ORIENTATION AND MECHANISM OF REACTIONS OF AROMATIC AMINES WITH SULFUR MONOCHLORIDE

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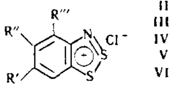
The reaction of m-substituted anilines with sulfur monochloride has been studied. It has been shown that cyclization with the formation of 1,3,2-benzothiazathiolium compounds takes place in the position para to the substituent. The introduction of methoxy groups into o-nitroanilines interferes with the displacement of the nitro group by the chlorine atom. A nucleophilic reaction mechanism has been proposed according to which the nitro group is displaced after the formation of the thiathioniaazine ring.

Aromatic amines having even one free ortho position react with sulfur monochloride forming benzo-1-thia-2-thionia-3-azine salts I–VII (Hertz compounds) [1].



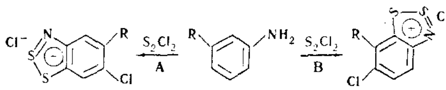
I–VII

I $R' = Cl$, $R'' = CH_3$, $R''' = H$;
II $R' = Cl$, $R'' = CH_3O$, $R''' = H$;
III $R' = CH_3O$, $R'' = CH_3O$, $R''' = H$;
IV $R' = R'' = Cl$, $R''' = H$;
V $R' = CH_3O$, $R'' = H$, $R''' = NO_2$;
VI $R' = CH_3O$, $R'' = H$, $R''' = Cl$;
VII $R' = R'' = CH_3O$, $R''' = NO_2$

If hydrogen or an electron-accepting substituent is present in the position para to the nitrogen atom in the initial amine, the substituent is displaced by chlorine [2]. Hertz compounds have long been used in the industrial synthesis of o-aminothiophenols, but their structure has been studied very little, which is due to the difficulty of their isolation, purification, and identification [3].

There is no information in the literature on how meta-substituted anilines react with sulfur monochloride. To determine the direction of the reaction, we synthesized Hertz compounds from m-toluidine, m-anisidine, m-chloroaniline, and 4-aminoveratrole. The reaction products were isolated in the form of the previously-unreported double salts with zinc chloride, which are readily obtained by the action of a solution of anhydrous zinc chloride in acetic acid on a solution of the benzothiazathiolium salts in anhydrous acetic or formic acid. The zinc chloride derivatives obtained proved to be considerably more stable than the chlorides.

Two variants of the reaction with sulfur monochloride are theoretically possible for the meta-substituted anilines, A and B.



PMR spectroscopy proved to be very convenient for determining the structure of the reaction products. Fig. 1 gives the spectra of the compounds synthesized, I–IV. In the spectra of the products studied, only the signals of isolated protons are seen, i.e., the reaction of the anilines with sulfur monochloride takes place in direction A.

It is known [4] that the action of sulfur monochloride on o-nitroaniline leads not only to chlorination in the para position but also the displacement of the nitro group by a chlorine atom. The possibility of determining in a simple manner the structure of the products obtained by using their PMR spectra has enabled this reaction to be studied in more detail. Assuming that it has a nucleophilic nature, we decided to investigate the influence of methoxy groups in the initial nitroaniline on the displacement of the nitro group. The reaction of 4-amino-3-nitroanisole with sulfur monochloride was recently performed by British workers [5], who isolated a product which did not contain a nitro group. The PMR spectra of the substances that we obtained by the reaction of 4-amino-3-nitroanisole and of 4-amino-3-nitroveratrole are given in Fig. 2. We see from these spectra that in the reaction of the aminonitroanisole (Fig. 2, part 1), a mixture of products V and VI, is formed. Two groups of signals from the ring protons and two signals from a methoxy group can be seen. The nitro derivative V is evidently represented by signals in weaker magnetic fields than that of the chloro derivative VI. We see from the ratio of the areas of the peaks of the methyl protons that the amount of nitro compound in the mixture is approximately 1.5 times greater than that of the chloro derivative. Elementary analysis shows that under these conditions only partial displacement of the nitro group takes place, the ratio of the chlorinated and nonchlorinated products being approximately 2 : 3. However, in the reaction of the aminonitroveratrole (Fig. 2, part 2) the NMR spectrum has two signals: one in the weak field corresponding to a ring proton, and the other (unresolved) corresponding to the protons of the methoxy groups, the intensity of the second signal being six times greater than that of the first. The elementary analysis of this product (VII) shows that the nitro group has not been displaced. Thus, the introduction of electron-donating methoxy groups into the o-nitroanilines prevents the replacement of the nitro group by chlorine, which confirms the nucleophilic nature of this reaction.

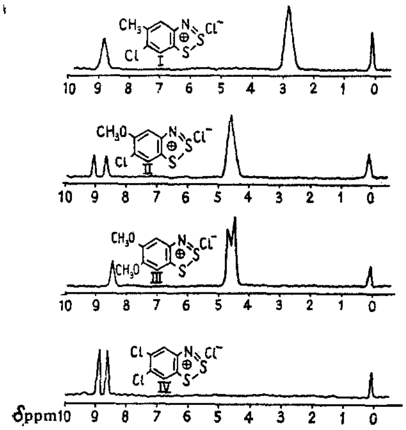
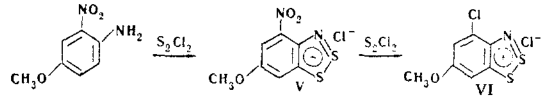


Fig. 1. PMR spectra of the reaction products of meta-substituted anilines with sulfur monochloride.

The question arises as to whether the displacement of the nitro group by chlorine takes place before or after the formation of the thiathioniaazine dithiazolium ring. To decide this, we heated for an additional six hours the mixture of products obtained from heating 4-amino-3-nitroanisole with sulfur monochloride under the conditions of the Hertz reaction for six hours. The elementary analysis of the compound obtained, VI, showed that with this treatment the nitro group was completely displaced. However, when the reaction was carried out for just two hours, only compound V which contains a nitro group was obtained. These facts show that in the reaction with sulfur monochloride the heterocycle is formed first and then the nitro group is replaced nucleophilically by a chlorine atom in the following manner.



EXPERIMENTAL

The benzothiazathiolium chlorides (I–III) were obtained by the following general method. At room temperature, 0.1 mole of an amine hydrochloride was mixed with 1 mole of sulfur monochloride and the mixture was slowly heated to 70–80° C under reflux, being protected from atmospheric moisture. Then it was stirred at this temperature until the evolution of hydrogen chloride ceased (5–7 hr), after which it was dissolved in 30 ml of dry benzene (all the solvents used in this work were carefully dehydrated). The solution was cooled and the precipitate was filtered off. Then it was carefully washed with carbon disulfide and ether and dried in vacuo. The crude product was crystallized from thionyl chloride [3], washed with petroleum ether, and dried in vacuo.

The benzothiathioniaazine chlorides (IV–VII) were obtained by the following general method. A solution or suspension of 0.1 mole of the corresponding amine in glacial acetic acid (50 ml) was added with stirring to 100 ml of sulfur monochloride at room temperature and the mixture was kept under these conditions for 3 hr. Then it was heated to 80–95° C for 30 min and dissolved in 100 ml of benzene. The precipitate was filtered off, washed with carbon disulfide, benzene, and ether, and dried in vacuo. The dried product was dissolved in formic acid (50 ml) with heating (50° C) and the solution was stirred with 0.1 g of animal charcoal for 1 hr. The charcoal was filtered off and the resulting solution was slowly added to 200 ml of ether. The precipitate that formed was filtered off, washed with ether, and dried in vacuo.

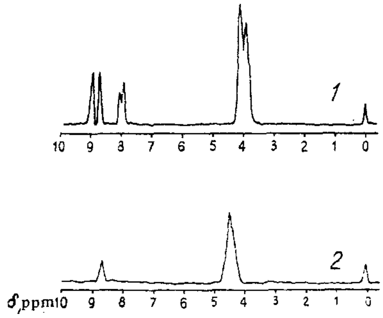


Fig. 2. PMR spectra of the reaction products of sulfur monochloride with 1) 4-amino-3-nitroanisole, i.e., V and VI, 2) 4-amino-3-nitroveratrole, i.e., VII.

The double salts of the Hertz compounds (I–VII) with zinc chloride were obtained by the following general method. A solution of 1 g of the compound in formic acid was treated with 0.1 g of animal charcoal. After the mixture had been stirred for half an hour, the charcoal was filtered off and the solution was treated with a small amount of a 10% solution of anhydrous zinc chloride in acetic acid. On standing a precipitate slowly deposited. This was filtered off, washed with acetic acid and ether, and dried in vacuo, after which it was crystallized from formic acid. The elementary analyses of the double salts are given in the table.

Double Salts of Hertz Compounds with Zinc Chloride

Double salt of compound	Empirical formula	Found, %			Calculated, %			Yield, %
		N	S	Cl	N	S	Cl	
I	$C_7H_5Cl_2NS_2 \cdot ZnCl_2$	—	17,00	37,91	3,74	17,15	37,78	90
II	$C_7H_5Cl_2NOS_2 \cdot ZnCl_2$	—	16,75	36,04	3,57	16,63	36,22	93
IV	$C_6H_2Cl_3NS_2 \cdot ZnCl_2$	—	16,05	44,78	3,55	16,25	44,95	87
III	$C_8H_6ClNO_2S_2 \cdot ZnCl_2$	—	16,78	27,38	3,67	16,62	27,61	98
VII	$C_8H_7ClN_2O_4S_2 \cdot ZnCl_2$	6,64	14,71	24,62	6,51	14,92	24,82	81
V	$C_7H_5ClN_2O_3S_2 \cdot ZnCl_2$	6,98	16,19	26,78	7,21	16,01	26,55	60
VI	$C_7H_5Cl_2NOS_2 \cdot ZnCl_2$	3,68	16,75	36,01	3,57	16,63	36,22	56
Mixture V+VI	—	4,84	16,39	29,83	—	—	—	60

The PMR spectra were recorded on a Perkin Elmer RK instrument with a working frequency of 60 MHz. The solvents used were deuteriosulfuric acid and hexamethanol. For the sulfuric acid solution tetramethylsilane in ethylbenzene was used as the internal standard.

REFERENCES

1. R. Hertz, Freidlender, **14**, 908, 1926.
2. W. Hixson and D. Gauwenberg, J. Am. Chem. Soc., **52**, 2118, 1930.
3. B. Kh. Strelets and L. S. Éfros, ZhOrKh, 5, 151, 1969.
4. K. Blomqust and L. Dinguid, J. Org. Chem., **12**, 718, 1947.
5. P. Hope and L. Wiles, J. Chem. Soc., 1642, 1967.

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