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SYNTHESIS OF 4-TRIHALOMETHYL-2-OXOBENZ-1,5,3-OXATHIAZEPINES AND 2-OXO-4-TRICHLOROMETHYLBENZ-1,5,3-DITHIAZEPINE AND THEIR CONVERSION TO 2-TRIHALOMETHYL-2-ISOCYANATOBENZ-1,3-OXATHIOLANES AND 2-ISOCYANATO-2-TRICHLOROMETHYLBENZ-1,3-DITHIOLANE

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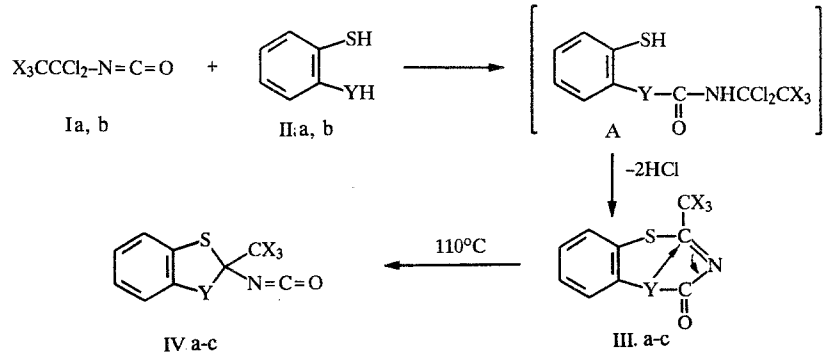
The reaction of perhaloethyl isocyanates with o-mercaptophenol and o-dimercaptobenzene gave 4-trihalomethyl-2-oxobenz-1,5,3-oxathiazepines and 2-oxo-4-trichloromethylbenz-1,5,3-dithiazepine, which at 100-110°C undergo contraction of the heteroring and are converted to the corresponding 2-trihalomethyl-2-isocyanato-1,3-oxathiolanes and a dithiolane.

We have previously proposed several methods for the synthesis of 2-isocyanato-1,3-dioxolanes [1, 2]. One of them is based on the direct reaction of perhaloethyl isocyanates with pyrocatechol. It was shown that the initially formed substances are products of addition at the isocyanato group — acyclic urethanes of the A type (see the scheme) containing an —NH—CCl_2— fragment, which were isolated and characterized [2]. It was assumed that the action of bases leads to their cyclization to seven-membered heterocycles, which, as a consequence of their low stability, undergo rearrangement to 2-isocyanato-1,3-dioxolanes. This assumption was based on the fact of the formation of benz-1,5,3-dioxazepine derivatives in the reaction of pyrocatechol with 1-functionally substituted alkyl isocyanates [3].

In this connection, it seemed of interest to study the reaction of perhaloethyl isocyanates Ia, b with thio analogs of pyrocatechol — o-mercaptophenol (IIa) and o-dimercaptobenzene (IIb). One might have expected that the increased nucleophilicity of the SH group as compared with the OH group should decrease the electrophilicity of the resulting seven-membered heterocycles and lead to an increase in their stabilities.

It was established that isocyanates Ia, b react with binucleophiles IIa, b in benzene solution in the presence of triethylamine and form 4-trihalomethyl-2-oxobenz-1,5,3-oxathiazepines IIIa, b and 2-oxobenz-4-trichloromethyl-1,5,3-dithiazepine (IIIc) in good yields.



I a X = Cl, b X = F; II a Y = O, b Y = S; III, IV a X = Cl, Y = O, b X = F, Y = O, c X = Cl, Y = S

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TABLE 1. Characteristics of the Synthesized IIIa-c and IVa-c

Compound	Empirical formula	mp, °C	^1H and ^{19}F NMR spectra, δ, ppm	IR spectrum, cm^{-1}, $\nu_{C=O}$, $\nu_{N=C=O}$*	Yield, %
IIIa	$C_9H_4Cl_3NO_2S$	74...75	7,17...7,44 (4H,m, C_6H_4)	1750	68
IIIb	$C_9H_4F_3NO_2S$	61...62	7,15...7,40 (4H,m, C_6H_4) 73,3(c, CF_3)	1755	57
IIIc	$C_9H_4Cl_3NOS_2$	96...97	7,27...7,54 (4H,m, C_6H_4)	1700	72
IVa	$C_9H_4Cl_3NO_2S$	50...51	7,07...7,30 (4H,m, C_6H_4)	2165*	40
IVb	$C_9H_4F_3NO_2S$	—	7,20...7,53 (4H,m, C_6H_4) 76,7 (c, CF_3)	2160*	37
IVc	$C_9H_4Cl_3NOS_2$	60...61	7,16 37,42 (4H,m, C_6H_4)	2165*	48

*Purified by reprecipitation from solution in diethyl ether by the addition of hexane.

Compounds IIIa-c are colorless crystalline substances that are stable without access to air moisture. Their structures were confirmed by their spectral characteristics. Thus the IR spectra of IIIa, b contain intense absorption bands of the C=O group of a urethane fragment at 1750-1755 cm^{-1} [4]; this excludes the alternative 2-trihalomethylbenz-4-oxo-1,5,3-oxathiazepine structure containing a thiourethane fragment, since in this case the absorption band of the C=O group should be shifted to 1700 cm^{-1} [5], which is observed for 2-oxobenz-4-trichloromethyl-1,5,3-dithiazepine (IIIc). In turn, the presence of strongly acceptor trihalomethyl groups in the 2 position of the heteroring leads to the absence of absorption bands of a C=N group in the IR spectra. The presence of one signal in the ^{19}F NMR spectra of both the reaction mixture and purified azepine IIIb constitutes evidence for high regioselectivity of the cyclization process, and the magnitude of its chemical shift (73.3 ppm) confirms the sp^2 valence state of the $C_{(4)}$ atom of the heteroring [4]. The ^{13}C NMR spectrum of this compound contains, in addition to signals of carbon atoms of an aromatic ring (129.75, 130.24, 130.60, and 135.20 ppm), quartets of signals of CF_3 groups (116.27 ppm, $^1J_{C-F}$ = 280.4 Hz) and a $C_{(4)}$ atom (164.70 ppm, $^2J_{C-F}$ = 36.3 Hz), as well as a singlet signal of a $C_{(2)}$ atom (171.32 ppm).

In refluxing toluene IIIa-c are converted to 2-isocyanatobenz-1,3-oxathiolanes IVa, b and 2-isocyanatobenz-1,3-dithiolane IVc in satisfactory yields in 3 h. Thus there is a 1,3 shift of the heteroatom (O or S) in the azaallyl fragment of the benz-1,5,3-oxathiazepine (-dithiazepine) system, which is accompanied by contraction of the seven-membered heteroring to a five-membered system with the simultaneous generation of an isocyanato group.

The structures of isocyanates IVa-c were confirmed by data from the IR and ^1H and ^{19}F NMR spectra (see Table 1).

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Varian Gemini 200 spectrometer with hexamethyldisiloxane (HMDS), tetramethylsilane (TMS), and $CFCl_3$, respectively, as the internal standards. The IR spectra of solutions in $CHCl_3$ were obtained with a UR-20 spectrometer.

The results of elementary analysis for halogen, N, and S, as well as the cryoscopically measured molecular masses, were in agreement with the calculated values.

4-Trihalomethyl-2-oxobenz-1,5,3-oxathiazepines IIa, b and 2-Oxo-4-trichloromethylbenz-1,5,3-dithiazepine (IIIc). A 0.01-mole sample of o-mercaptophenol (IIa) or o-dimercaptobenzene (IIb) was added to a solution of 0.01 mole of isocyanate Ia, b in 40 ml of dry benzene, after which 2.0 g (0.02 mole) of triethylamine in 15 ml of benzene was added with stirring. The reaction mixture was stirred for 3 h, after which the precipitated triethylamine hydrochloride was removed by filtration, the filtrate was evaporated, and the residue was purified by crystallization from hexane.

2-Trihalomethyl-2-isocyanatobenz-1,3-oxathiolanes IVa, b and 2-Isocyanato-2-trichloromethylbenz-1,3-dithiolane (IVc). A solution of 0.005 mole of IIIa-c in 20 ml of toluene was refluxed for 3 h, after which the solvent was removed at reduced pressure, and the residue was purified by crystallization from hexane or by reprecipitation from an ether solution by the addition of hexane.

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