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Rearrangements of Tertiary Amine Oxide. XV.[1] The Reaction of Heterocyclic *N*-Oxides with *p*-Nitrobenzenesulfinyl Chloride

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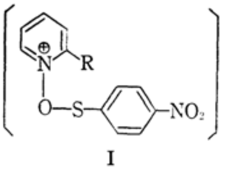
In the reaction of pyridine and α-picoline *N*-oxide with *p*-nitrobenzenesulfinyl chloride, the N–O bond of the intermediate salt appears to cleave homolytically, as in the case of *N*-oxide with *p*-nitrobenzenesulfenyl chloride, and the *p*-nitrosulfonyl radical which arises from the homolytic cleavage of the N–O bond is considered to be so stable that only the secondary reaction products from the sulfonyl radical, and no heteroring-substituted products, are obtained. It is the same in the case of unsubstituted benzenesulfinyl chloride.

We have reported earlier that, in the reaction of *p*-nitrobenzenesulfenyl chloride with pyridine and α-picoline *N*-oxides, the N–O bond of the incipient salt I was homoliticaly cleaved, giving only reduced pyridine bases, while neither ring-substituted rearrangement products nor unreacted *N*-oxides were obtained.[2]



R=H, CH$_3$

I

On the other hand, the reactions of pyridine and isoquinoline *N*-oxide with tosyl chloride gave ring-substituted rearrangement products, apparently

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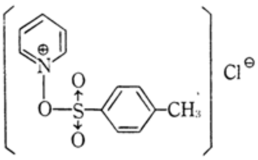
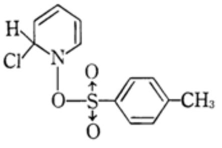
[1] Part XIV: S. Oae and S. Kozuka, *Tetrahedron*, **21**, 1971 (1965).

[2] S. Oae and K. Ikura, This Bulletin, **38**, 58 (1965).

formed through the heterolytic cleavage of the N–O linkage of the intermediate IIA, formed by the nuclear addition of Cl ion to the II salt.[3]



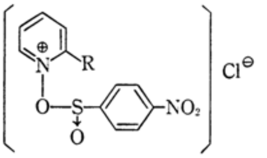
II



IIA

The marked difference between these two reactions may lie in the difference in the reacting organic sulfur chlorides. Namely, the former, *p*-nitrobenzenesulfenyl chloride, is electronically neutral, while the latter has the positive character of the sulfur atom, which would cause a facile heterolytic cleavage of the N–O bond. This may lead to the idea that sulfinyl chlorides, which has a more positive sulfur atom than sulfenyl chlorides and a less positive sulfur atom than sulfonyl chlorides, would give rise to a reaction between the two above reactions.

Thus we have investigated the reaction of *p*-nitrobenzenesulfinylchloride with pyridine and α-picoline *N*-oxides, a reaction which involves the incipient formation of the III salt.

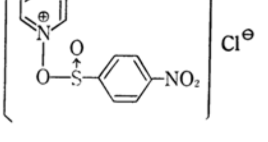


R=H, CH$_3$

III

Results and Discussion

p-Nitrobenzenesulfinyl chloride was prepared by chlorinating *p*, *p*′-dinitrodiphenyldisulfide in glacial acetic acid with chlorine gas, and it was identified by means of the reaction product with acetone, which has the analytical composition of the α-sulfinylacetone. When equivalent amounts of pyridine *N*-oxide and *p*-nitrobenzenesulfinyl chloride were mixed in a benzene solution, colorless crystalline precipitates were formed immediately, with an evolution of heat. The crystals, which are very hygroscopic, have the analytical composition of the salt IV, as is shown below:



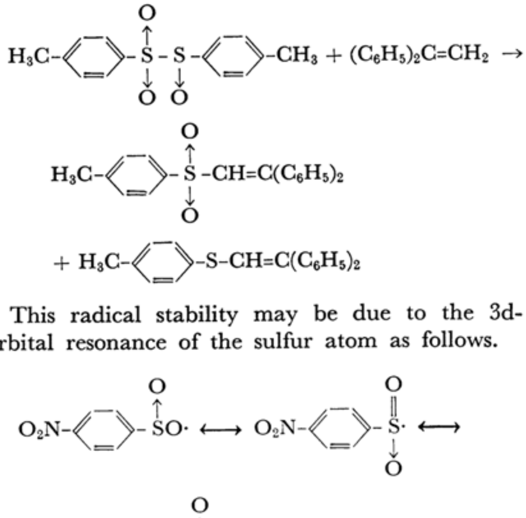
IV

The IV salt was obtained after the thorough removal of the solvent benzene under the vaccum; the salt was then heated at 180—200°C for two hours under a nitrogen stream. It began to melt at around 80°C, but no color change was observed until around 180°C; at around 180°C the salt started to melt, giving a dark, oily mass, and sulfur dioxide was evolved.

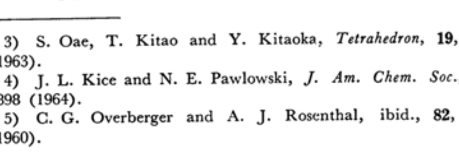
Among the reaction products isolated were pyridine, *p*-nitrochlorobenzene, *p*-nitrobenzenesulfonic acid, and *p*, *p*′-dinitrodiphenyldisulfide.

Neither a ring-substituted rearrangement product nor unreacted pyridine *N*-oxide was isolated among the products. These reaction products and their distributions seem to indicate that this reaction is also initiated by the cleavage of the N–O bond of the IV salt, just as in the case of *N*-oxide with *p*-nitrobenzenesulfenyl chloride, and not like the case of *N*-oxide with tosyl chloride. Here again the sulfonyl radical, V, which was presumed to be formed at first by the cleavage of the N–O bond of the IV salt, is apparently stable.

The existence of this radical was reported previously by Kice[4] and Overberger[5]. Namely, Kice has reported that the thermal decomposition of aromatic sulfinyl sulfonate gives the tolyl sulfonyl radical, which can be trapped with gulvinoxyl. He has also shown that the radical can add to an olefine to give a stable addition product, as is shown below:



This radical stability may be due to the 3d-orbital resonance of the sulfur atom as follows.



If the reaction would follow a path similar to that of pyridine *N*-oxide with tosyl chloride, one

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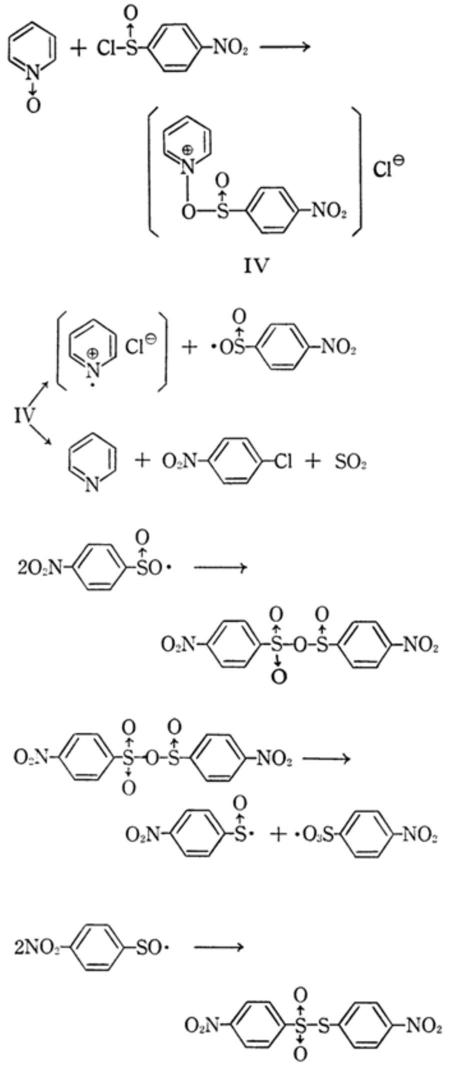
[3] S. Oae, T. Kitao and Y. Kitaoka, *Tetrahedron*, **19**, 827 (1963).

[4] J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, **86**, 4898 (1964).

[5] C. G. Overberger and A. J. Rosenthal, ibid., **82**, 117 (1960).

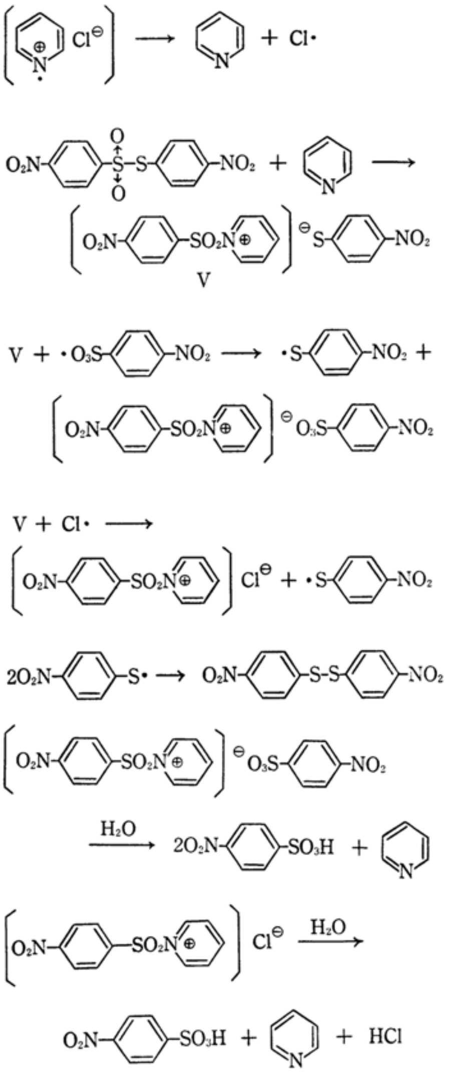
would expect some pyridine ring-substituted compound among the product mixture, for the heterolytically-cleaved species, presumably the nitrobenzene sulfonium ion, is considered to react with the other cleaved partner to give perhaps a very stable sulfonyl product.

In this reaction, however, there was apparently no formation of any heteroring-substituted product, and the yield of the pyridine recovered was nearly quantitative. The entire reaction is quite similar to the reaction with *p*-nitrobenzenesulfenyl chloride. These findings, and the results of the previous work on the thermal decomposition of aromatic sulfinyl sulfonate, seems to favor the homolytic cleavage of the N–O bond of the IV salt. Thus, the overall reaction scheme may be formulated nicely as below:



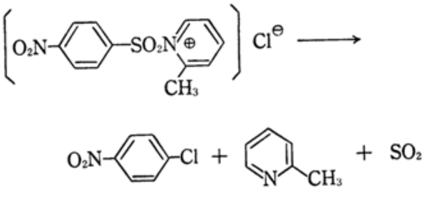
(1) (2) (3) (4) (5) (6)

p-Nitrochlorobenzene was probably formed by step 3. Here again the *p*-nitrochlorobenzene was

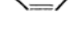


(7) (8) (9) (10) (11) (12) (13)

obtained as in the case of the reaction of *p*-nitrobenzenesulfenyl chloride with α-picoline *N*-oxide, where the formation of *p*-nitrochlorobenzene was considered to proceed through the following pathway:[2)]

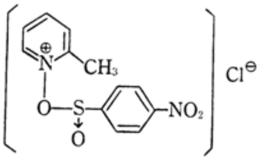


In this reaction the amount of this compound actually isolated was rather large as compared to those of the disulfide and *p*-nitrobenzenesulfonic acid.

About the formation of the radical, (O_2N–  –$SO_3\cdot$) is now yet questionable, but if step

5 is assumed, the reaction products are cleverly explained, and this radical might be occur with the charge transfer with V, as is shown by step 9.

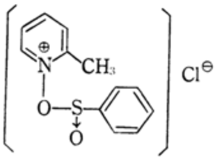
The same reaction was applied to α-picoline *N*-oxide. In this case, too, equimolar amounts of α-picoline *N*-oxide and *p*-nitrobenzenesulfinylchloride were mixed in a benzene solution. White crystalline precipitates gradually formed, with an evolution of heat; these precipitates changed to a dark oil during the removal of the solvent. The dark oil was found by analysis to have the composition derived from the VI salt.



VI

This salt was heated at 140—150°C for two hours under a nitrogen stream. The evolution of hydrogen chloride began at around 140°C, and sulfur dioxide gas was also observed during the heating, although the amounts of both gases were small. The reaction products isolated were α-picoline, *p*, *p*′-dinitrodiphenyl disulfide, and *p*-nitrobenzenesulfonic acid. Here again an undetectable amount of any hetero ring-substituted products was obtained among the reaction products in spite of the noticeable amounts of hydrogen chloride evolved. Here, *p*-nitrochlorobenzene was not obtained. However, the amount of disulfide was larger than in the case of pyridine *N*-oxide. Judging from these reaction products, therefore, the reaction also seems to proceed via a similar homolytic cleavage of the N–O bond of the VI salt, and the overall reaction scheme may be considered to be quite analogous to the one previously postulated for that with pyridine *N*-oxide except for step 3.

We have also extended the reaction to unsubstituted benzenesulfinyl chloride with α-picoline *N*-oxide. When equimolar amounts of α-picoline *N*-oxide and benzenesulfinyl chloride were mixed in a benzene solution, heat evolved and a dark red oil was gradually precipitated. Apparently the decomposition of the conceivable incipient salt was very facile, and the resultant dark oil was a reacted mixture. However, in this case, it is considered that the reaction proceeds through the formation of the VII salt. The reaction products isolated were α-picoline, diphenyl disulfide, and benzenesulfonic acid.



VII

This reaction was also considered to proceed like the other two reactions.

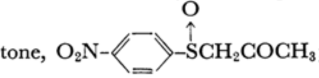
Experimental

The Preparation of *p*-Nitrobenzenesulfinyl Chloride.—*p*, *p*′-Dinitrodiphenyl disulfide was mixed with exactly twice as much glacial acetic acid in chloroform, and chlorine gas was introduced at -5—-10°C until no hydrogen chloride evolution was recognized. Then the chloroform and acetyl chloride formed were thoroughly removed in vacuo at room temperature.

The residue formed cubic crystals. This was used for the succeeding reaction without further purification; m. p. 58—60°C.

Found: N, 7.12. Calcd. for $C_6H_4NO_3SCl$: N, 6.81%.

This chloride was identified by reacting it with acetone at room temperature until its derivatives were produced. The product has the correct analytical composition of the α-sulfinylacetone,



$O_2N-C_6H_4-\overset{O}{\overset{\uparrow}{S}}CH_2COCH_3$; m.p. 66—67°C.

Found: C, 47.56; H, 4.02; N, 6.64; S, 14.90. Calcd. for α-sulfinylacetone: C, 47.56; H, 3.99; N, 6.16; S, 14.11%.

The Reaction of Pyridine *N*-Oxide with *p*-Nitrobenzenesulfinyl Chloride.—When both a benzenes solution of pyridine *N*-oxide (1.00 g.) and *p*-nitrobenzenesulfinyl chloride (2.00 g.) were mixed at room temperature, the white salt, IV, precipitated at once. Then the solvent was removed in vacuo at room temperature, and the residue was heated at around 180—200°C for two hours under a nitrogen stream. The reaction mixture became a dark, oily mass, and sulfur dioxide was evolved. After the reaction, dilute hydrochloric acid was added, and the mixture was extracted with chloroform.

The removal of the solvent chloroform gave *p*-nitrochlorobenzene (1.10 g.) and *p*, *p*′-dinitrodiphenyl disulfide (0.05 g.).

The aqueous layer was made neutral with sodium carbonate and extracted with chloroform. The removal of the solvent gave pyridine (0.6 g.). Then, a 10% ethanol solution of benzylisothiourea hydrochloride salt was added to the aqueous mother solution, from which pyridine had already been recovered, and the crystals thus precipitated was collected and recrystallized from a water-ethanol mixture. These crystals were thiuronium salt of *p*-nitrobenzenesulfonic acid (0.78 g.).

The sulfur dioxide was trapped by passing it through a solution of barium hydroxide; the quantity of SO_2 was 0.36 g.

The Isolation of 1-*p*-Nitrobenzenesulfinylpyridinium Salt IV.—The hygroscopic crystalline precipitate obtained by reacting *p*-nitrobenzenesulfinyl chloride and pyridine *N*-oxide was washed with ethanol, dried, and analyzed; m. p. 98—100°C.

Found: C, N, 9.62. Calcd. for $C_{11}H_9N_2O_4SCl$: N, 9.32%.

The Reaction of α-Picoline *N*-Oxide with *p*-Nitrobenzenesulfinyl Chloride. — α-Picoline *N*-

oxide (2.0 g.) and *p*-nitrobenzenesulfinyl chloride (4.0 g.) were used. The colorless salt which was gradually precipitated changed to a dark oil during the removal of the solvent. After the solvent had been removed, the dark oil was heated at 140—150°C for two hours under a nitrogen stream. The treatment of the reaction products was exactly the same as in the case of pyridine *N*-oxide.

The product from the chloroform layer was *p*, *p'*-dinitrodiphenyl disulfide (2.1 g.). From the aqueous layer *α*-picoline (1.3 g.) and *p*-nitrobenzenesulfonic acid (1.6 g.) were obtained.

The Isolation of 1-*p*-Nitrobenzenesulfinyl-2-picolinium Salt VI.—The dark oil precipitate obtained by reacting *p*-nitrobenzenesulfinyl chloride and *α*-picoline *N*-oxide was washed well with water and recrystallized from a water-ethanol mixture; m. p. 174—177°C.

Found: N, 9.09. Calcd. for $C_{12}H_{11}N_2O_4SCl$: N, 8.90%.

The Reaction of *α*-Picoline *N*-Oxide with Phenylsulfinyl Chloride.—*α*-Picoline *N*-oxide (1.5 g.) and phenylsulfinyl chloride (2.1 g.) were reacted as usual in a benzene solution. Apparently the reaction got started immediately, forming no precipitated salt, but a dark red oil was gradually precipitated while the solvent was bing removed with a vigorous reaction. Then the dark oil was heated an additional hour at around 160°C. The treatment of the reaction products was exactly the same as in the above two cases.

The product from the chloroform layer was diphenyl disulfide (1.1 g.). From the aqueous layer, *α*-picoline (1.0 g.) and benzenesulfonic acid (0.8 g.) were obtained.

All the compounds were identified by mixed melting point, infrared spectra, and elemental analyses.