.[1] A similar mode of C–O bond scission has been observed in the rearrangements of both benzyl *p*-toluenesulfenate[2] and cyclohexenyl benzenesulfenate.[3]

However, the reaction of *N,N*-disubstituted hydroxylamines with the sulfenyl chloride could also lead to the formation of sulfinamide (III) by rearrangement as in the case of the allylic sulfenates as shown below. However, no such reaction has yet been investigated.



(I) (II) (III)

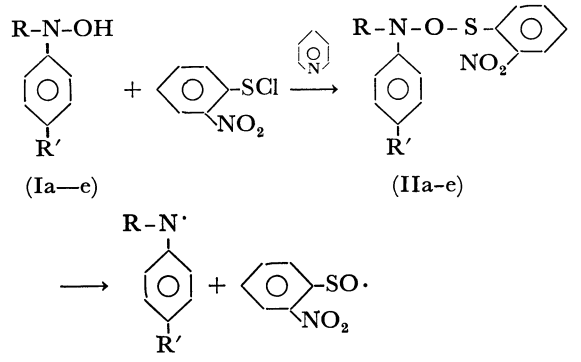
This paper describes the reaction of *N*-aroyl-*N*-arylhydroxylamines with *o*-nitrobenzenesulfenyl chloride, comparing the reaction route of the hydroxylamine with that of the corresponding alcohol.

Results and Discussion

The *N*-aroyl-*N*-arylhydroxylamines (Ia—e) were allowed to react with an equimolar amount of *o*-nitrobenzenesulfenyl chloride, and *S*-(*o*-nitrophenyl) *o*-nitrobenzenethiosulfonate and the corresponding *N*-aroylarylamines were obtained in good yields along with small amounts of *o,o′*-dinitrodiphenyl disulfide as shown in the Table. No rearrangement product (III) was found among the products.

Apparently, the more polar the solvent used, the greater was the yield of the unexpected reduction products, the *N*-aroylaryamines, while the introduction of an electron-releasing *p*-methyl group into the phenyl ring of the hydroxylamines resulted in an increase of the amount of the reduction product. Futhermore, the yield of the reduction product was not affected very much by the functional group (R) directly attached to the nitrogen atom of the hydroxylamines.

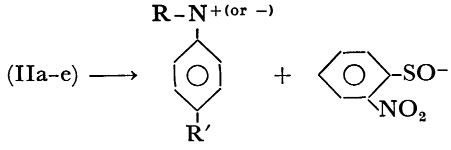
The *p*-nitrobenzenesulfinyl radical is known to be quite stable due to the electron-sharing 3d-orbital resonance, and to dimerize readily eventually yielding *S*-(*p*-nitrophenyl) *p*-nitrobenzenethiosulfonate.[4,5] Therefore, one may safely assume that the hydroxylamines (Ia—e) react with the sulfenyl chloride to give the intermediate (IIa—e), which undergoes homolytic scission of the N-O bond in (IIa—e) as shown below. The resulting acylamino radical undoubtedly affords the *N*-aroylarylamine by hydrogen abstraction and the *S*-(*o*-nitrophenyl) *o*-nitrobenzenethiosulfonate is formed by the dimerization of *o*-nitrobenzenesulfinyl radical, like the *p*-nitrobenzenesulfinyl radical.



(Ia—e) (IIa-e)

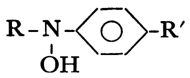
R=PhCO, R′=H (Ia); R=PhCO, R′=CH_3 (Ib); R=PhCO, R′=Cl (Ic); R=CH_3CO, R′=H (Id); R=Ts, R′=H (Ie)

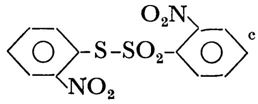
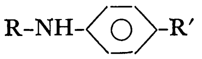
If the N–O bond of (IIa—e) is assumed to cleave heterolytically, there are the following two possibilities for heterolysis.



These possibilities, however, may be ruled out by the following observations: (1) no substantial formation of the disulfide whose amount must be comparable to that of the thiosulfonate[5a,6] and (2) little influence by any polar functional group (R) on the yield of the reduction product was observed, unlike the reduction of *O*-(3,5-dinitrobenzoyl)-*N*-aroyl-*N*-arylhydroxylamines by cyanide ions in a dipolar aprotic solvent.[7] If the N–O bond of (IIa—e) were cleaved heterolytically, the nucleophilic attack of the chloride ion on the sulfenate-sulfur atom of (IIa—e) should give *o*-nitrobenzenesulfinyl chloride and the anilide anion. Thus, the alternative mechanism involving the homolysis of the N–O bond remains the most plausible possibility.

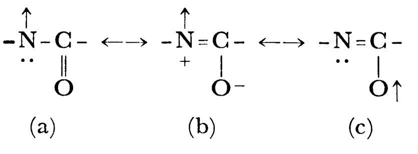
The lone-pair electron of the acylamino radical has been suggested to be extensively delocalized into the carbonyl group as shown by (b) in preference to the allylic resonance (c), placing the odd electron on the oxygen atom, being quite unimportant.[8]

Table 1. The products of the reaction of  with *o*-nitrobenzenesulfenyl chloride at room temperature$^{a,b)}$

Substituents		Reaction Condition		Products and Yields, %	
R	R′	Solvent	Time (hr)	 c)	 d)
PhCO	H	CH_2Cl_2	24	41	57
PhCO	H	CH_3CN	24	60	76
PhCO	CH_3	CH_2Cl_2	24	57	86
PhCO	Cl	CH_2Cl_2	24	50	57
CH_3CO	H	CH_2Cl_2	24	46	53
Ts	H	CH_2Cl_2	24	46	57

Ts=p-$CH_3C_6H_4SO_2$-

a) The reactions were carried out in the presence of dissolved oxygen. b) A small amount of *o,o′*-dinitrodiphenyl disulfide was obtained in each run. c) Yield based on the sulfenyl chloride used. d) Yield based on the hydroxylamine used.



In addition, ESR spectroscopy revealed the electronic ground state of the acylamino radical to possess not a σ-, but a π-character. The π-radical is stabilized by the π-delocalization of an odd electron on the nitrogen atom in the phenyl ring. Consequently, the effects of the solvent and the subststituent R′ on the amount of the reduction product can be interpreted in terms of the enhanced stability of the acylamino radical, formed by the homolytic scission of the N–O bond. The absence of any appreciable effect of the substituent R may be due to the negligible contribution of the allylic resonance (c) in the acylamino radical.

Thus, the different behaviors of the hydroxylamine and the alcohol in the reaction with the sulfenyl chloride appears to be attributable to the difference in the thermodynamical stabilities of the sulfinamide and the sulfoxide.

Experimental

Materials and Solvent. *N*-Aroyl-*N*-arylhydroxylamines (Ia—e) were prepared by the reactions of the corresponding *N*-arylhydroxylamines (2 mol) with aroyl chloride (1 mol) in dry ether at 0 °C. Repeated recrystallization from benzene-hexane gave mp, 121.5—122.0 °C (Ia), 110—111 °C (Ib), 156—157 °C (Ic), 68.5—69.5 °C (Id), and 145—146 °C (Ie; Found; C, 59.06; H, 4.98; N, 5.38%. Calcd for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.97; N, 5.32%). *o*-Nitrobenzenesulfenyl chloride was synthesized by the chlorination of *o,o′*-dinitrodiphenyl disulfide with dry chlorine gas in chloroform at room temperature. Repeated recrystallization from hexane gave light yellow needles, mp 74—75 °C (lit, 73—74.5 °C)$^{10)}$. All the solvents used were purified by the usual methods.

General Procedure for the Reactions of (Ia—e) with o*-Nitrobenzenesulfenyl Chloride.* Solutions of *o*-nitrobenzenesulfenyl chloride (4.58—6.62 mmol) in 20 ml of methylene chloride were dropped for 10 min with stirring into solutions of *N*-aroly-*N*-arylhydroxylamines (4.58—6.62 mmol) and pyridine (4.58—6.62 mmol) in 30 ml of methylene chloride at 0 °C. After keeping the mixtures at room temp. for 24 hr, the solutions were washed with water and dried over anhyd. sodium sulfate. Evaporation of the solvent afforded residual solids, which were then separated by column chromatography packed with silica gel using methylene chloride as the eluent. The structures of the products (shown in the Table) were identified by comparing their melting points and IR spectra with those of authentic compounds.

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