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SMILES REARRANGEMENT OF TETRACHLOROPYRIDYL METHYL-HYDROXYPHENYL SULFONE

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In the present work we have investigated the Smiles rearrangement [1] for compounds which contain as activated aromatic system a tetrachloropyridyl residue bonded to a benzene ring by a sulfide or sulfonyl bridge. To prepare compounds of this type, we investigated the reaction of 2,3,5,6-tetrachloropyridyl-4-sulfenyl chloride (I) with p-cresol and p-chloro phenol. In the IR spectrum of the compound obtained as a result of the condensation with p-cresol, an absorption band in the 3500 cm^{-1} region was detected (OH group), which unequivocally demonstrates that the attack of the sulfenyl chloride I is directed to one of the carbon atoms of the benzene ring, namely, to the ortho position to the hydroxyl group, whose donor properties exceed those of the methyl group, as a result of which 2,3,5,6-tetrachloropyridyl 4-(2'-hydroxyl-5'-methylphenyl)sulfide (IIa) is formed. Replacement of the methyl group in p-cresol by the electronegative chlorine atom considerably retards the reaction rate.

In the action of aqueous or alcoholic alkali on the sulfides IIa and IIb, the solution rapidly acquires a stable bright-yellow coloration (λ_{max} = 390 nm), which indicates the formation of the spiro Meisenheimer complex (A). It should be noted that ionization of the hydroxyl group can be effected only with the aid of a sufficiently strong base, for example, sodium hydroxide or potassium hydroxide, or alkali metal alcoholates. In the presence of triethylamine or piperidine, complex A is not formed [2].

Upon the action of hydrochloric acid or dimethyl sulfate on the complex A, there are formed, respectively, the sulfides IIa and b, or 2,3,5,6-tetrachloropyridyl-4-2'-methoxy-5'-methyl(or chloro)phenyl sulfides (IIIa, b). In spite of the higher nucleophilicity of the sulfur atom as compared with oxygen, opening of the oxathiolane ring of complex A under the action of electrophiles takes place, not at the C—S bond, but at the C—O bond. This is apparently explained by the stability of the phenolate anion [3], as a result of which the reaction inverse to the formation of complex A takes place easily. At 50° the orange coloration of complex A disappears, and cyclization products separate from the solutions; in the UV spectra of these an absorption band at 296 nm is detected, and in the IR spectra hydroxyl group absorption is absent. In the mass spectra of the cyclization products peaks for molecular ions at 317 and 337 are observed, respectively. If cyclization takes place with involvement of an oxygen anion (compound B), which attacks the 3-position, the reaction products will be the corresponding 3-azaphenoxathines (IVa and b). In the case of a preliminary Smiles rearrangement, the formation of isomeric 2-azaphenoxathiines is possible. We suggest that, thanks to the insufficient stability of the spiro-complex A, and by analogy with polynitrobenzene derivates [3], we obtained the isomers IV.

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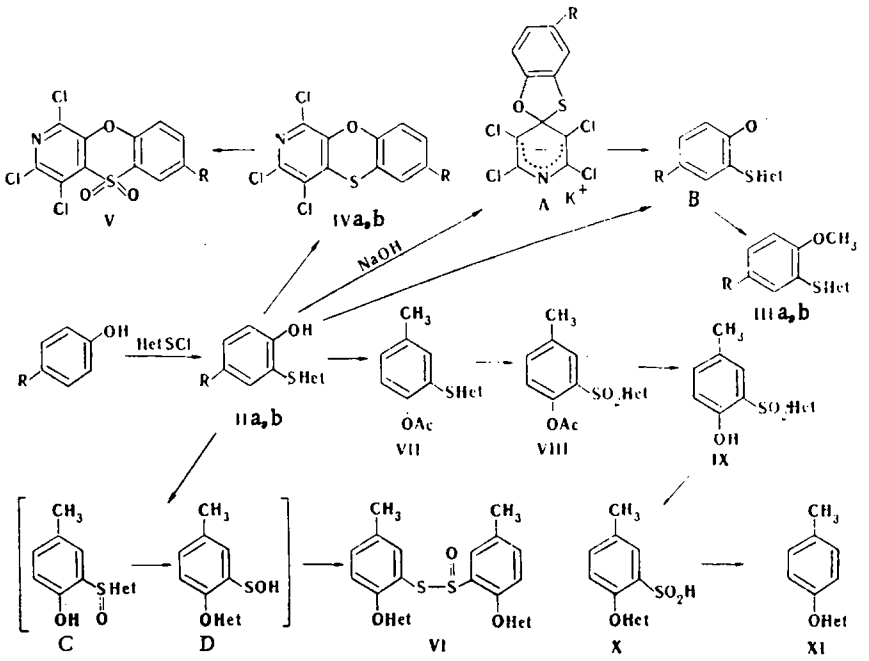
On oxidation of compound IVb with peracetic acid, the dioxide V is formed.



Het = 2,3,5,6-tetrachloro-4-pyridl; a R=CH3, b R=Cl

By oxidation of the sulfide IIa with hydrogen peroxide in acetic acid, instead of the expected sulfoxide we obtained bis[2-(2'3',5',6'-tetrachloropyridyloxy)-5-methylphenyl] sulfide sulfoxide (VI) as a result of a Smiles rearrangement of sulfoxide B into the unstable sulfenic acid D, which is converted into product VI. The structure of compound VI was confirmed by use of IR and mass spectra.

To obtain the corresponding sulfone from sulfide IIa, with the objective of protecting the hydroxyl group the latter was acetylated to the corresponding (2-acetoxy-5-methylphenyl) sulfide (VII). Oxidation of compound VII leads to the formation of sulfone VIII. On hydrolysis of the acetoxy group in compound VIII in acid medium, compound IX was obtained, which is transformed by the action of sodium hydroxide into the stable Smiles rearrangement product — 2-(2',3',5',6'-tetrachloropyridyloxy)-5-methylbenzenesulfinic acid (X). At 150° compound X evolves sulfur dioxide and is converted into 4-(4'-methylphenoxy)-2,3,5,6-tetrachloropyridine (XI). The structure of the latter was confirmed by an independent synthesis of it from pentachloropyridine and sodium p-cresolate. According to gas-chromatographic evidence, the latter reaction leads to the formation of a mixture of the 4- and 2-isomers (92 and 8%, respectively). Under the action of gaseous ammonia, product XI is converted into the known 4-amino-2,3,5,6-tetrachloropyridine [5].

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument, in KBr disks; the UV spectra, in a Specord UV-vis instrument, in ethanol. Gas-chromatographic analysis was performed on a "Tsvet-4" chromatograph using a flame ionization detector, on SE-30 siloxane polymer deposited on chromosorb W. The column temperature was 230°; that of the vaporizer, 350°; the carrier gas (nitrogen) velocity was 30 ml/ml. Molecular weights of the compounds were measured on an MS-1302 mass-spectrometer having a system of direct introduction of the specimen into the ion source; ionization chamber temperature, 250°; ionizing electron energy, 70 eV. Characteristics of the synthesized substances are given in Table 1.

2,3,5,6-Tetrachloropyridyl-4[2'-hydroxy-5'-methyl(or chloro)phenyl] Sulfides (II a, b). A mixture of 10 mmole of 2,3,5,6-tetrachloropyridyl-4-sulfenyl chloride (I) and 13 mmole of p-cresol or p-chlorophenol plus 0.1 g of $AlCl_3$ was boiled in 30 ml of dichloroethane for 20 min. The reaction mixture was treated with 30 ml of 0.1 N HCl, and the organic layer was separated and dried with $CaCl_2$. The solvent was distilled off under vacuum. UV spectrum in ethanol, λ_{max} = 230, 320 nm.

TABLE 1. Characteristics of Synthesized Compounds

Compound	mp, °C	Found, %		Empirical formula	Calculated, %		Yield, %
		Cl	S		Cl	S	
IIa	140—141	39,9	9,0	$C_{12}H_7Cl_4NOS$	40,0	9,0	91
IIb	146—148	47,5	8,6	$C_{11}H_4Cl_5NOS$	47,3	8,5	90
IIIa	150—151	—	8,8	$C_{13}H_9Cl_4NOS$ b	—	8,7	95
IIIb	156—158	—	8,2	$C_{12}H_6Cl_5NOS$ c	—	8,2	87
IVa	140—141	33,6	10,0	$C_{12}H_6Cl_3NOS$	33,4	10,0	55
IVb	172—173	41,9	9,5	$C_{11}H_3Cl_4NOS$	41,8	9,4	88
V	215—216	38,6	8,7	$C_{11}H_3Cl_4NO_3S$	38,4	8,6	85
VI	266—268	38,9	8,9	$C_{24}H_{12}Cl_8N_2O_3S_2$	39,2	8,8	90
VII	124—125	35,6	8,0	$C_{14}H_9Cl_4NO_2S$	35,8	8,1	88
VIII	166—168	33,0	7,5	$C_{14}H_9Cl_4NO_4S$	33,1	7,4	70
IX	187—188	36,5	8,2	$C_{12}H_7Cl_4NO_3S$	36,7	8,2	85
X	146—147	36,9	8,3	$C_{12}H_7Cl_4NO_3S$	36,7	8,2	90
XI	108—110	43,9	—	$C_{12}H_7Cl_4NO$ d	43,4	—	62

[a]Compound IIb was crystallized from heptane, VI and VIII, from CH_3COOH, the rest, from aqueous alcohol. [b]Found: CH_3O, 8.5%, Calculated: CH_3O, 8.4%; [c]Found: CH_3O. 8.0%. Calculated: CH_3O. 7.9%; [d]Found: N, 4.2%. Calculated: N, 4.3%.

2,3,5,6-Tetrachloropyridyl-4 [2'-methoxy-5'-methyl(or chloro)phenyl] Sulfides (IIIa and b). The sulfide (IIa or IIb) (10 mmole) was dissolved in 20 ml of 2 N NaOH, 6 ml of dimethyl sulfate was added, and the mixture was heated for 1 h at 100°.

1,2,4-Trichloro-8-methyl(or chloro)-3-azaphenoxathiines (IV a and b). To a solution of 10 mmole of sulfide IIa or IIb in 50 ml of tert.-butyl alcohol was added 0.01 g-atom of potassium in 15 ml of tert.-butyl alcohol. The orange-colored solution was boiled for 30 min.

1,2,4,8-Tetrachloro-3-azaphenoxathiine-10,10-dioxide (V). To a solution of 10 mmole of compound IVb in 60 ml of glacial acetic acid was added 20 ml of 30% H_2O_2. The mixture was boiled for 2 h. Yield, 3.15 g.

Bis-[2-(2',3',5',6'-tetrachloropyridyloxy)-5-methylphenyl]Sulfide Sulfoxide (VI). To a solution of 28 mmole of sulfide IIa in 20 ml of acetic acid was added 5 ml of 30% H_2O_2 and the mixture was boiled for 30 min. The precipitate which settled out was filtered off. Yield, 1 g. IR spectrum: 1100 cm^{-1} (SO). Found: M, 720; calculated, M 724.

2,3,5,6-Tetrachloropyridyl-4 (2'-acetoxy-5'-methylphenyl) Sulfide (VII). To a solution of 10 mmole of sulfide IIa in 30 ml of acetic anhydride was added 2 ml of pyridine and the mixture was heated for 1 h at 100°; then it was poured into water. Yield, 2.8 g.

2,3,5,6-Tetrachloropyridyl-4 (2'-acetoxy-5'-methylphenyl) Sulfone (VIII). To a solution of 1.25 mmole of sulfide VII in 15 ml of acetic anhydride was added 3 ml of 30% H_2O_2, and the mixture was heated for 2 h at 110°. Then it was poured onto ice. Yield, 0.38 g.

2,3,5,6-Tetrachloropyridyl-4 (2'-hydroxy-5'-methylphenyl) Sulfone (IX). Sulfone VII (0.7 mmole) was heated at 100° in a mixture of 10 ml of CH_3COOH and 10 ml of 80% H_2SO_4 for 20 min. The mixture was poured into water. Yield, 0.24 g.

2-(2',3',5',6'-Tetrachlropyridyloxy)-5-methylbenzenesulfinic Acid (X). Sulfone IX (0.7 mmole) was dissolved in 30 ml of 0.1 N NaOH, the mixture was acidified with HCl to a weakly acid reaction, and the precipitate which separated was filtered off. Yield, 0.27 g.

4-(4'-Methylphenoxy)-2,3,5,6-tetrachloropyridine (XI). A) The acid X (0.26 mmole) was heated for 10 min at 170°. The product was treated with 10 ml of 0.1 N NaOH, and the precipitate was filtered off. Yield, 0.05 g.

B) A mixture of 10 mmole of pentachloropyridine, 10 mmole of sodium p-cresolate, and 25 ml of dimethylformamide was heated for 4 h at 100°, and then was poured into water. Yield, 3.2 g (92%).

4-Amino-2,3,5,6-tetrachloropyridine (XII). Dry ammonia was passed into a solution of 20 mmole of compound XI in 10 ml of dimethylformamide for 2 h at 130°. The mixture was poured into water. Yield, 0.35 g (76%). Mp 218° (from aqueous ethanol). Lit. [5]: mp 220-221°.

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REACTIONS OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH AMINES

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The literature contains highly contradictory data on products of the reaction of 2H-azirines with aromatic and cyclic amines, and there are no data at all on the reaction of azirine I with aliphatic amines. As a result of heating of 2-phenylazirine with aniline and its derivatives, six types of compounds were obtained: benzanilide, pyrazine, phenacylaniline, indole, pyrrole, and an enediamine [1]. The reaction of 5-aminoisoxazoles with aniline and its analogs gives N,N-diarylureas and substituted pyrazine-2,5-dicarboxamides, products of the reaction of amines with the intermediate 2H-azirine [2, 3]. As a result of 1,3-dipolar cycloaddition of substituted aziridines to 2-phenyl-2H-azirine, diazabicyclohexanes are formed [4].

We investigated the reactions of 2,2-dimethyl-3-phenylazirine (I) with ammonia, methylamine, aziridine, pyrrolidine, and piperidine. As a result of the reaction of azirine I with ammonia and methylamine, adducts (III and IV) of the reacting substances in 2:1 and 1:1 ratios, respectively, were isolated. The vibrational spectra of the obtained compounds contained bands of NH_2-group vibrations (3300 and 3380 cm^{-1}); the spectrum of compound III also contained a band of NH-group stretching vibrations (3250 cm^{-1}); and the spectrum of compound IV contained a band of the C=N bond (1650 cm^{-1}). To determine the structure, we investigated the ^1H and ^{13}C NMR spectra of the obtained compounds (the spectral data are given in the experimental part). In the proton NMR spectrum of adduct III, we observed a broadened NH-group singlet and also the presence of two groups of phenyl protons. In the region of 176 ppm, its ^{13}C NMR spectrum contained a singlet which could be assigned only to resonance of the carbon atom of the C=N group (in the IR spectrum, the band of C=N bond stretching vibrations apparently overlapped the band of aromatic-ring vibrations). The presence of nonequivalent resonance signals of the four C-CH_3 groups in the ^1H and ^{13}C NMR spectra of compound III indicates the involvement of two molecules of azirine I in the reaction with ammonia (as confirmed by the data of elemental analysis) and also indicates the cyclic structure of the obtained compound III.

The ^{13}C NMR spectrum of compound IV contained only one carbon-atom C=N singlet (see the experimental part), and it should therefore have an acyclic structure. This was also confirmed by the equivalence of the CH_3 groups in the ^1H and ^{13}C NMR spectra. Mass-spectrometric analysis of IV showed the presence of M^+ 176 corresponding to the empirical formula of IV. Thus, on the basis of spectral and analytical data, we can consider that 2-amino-3,3,6,6-tetramethyl-2,5-diphenyl-2,3,5,6-tetrahydropyrazine (III) was formed in the reaction of azirine I with ammonia and that N-(2-amino-2-methyl-1-phenylpropylidene)methylamine (IV) was formed in the case of the similar reaction with methylamine.

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