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A Novel Reduction of the *O*-(3,5-Dinitrobenzoyl)-*N*,*N*-(aroylaryl)hydroxylamines by the Cyanide Ion in Dipolar Aprotic Solvents

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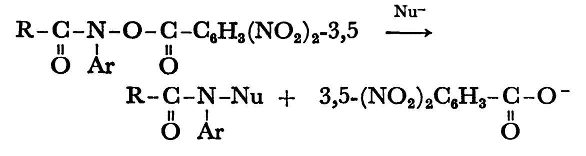
Synopsis. The reaction of *O*-(3,5-dinitrobenzoyl)-*N*,*N*-(aroylaryl)hydroxylamines with the cyanide ion in dipolar aprotic solvents was found to afford the corresponding reduction products, *i.e.*, *N*-aroylarylamines, in good yields *via* decarboxylation. The mechanism of this novel reduction was discussed.

In the preceding paper we have shown that *N*,*N*-dibenzyl-*O*-(*p*-nitrobenzoyl)hydroxylamine is a good model compound for studying both nucleophilic substitution and elimination reactions on the trivalent nitrogen atom.[1]

As an extension of the earlier study, we have now prepared *O*-(3,5-dinitrobenzoyl)-*N*,*N*-(aroylaryl)hydroxylamines and allowed them to react with various nucleophiles in dimethyl sulfoxide (DMSO), expecting that the reaction would proceed *via* nucleophilic substitution on the nitrogen atom as follows:

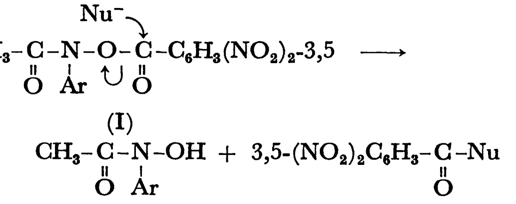


$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{Ar}{|}}{N}{-}O{-}\underset{\underset{O}{\|}}{C}{-}C_6H_3(NO_2)_2\text{-}3,5 \xrightarrow{Nu^-} R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{Ar}{|}}{N}{-}Nu + 3,5\text{-}(NO_2)_2C_6H_3{-}\underset{\underset{O}{\|}}{C}{-}O^-}$$

R = $\mathrm{CH_3}$, Ph

Results and Discussion

The reaction of *O*-(3,5-dinitrobenzoyl)-*N*,*N*-acetyl-(*p*-chlorophenyl)hydroxylamine (I) with nucleophiles in DMSO or DMF at room temperature was found to give products which appear to be formed by the attack of the nucleophile upon the carbonyl-carbon of the reactant, as is shown below, except for the reaction with cyanide ion, as is indicated in Table 1. When the cyanide ion was allowed to react with I, an unexpected reduction product was obtained in a substantial yield, while no substitution product was detected.

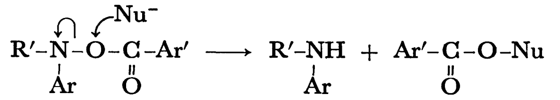


$$\mathrm{CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{Ar}{|}}{N}{-}O{-}\overset{Nu^-}{\underset{\underset{O}{\|}}{C}}{-}C_6H_3(NO_2)_2\text{-}3,5 \longrightarrow CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{Ar}{|}}{N}{-}OH + 3,5\text{-}(NO_2)_2C_6H_3{-}\underset{\underset{O}{\|}}{C}{-}Nu}$$

(I)

Ar = p-$\mathrm{ClC_6H_4}$

Thus, the effects of substituent on the yields of the reduction products and on the course of the reaction were investigated in order to clarify the mechanism of this novel reduction by the cyanide ion. The results are listed in Table 2. An inspection of the data in Table 2 clearly indicates that the novel reduction occurred only when the leaving group was 3,5-dinitrobenzoyloxy group, since no hydroxylamine (V) with *p*-nitrobenzoyloxy group as the leaving group gave the reduction product in the reaction. Moreover, the yield of the reduction tends to increase with the increase in the electron-withdrawing ability of the substituent which is attached directly to the nitrogen atom.



$$\mathrm{R'{-}\underset{\underset{Ar}{|}}{N}{-}O{-}\overset{Nu^-}{\underset{\underset{O}{\|}}{C}}{-}Ar' \longrightarrow R'{-}\underset{\underset{Ar}{|}}{N}H + Ar'{-}\underset{\underset{O}{\|}}{C}{-}O{-}Nu}$$

R′ = $\mathrm{CH_3CO}$ (II), PhCO (III), p-$\mathrm{CH_3C_6H_4SO_2}$ (IV);
Ar = Ph
R′ = $\mathrm{CH_3CO}$; Ar = p-$\mathrm{ClC_6H_4}$ (I); Ar′ = $\mathrm{-C_6H_3(NO_2)_2}$-3,5

One mechanism to explain the product distribution of the reaction with the cyanide ion may involve the nucleophilic substitution on the oxygen atom which has been observed in the reactions of peroxides with nucleophiles.[2] This mechanism, however, seems un-

Table 1. Reaction of I with various nucleophiles at room temperature

Nucleophile	Solvent	Product (Yield %)	Reaction time (hr)
$\mathrm{NaN_3}$	DMSO	$\mathrm{Ac{-}\underset{\underset{OH}{\mid}}{N}{-}Ar}$ (66), $\mathrm{Ar'CO_2Na}$ (12)	26
NaSPh	DMSO	$\mathrm{Ac{-}\underset{\underset{OH}{\mid}}{N}{-}Ar}$ (74), $\mathrm{Ar'CO_2Na}$ (27), PhSSPh (67)	25
p-$\mathrm{CH_3C_6H_4SH}$	DMF	$\mathrm{Ac{-}\underset{\underset{OH}{\mid}}{N}{-}Ar}$ (96), p-$\mathrm{CH_3C_6H_4{-}S{-}\underset{\underset{O}{\|}}{C}{-}Ar'}$ (83)	48
$\mathrm{NaOCH_3}$	DMSO	$\mathrm{Ac{-}\underset{\underset{OH}{\mid}}{N}{-}Ar}$ (57), $\mathrm{Ar'CO_2CH_3}$ (41)	25
NaCN	DMSO	$\mathrm{Ac{-}\underset{H}{N}{-}Ar}$ (52)	26

Ac = $\mathrm{CH_3CO}$ Ar = p-$\mathrm{ClC_6H_4}$ Ar′ = $\mathrm{-C_6H_3(NO_2)_2}$-3,5

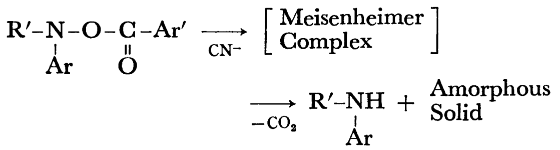
TABLE 2. REACTION OF $R'-\underset{Ph}{N}-O-\underset{O}{C}-Ar'$ WITH SODIUM CYANIDE AT ROOM TEMPERATURE

Substituent R′	Solvent	Yield of reduction product (%)	Reaction time (hr)
CH_3CO (II)	DMSO	63	26
PhCO (III)	DMSO	90	26
PhCO (III)	DMF	76	26
p-$CH_3C_6H_4SO_2$ (IV)	DMSO	94	26
$Ac-\underset{Ar}{N}-O-\underset{O}{C}-C_6H_4-NO_2$-$p$ (V)	DMSO	$Ac-\underset{Ar}{N}-OH$ (81), p-$NO_2C_6H_4CO_2Na$ (37)	25

$Ac=CH_3CO$ $Ar=p$-ClC_6H_4 $Ar'=-C_6H_3(NO_2)_2$-3,5

likely because the reduction product of (IV) was obtained in a high yield in spite of the large steric and electronic repulsions between the sulfonyl oxygen and charged nucleophiles, serving to suppress the reduction.

A more probable mechanism is that the reduction proceeds *via* the decarboxylation of a Meisenheimer-type complex formed as an intermediate as in the displacement reaction of polynitroaromatics.[3] This mechanism explains the observation that the reduction proceeds more readily when the electron-withdrawing power of the R′ substituents increases. Another strong support for this mechanism is that carbon dioxide was trapped as barium carbonate by bubbling through an aqueous solution of barium hydroxide, with nitrogen gas as a carrier gas, in the reaction of hydroxylamine (III) with the cyanide ion in DMSO at room temperature, though the yield of carbon dioxide thus evolved was relatively low (*ca.* 10%).



$$\underset{Ar}{R'-N}-O-\underset{O}{C}-Ar' \xrightarrow[CN^-]{} \left[\begin{matrix}\text{Meisenheimer}\\ \text{Complex}\end{matrix}\right] \xrightarrow[-CO_2]{} R'-\underset{Ar}{NH} + \begin{matrix}\text{Amorphous}\\ \text{Solid}\end{matrix}$$

$R'=CH_3CO$ (II), PhCO (III), p-$CH_3C_6H_4SO_2$ (IV);
$Ar=Ph$
$R'=CH_3CO$; $Ar=p$-ClC_6H_4 (I); $Ar'=-C_6H_3(NO_2)_2$-3,5

It has been recently established that the species more readily formed in the interaction of aromatic polynitro compounds with the cyanide ion in a dipolar aprotic solvent than in alcoholic or ketonic solvents, may be formulated as Meisenheimer complexes on the basis of their UV, IR, and NMR spectra.[4] Therefore, the intermediate whose strong absorption band appeared at $\lambda_{max}=576$ nm may safely be ascribed to the Meisenheimer-type complex formed by the interaction of (III) with sodium cyanide in DMF.

TABLE 3. PHYSICAL PROPERTIES OF I, II, III, IV, AND V

Compound	Mp (°C)	IR (KBr, cm^{-1})
(I)	137—138	3100, 1780, 1690, 1540, 1340, 1250
(II)	103—104	3060, 1770, 1675, 1530, 1340, 1245
(III)	---[a]	3100, 1780, 1680, 1545, 1350, 1250
(IV)	---[a]	3100, 1780, 1550, 1365, 1340, 1255, 1170
(V)	135—136	1770, 1705, 1530, 1340, 1240

a) The melting points could not be precisely determined because thermal rearrangement occurred before melting.

Experimental

Materials. The *O*-(3,5-dinitrobenzoyl)-*N,N*-(aroylaryl)-hydroxylamines used were prepared from 3,5-dinitrobenzoyl chloride and the corresponding *N,N*-aroylarylhydroxylamines under the usual Schotten-Bauman conditions. The *O*-(*p*-nitrobenzoyl)-*N,N*-acetyl-(*p*-chlorophenyl)hydroxylamine was synthesized similarly. The mp and the IR spectrum of these hydroxylamines are shown in Table 3.

General Procedure for the Reaction of I, II, III, IV and V with Nucleophiles. A small excess of a nucleophile (1.1—1.7 mM) was added to 6 ml of a DMSO solution of I—V (0.9—1.6 mM) in a reaction vessel, after which the whole solution was stirred with a magnetic stirrer at room temperature for 25—48 hr. After the reaction, the contents were poured into a large excess of water, and then the products were extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water several times and dried over Na_2SO_4. The subsequent evaporation of $CHCl_3$ afforded a residue, which was then subjected to column chromatography through silica gel, using CH_2Cl_2 as the eluent. The water solution was acidified slightly with a dil-HCl aqueous solution, and the aqueous solution was extracted with $CHCl_3$. The evaporation of $CHCl_3$ gave the crude *p*-nitro- and 3,5-dinitrobenzoic acids respectively. The structures of the products isolated were determined by comparison with authentic samples.

References

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