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STEREOCHEMISTRY OF THE ALKALINE HYDROLYSIS OF N-CHLOROSULFIMIDES TO SULFOXIMIDES

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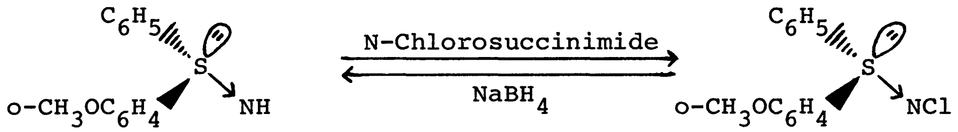
(-)-(S)-N-Chloro-S-o-methoxyphenyl-S-phenylsulfimide was prepared and its alkaline hydrolysis afforded the corresponding sulfoximide. This hydrolysis was found to proceed with a retention of configuration at the reaction center.

One of the interesting derivatives of free sulfimides is the N-halo derivatives which can be obtained by treating the corresponding free sulfimides ($^{R}_{R'}\!\!>S\rightarrow NH$) with halogenating reagents. N-Halosulfimides react readily with soft nucleophiles such as sulfides, phosphines, and tertiary amines to afford the corresponding N-sulfonio-, N-phosphonio-, and N-ammoniosulfimide salts. However, upon treatment with such a hard nucleophile as hydroxide, N-halosulfimides give what appears to be a rearranged product, i.e., the corresponding sulfoximide.1) Earlier we suggested that the reaction of N-halosulfimides with sulfides or phosphines proceeded via an initial attack of sulfides or phosphines on the halogen atom of N-halosulfimides forming either the corresponding halosulfonium or halophosphonium salts as intermediates which then undergo nucleophilic substitution on either the sulfur atom or the phosphorus atom, while in the reaction with tertiary amines, a direct nucleophilic substitution on the nitrogen atom of N-halosulfimides took place, eventually affording the final products, i.e., the corresponding N-ammoniosulfimide salts.2)

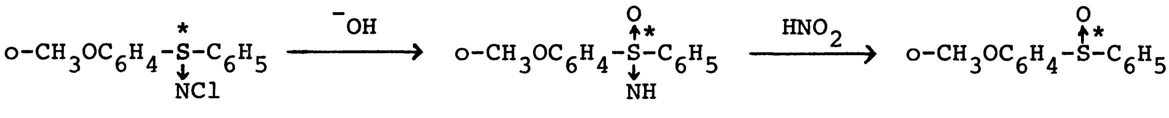
In order to understand the mechanism of the reaction of N-halosulfimides with hard nucleophiles, we carried out alkaline hydrolysis of (-)-(S)-N-chloro-S-o-methoxyphenyl-S-phenylsulfimide and obtained the corresponding sulfoximide which retained fully its configuration around the sulfur atom. Thus, we wish to report briefly the result and its implication for understanding the mechanism.

Optically active (-)-(S)-S-o-methoxyphenyl-S-phenylsulfimide (I) was conveniently prepared by the hydrolysis of the corresponding N-p-tosylsulfimide (II) in conc. sulfuric acid.3) The hydrolysis of II to I was found to proceed without racemization, since I was quantitatively converted back to II upon treatment with tosyl chloride in the presence of pyridine and the sign of optical rotation of II was identical to that of the starting compound.3) Conversion of I [$[\alpha]_D^{25}=-73.9°$ (c, 1.44, $CHCl_3$, optical purity, 38.1%4))] to (-)-(S)-N-chloro-S-o-methoxyphenyl-S-phenylsulfimide (III) was carried out by treatment with N-chlorosuccinimide in 67.0% yield, m.p. 79-80°C (dec), $[\alpha]_D^{25}=-33.1°$ (c, 0.29, $CHCl_3$). Reduction of III with sodium borohydride afforded the original I with 96% retention of configuration around the sulfur atom. Accordingly, the chlorination of I did not change the configuration around the sulfur atom and hence (-)-III can be assigned as (S)-configuration.



(-)-(S)-(I) (-)-(S)-(III)

Alkaline hydrolysis of (-)-(S)-III was carried out with sodium hydroxide in methanol at room temperature for 1 hr. Then, a careful work-up afforded optically active S-o-methoxyphenyl-S-phenylsulfoximide (IV) in 92.5% yield [m.p. 131-2°C, $[\alpha]_D^{25}$=+0.3° (c, 0.67, $CHCl_3$)]. In order to examine the stereochemical path of this reaction, (+)-IV was treated with sodium nitrite and conc. sulfuric acid (H_2O, 20°C, 1 hr) to afford (+)-(R)-o-methoxyphenyl phenyl sulfoxide (V) in 95.0% yield [$[\alpha]_D^{25}$=+79.0° (c, 0.62, $CHCl_3$, optical purity, 36.1%[5])].

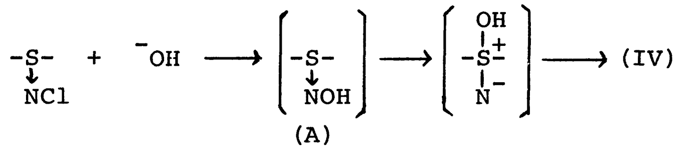


$$\text{o-}CH_3OC_6H_4\text{-}\underset{\underset{NCl}{\downarrow}}{\overset{*}{S}}\text{-}C_6H_5 \xrightarrow{^{-}OH} \text{o-}CH_3OC_6H_4\text{-}\underset{\underset{NH}{\downarrow}}{\overset{\overset{O}{\uparrow *}}{S}}\text{-}C_6H_5 \xrightarrow{HNO_2} \text{o-}CH_3OC_6H_4\text{-}\overset{\overset{O}{\uparrow *}}{S}\text{-}C_6H_5$$

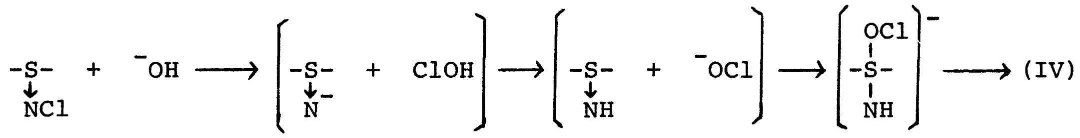
(-)-(S)-(III) (+)-(IV) (+)-(R)-(V)

Since the conversion of IV ⟶ V is known to proceed with a retention of configuration around the sulfur atom,[6] (+)-V should possess (R)-configuration. Thus, the alkaline hydrolysis of III to V is considered to proceed with 98% retention of configuration around the sulfur atom.[7]

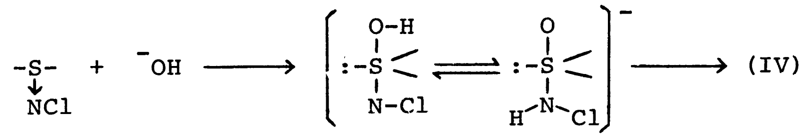
As to the probable mechanism for this reaction, the following three processes are conceivable; namely, the first one involves an initial attack by hydroxide ion on the nitrogen atom of III to afford an N-hydroxysulfimide intermediate (A), from which the hydroxy group migrates intramolecularly to afford IV. The second one involves an initial attack by hydroxide ion on the chlorine atom of III liberating hypochlorous acid, which then oxidizes the sulfimide to afford IV. The third one involves an initial attack by hydroxide ion on the sulfur atom of III to afford a sulfurane-like intermediate (B), which then decomposes rapidly to the corresponding sulfoximide (IV) and chloride ion. These mechanisms are shown below.

1) 

$$\underset{\underset{NCl}{\downarrow}}{\text{-S-}} + {}^{-}OH \longrightarrow \left[\underset{\underset{NOH}{\downarrow}}{\text{-S-}}\right] \longrightarrow \left[\underset{\underset{N^{-}}{|}}{\overset{\overset{OH}{|}}{\text{-S}^{+}\text{-}}}\right] \longrightarrow \text{(IV)}$$

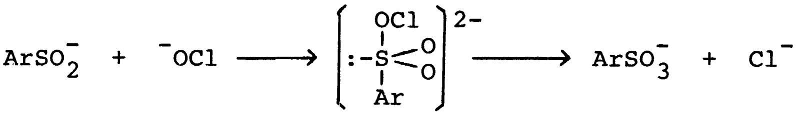
2) 

$$\underset{\underset{NCl}{\downarrow}}{\text{-S-}} + {}^{-}OH \longrightarrow \left[\underset{\underset{N^{-}}{\downarrow}}{\text{-S-}} + ClOH\right] \longrightarrow \left[\underset{\underset{NH}{\downarrow}}{\text{-S-}} + {}^{-}OCl\right] \longrightarrow \left[\underset{\underset{NH}{|}}{\overset{\overset{OCl}{|}}{\text{-S-}}}\right]^{-} \longrightarrow \text{(IV)}$$

3)

(B)

In order to examine the first possibility, we tried to isolate dimethyl- and diphenyl-N-hydroxysulfimide (A) by treating the sulfide-bromine complexes, prepared from dimethyl and diphenyl sulfide and bromine, with hydroxylamine, but failed to obtain either the corresponding N-hydroxysulfimides or sulfoximides, only the sulfoxides being obtainable. A similar attempt to obtain N-aminosulfimides by treating the sulfide-bromine complexes with hydrazine was also unsuccessful. Therefore, the 1st mechanism is quite unlikely. If the reaction would follow the 2nd mechanistic route, treatment of free diphenylsulfimide with NaOCl under alkaline condition should yield the corresponding sulfoximide. However, actual treatment of free diphenylsulfimide with NaOCl under alkaline condition for 1 hr did not give the corresponding sulfoximide, but afforded only N-chlorodiphenylsulfimide, suggesting that hypochlorite ion is a good chlorinating agent of the free sulfimide but not a good oxidizing agent to afford the sulfoximide. Thus, the best conceivable mechanism is the 3rd one in view of these stereochemical observations.

Recently, Kice and Puls[8)] also suggested that the most plausible mechanism of the reaction of arylsulfinate with hypochlorite ion to involve a sulfurane intermediate as shown below.



Oxidation of sulfoxides[9)] and sulfonium salts[10)] with perbenzoate anion has also been considered to proceed via similar intermediates.

References and Footnotes

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4) Optically pure (I) has $[\alpha]_D^{25}$=-194° ($CHCl_3$).[3-b)]

5) Optically pure (-)-(S)-(V) was prepared according to the usual method*; $[\alpha]_D^{25}$=-196° (c, 1.12, $CHCl_3$). *K. Mislow et al., J. Am. Chem. Soc., 87,

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7) Oxidation and reduction of the sulfimide (I) were reported previously to proceed with retention of configuration around the sulfur atom.[3-b] ((-)-(S)-(I) $[\alpha]_D^{25}=-194°$ ($CHCl_3$) ⟶ (+)-(R)-(V) $[\alpha]_D^{25}=+219°$ ($CHCl_3$))

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