OXIDATIVE IMINATION OF SULFUR-CONTAINING HETEROCYCLES

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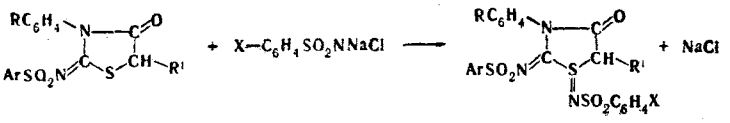
For the first time, the sulfur heteroatom of 4-oxothiazolidines has been iminated with sodium salts of chloroamides of arenesulfonic acids and N-chloroamides of carboxylic acids. The effect of the substituents and the size of the ring on the ability of the ring sulfur atom to undergo oxidative imination was studied.

The study of compounds of the thiazolidine series is attracting special attention because of their high biological activity [1, 2] and the possibility of their application as vulcanizing agents [3].

The oxidative imination of sulfur-containing heterocycles makes it possible to synthesize previously unknown forms of sulfimines. Up until now, only the reaction of sodium salts N-chloroarenesulfonamides with di- and trithians [4, 5], thioxanthenes and thioxanthones [6, 7] has been studied, and the imination of o-carboxybenzenesulfenic acid imide has been accomplished [8].

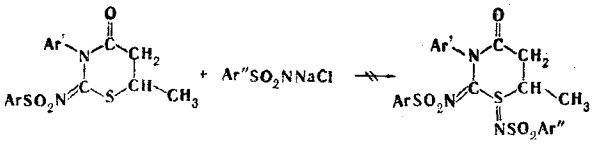
A study of sulfur-containing heterocyclic compounds has shown that the attack on the endocyclic sulfur atom by nucleophilic reagents proceeds much more rapidly than in the case of their noncyclic analogs. Their relative reactivities, which increase as a function of the size of the ring in the order five-membered > seven-membered ≫ six-membered > noncyclic system [9], were determined in the case of organic sulfoxides and disulfides [9]. Thus the oxidation of 1,2-dithiolanes takes place relatively rapidly, whereas noncyclic disulfides and seven-membered dithians do not undergo this reaction [10-12].

For the first time, we have carried out the oxidative imination of the sulfur heteroatom of 4-oxothiazolidines and 4-oxothiazans with sodium salts of N-chloroarenesulfonamides and N-chloroamides of carboxylic acids. The divalent sulfur in the 2-arenesulfonimido-3-phenyl-4-oxo-5-alkylthiazolidine ring is readily iminated in refluxing acetone in 3-5 min if there are alkyl substituents bonded to the carbon atom in the 5 position:



Ia-n

The character and structure of the substituents bonded to the adjacent C_5 atom affect the ability of the ring sulfur atom to undergo oxidative imination in the series of 4-oxothiazolidines that we investigated: when R = CH_3 or C_2H_5, the reaction is complete in a few minutes, whereas an imination product cannot be obtained when R = H or iso-C_3H_7. Six-membered 4-oxothiazans also do not undergo oxidative imination:



The N-chloroamides of carboxylic acids react with 4-oxothiazolidines in the presence of an organic base at room temperature. As the reaction proceeds, the starting thiazolidone dissolves, and crystals of triethylamine hydrochloride precipitate:

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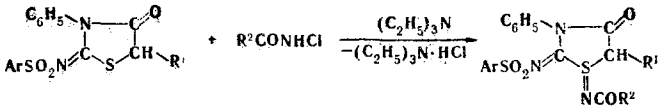
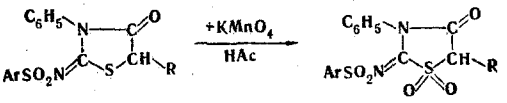


IIa-f

The well-known principle in the oxidation of sulfur-containing [9-12] heterocycles is also observed in the reaction of 4-oxothiazolidines and 4-oxothiazans with potassium permanganate: Sulfoxides can be obtained only for the five-membered heterocycle.



The 1-arenesulfonimido(aroyl)-2-arene(alkane)sulfonimido-3-phenyl-4-oxo-5-alkylthiazolidines, which are obtained in high yields, are colorless crystalline substances that are soluble in alcohol, acetone, and benzene but insoluble in water and petroleum ether. The incorporation of an arenesulfonimido group in the 4-oxothiazolidines increases the stability of the ring with respect to the action of acids and alkalis considerably: The molecule does not undergo decomposition when the compound is refluxed for many hours in hydrochloric acid, dissolved in concentrated H_2SO_4, and poured over ice.

A band of carbonyl absorption at 1740-1750 cm^{-1}, which is shifted 20-25 cm^{-1} as compared with the absorption of this group in the spectra of the starting thiazolidones, is observed in the IR spectra of 1-arenesulfonimido-2-arene(alkane)sulfonimido-3-phenyl-4-oxo-5-alkylthiazolidines. It is known [13] that a 28 cm^{-1} shift in the band of the carbonyl bond to the short-wave region is also observed in the oxidation of penicillin and 3-acylated thiazolidines. The characteristic peak at 1550 cm^{-1} can be assigned to the skeletal vibrations of the thiazolidine structure [14]. This very strong absorption band is observed at 1515-1560 cm^{-1} in the spectra of the thiazolidines that we synthesized. Absorption of symmetrical and asymmetrical vibrations of the SO_2 group is observed at 1370 and 1160 cm^{-1}, respectively.

TABLE 1. 1-Arenesulfonimido-2-arene(alkane)sulfonimido-3-phenyl-4-oxo-5-alkylthiazolidines (I)

Compound	Ar	R	R'	X	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
						C	N	S		C	N	S	
Ia	C_6H_5	H	CH_3	H	183	52,2	8,4	19,3	$C_{22}H_{19}N_3O_5S_3$	52,68	8.38	19,18	92
Ib	p-BrC_6H_4	H	CH_3	H	166—167	45,8	7,3	16,7	$C_{22}H_{18}BrN_3O_5S_3$	45,51	7,24	16,57	78
Ic	p-ClC_6H_4	H	CH_3	H	176—177	48,9	7,6	17,4	$C_{22}H_{18}ClN_3O_5S_3$	49,30	7,84	17,94	75
Id	p-$CH_3C_6H_4$	H	CH_3	p-Cl	171—172	50,5	7,9	17,5	$C_{23}H_{20}ClN_3O_5S_3$	50,22	7,64	17,49	91
Ie	C_6H_5	H	C_2H_5	H	109—110	53,8	8,2	18,3	$C_{23}H_{21}N_3O_5S_3$	53,58	8,16	18,65	77
If	p-ClC_6H_4	H	C_2H_5	p-CH_3	116	51,6	7,2	17,2	$C_{24}H_{22}ClN_3O_5S_3$	51,10	7,50	17,05	76
Ig	p-ClC_6H_4	H	C_2H_5	p-Cl	118	47,1	7,2	16,7	$C_{23}H_{19}Cl_2N_3O_5S_3$	47,26	7,19	16,46	79
Ih	p-$CH_3C_6H_4$	H	C_2H_5	p-CH_3	114	55,4	7,8	17,8	$C_{25}H_{25}N_3O_5S_3$	55,23	7,73	17,69	81
Ii	C_6H_5	p-Br	CH_3	H	163—164	45,8	7,2	16,7	$C_{22}H_{18}BrN_3O_5S_3$	45,52	7,24	16,57	84
Ij	p-$CH_3C_6H_5$	p-Cl	CH_3	H	188—189	50,0	7,3	17,6	$C_{23}H_{30}ClN_3O_5S_3$	50,22	7,64	17,49	98
Ik	C_6H_{13}	p-Cl	CH_3	H	204—205	48,6	7,7	17,8	$C_{22}H_{26}ClN_3O_5S_3$	48,56	7,72	17,68	89
Il	CH_3	p-Cl	CH_3	H	160—161	43,5	8,9	20,2	$C_{17}H_{16}ClN_3O_5S_3$	43,08	8,87	20,33	92
Im	C_6H_{13}	p-Cl	CH_3	p-Cl	208	45,7	7,4	16,5	$C_{22}H_{25}Cl_2N_3O_5S_3$	45,67	7,26	16,63	96
In	p-ClC_6H_4	p-Br	CH_3	p-Cl	207	40,6	6,5	14,7	$C_{22}H_{16}BrCl_2N_3O_5S_3$	40,69	6,47	14,81	78

TABLE 2. 1-Alkanoylimino-2-arenesulfonimido-3-phenyl-4-oxo-5-alkylthiazolidines (II)

Compound	Ar	R'	R''	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
					C	N	S		C	N	S	
IIa	C_6H_5	CH_3	C_6H_5	186—187	59,2	9,1	13,6	$C_{23}H_{19}N_3O_4S_2$	59,34	9,02	13,77	76
IIb	p-$CH_3C_6H_4$	CH_3	C_6H_5	183—184	60,2	8,5	13,2	$C_{24}H_{21}N_3O_4S_2$	60,11	8,76	13,37	84
IIc	p-ClC_6H_4	CH_3	C_6H_5	179—180	55,6	8,7	12,9	$C_{23}H_{18}ClN_3O_4S_2$	55,25	8,40	12,82	82
IId	C_6H_5	CH_3	CH_3	184	54,0	10,8	15,6	$C_{18}H_{17}N_3O_4S_2$	53,59	10,42	15,90	78
IIe	C_6H_5	C_2H_5	C_6H_5	127—128	60,3	8,9	13,5	$C_{24}H_{21}N_3O_4S_2$	60,11	8,76	13,37	80
IIf	p-$CH_3C_6H_4$	C_2H_5	C_6H_5	123—124	60,9	8,8	13,0	$C_{25}H_{23}N_3O_4S_2$	60,83	8,51	12,99	83

Regardless of the iminating agent, a distinct intense band at 1490 cm^{-1}, which evidently belongs to the vibrations of the S=N bond, appears in the IR spectra of all of the iminated thiazolidines. An absorption band corresponding to C=N vibrations is located at 1590 cm^{-1}.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

1-Arenesulfonimido-2-arene(alkane)sulfonimido-4-oxo-5-alkylthiazolidines. A mixture of 0.02 mole of 2-arene(alkane)sulfonimido-3-phenyl-4-oxo-5-alkylthiazolidine and 0.02 mole of the sodium salt of the N-chloroarenesulfonamide in 30 ml of acetone was refluxed until it no longer gave a positive reaction for active chlorine (10 min), during which the starting reagents dissolved, and the solution initially turned bright yellow and then became colorless as NaCl precipitated. The mixture was cooled and diluted with water, and the precipitated reaction product was removed by filtration and crystallized from acetone—water (1:1). The melting points, yields, and results of elementary analysis of Ia-n obtained by this method are indicated in Table 1.

1-Alkanoylimino-2-arene(alkane)sulfonimido-4-oxo-5-alkylthiazolidines. A solution of 0.02 mole of the carboxylic acid N-chloroamide in 15 ml of dry acetone was added with vigorous stirring to a suspension of 0.02 mole of 2-arene(alkane)sulfonimido-3-phenyl-4-oxo-5-alkylthiazolidine and 0.02 mole of triethylamine in 40 ml of dry acetone, and the mixture was then stirred in the cold until the starting thiazolidine dissolved completely and the mixture no longer gave a positive test for active chlorine (20-30 min). The precipitated triethylamine hydrochloride was removed by filtration, the solvent was removed by evaporation, and the residue was recrystallized from aqueous acetone. The IIa-f synthesized by this method are presented in Table 2.

2-Benzenesulfonimido-3-phenyl-4-oxo-5-methylthiazolidine 1,1-Dioxide. A 0.01-mole sample of 2-benzenesulfonimido-3-phenyl-4-oxo-5-methylthiazolidine was dissolved by heating in 70 ml of glacial acetic acid, and the resulting solution was cooled to room temperature and treated dropwise with a solution of 2 g of $KMnO_4$ in 20 ml of H_2O. After 30 min, the reaction mixture was decolorized with sodium bisulfite and diluted with water. The resulting precipitate was removed by filtration, dried, and crystallized from alcohol—benzene (1:1) to give a product with mp 135-136°C in 54% yield. Found: C 51.1; N 7.5; O 21.7; S 17.4%. $C_{16}H_{14}N_2O_5S_2$. Calculated: C 50.78; N 7.40; O 21.14; S 16.93%.

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