7. F. C. Eichel and D. F. Otmer, Ind. Eng. Chem., 41, 2623 (1949).
8. J. Kamija, J. Catalysis, 33, 480 (1974).
9. E. T. Denisov, N. I. Mitskevich, and V. V. Agabekov, Mechanism of the Liquid-Phase Oxidation of Oxygen-Containing Compounds [in Russian], Minsk (1975).
10. P. A. Konstantionov, T. V. Shchedrinskaya, I. V. Zakharov, and M. N. Volkov, Zh. Org. Khim., 8, 2590 (1972).
11. A. Weissberger, O. Proskauer, G. Riddick, and A. Toops, Organic Solvents [Russian translation], Moscow (1958).
12. D. B. Sharp and T. M. Patric, J. Org. Chem., 26, 1389 (1961).
13. A. Weston and R. Michaelis, Organic Syntheses [Russian translation], Vol. 4, I. L., Moscow (1953), p. 476.
14. W. R. Biggerstaff, H. Arzoumanian, and K. L. Stevens, J. Med. Chem., 7, 110 (1964).
15. B. Weinstein, J. Am. Chem. Soc., 77, 6709 (1955).
16. W. S. Emerson and T. M. Patric, J. Org. Chem., 14, 790 (1949).

HYDROXYMETHYLATION AND AMINOMETHYLATION OF 2-IMINO-5-ARYLIDENETHIAZOLIDIN-4-ONES

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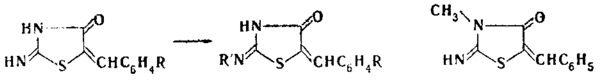
The hydroxymethylation and aminomethylation of 2-imino-5-arylidenethiazolidin-4-ones lead to the formation of 2-hydroxymethylimino- and 2-piperidinomethylimino-5-arylidenethiazolidin-4-ones. The structures of the synthesized compounds are discussed on the basis of the spectral data.

In [1] it was shown that the aminomethylation of 2-imino-5-benzylidenethiazolidin-4-one (Ia) in benzene leads to the formation of 3-aminomethyl derivatives, while aminomethylation products could not be isolated when the reaction was carried out in ethanol or acetic acid. The hydroxymethylation of 2-imino-5-arylidenethiazolidin-4-ones Ia-c has not been previously studied.



I a-c II-III a-c IV V

I-III a R = H; b R = p-NO_2; c R = p-OCH_3; II a-c R′ = CH_2OH;
III a-c R′ = piperidinomethyl R = H; R′ = CH_3

The hydroxymethyl derivatives (IIa-c) that we obtained (Table 1) were found to be unstable substances that undergo decomposition to the starting Ia-c during chromatography in thin layers of silica gel and during attempts to determine their melting points or recrystallize them. According to the derivatographic data, the weight loss of a solid sample, which begins at 110-115°C, corresponds to splitting out of one molecule of formaldehyde. The formation of unstable adducts with formaldehyde has also been demonstrated for the similarly constructed 3-aryl-2-iminothiazolidin-4-ones [3].

In contrast to IIa-c, aminomethyl derivatives IIIa-c have fixed melting (decomposition) points; however,

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*Deceased.

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TABLE 1. 2-Imino-5-benzylidenethiazolidin-4-ones and Their Derivatives

Compound	R	mp, °C	UV spectrum, λ_{max}, nm ($\log \varepsilon$)	IR spectrum, ν, cm^{-1}		PMR spectrum, δ, ppm				Found, %		Empirical formula	Calc., %		Yield, %
				C=O	C=N+Het	NH	OH	CHAr	CH_2	N	S		N	S	
Ia	H	286 (284) [2]	238 (4,00), 288 (4,12), 330 (4,34)	1665	1445, 1510	9,19; 9,49[a]	—	7,65	—	14,3	15,2	$C_{10}H_8N_2OS$	13,7	15,7	46
Ib	p-NO_2	302 (dec.)[b] (305) [2]	224 (4,05), 293 (4,12), 354 (4,29)	1650, 1670	1540sh	9,47; 9,74	—	7,78	—	16,6	12,5	$C_{10}H_7N_3O_3S$	16,8	12,9	30
Ic	p-OCH_3	288 (dec.)[b] (287) [2]	246 (4,09), 296 (3,93), 350 (4,39)	1680	1425 sh 1510	9,15; 9,40	—	7,71	—	12,4	13,6	$C_{11}H_{10}N_2O_2S$	12,0	13,7	41
IIa	H	284	238 (3,96), 287 (4,08), 331 (4,29)	1685	1445, 1570	10,11	6,45	7,83	4,89	12,1	13,2	$C_{11}H_{10}N_2O_2S$	12,0	13,7	72
IIb	p-NO_2	300 (dec.)	223 (4,05), 299 (4,09), 355 (4,28)	1650 sh 1670	1540 sh	10,42	6,51	7,78	5,05	15.5	11,7	$C_{11}H_9N_3O_4S$	15,0	11,5	68
IIc	p-OCH_3	288 (dec.)	246 (3,86), 295 (3,70), 351 (4,13)	1670	1545	10,10	6,48	7,79	4,89	10,8	11,8	$C_{12}H_{12}N_2O_3S$	11,3	12,3	74
IIIa	H	157	231 (4,06), 286 (4,10), 331 (4,31)	1680	1445, 1510, 1570	No signal was observed	—	7,77	4,45[c]	13,7	10,2	$C_{16}H_{19}N_3OS$	13,9	10,6	65
IIIb	p-NO_2	168	224 (4,03), 294 (4,11), 355 (4,28)	1665	1475, 1550	" " "	—	7,72	4,40[c]	16,1	9,6	$C_{16}H_{18}N_4O_3S$	16,2	9,3	54
IIIc	p-OCH_3	174	246 (4,08), 293 (3,94), 349 (4,37)	1665	1480, 1555	" " "	—	7,67	4,39[c]	12,2	9,8	$C_{17}H_{21}N_3O_2S$	12,7	9,7	61
IV	H	225 (227) [2]	240 (3,83), 293 (4,04), 331 (4,28)	1685	1470, 1590	9,54	—	7,71	—	12,7	14,2	$C_{11}H_{10}N_2OS$	12,8	14,7	9
V	H	159 (161) [2]	232 (3,95), 254 (3,82), 325 (4,35)	1695	1595	9,93	—	7,78	—	12,5	14,3	$C_{11}H_{10}N_2OS$	12,8	14,7	33

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[a] For a sample of Ia obtained from Mannich base IIIa, δNH 9.35 ppm. [b] These compounds from stable monosolvates with acetic acid, while Ib–i form stable monosolvates with dioxane; the solvate shell is removed by drying at 100°C (2 mm) for 4 h. [c] The δCH_2 signals of the piperidyl group are observed at 1.45 and 2.51 ppm.

like IIa-c, they undergo decomposition to starting Ia-c, i.e., they are deaminomethylated, during chromatography on Silufol and recrystallization.

According to the results of elementary analysis and data from the PMR spectra, IIa-c and IIIa-c are monosubstituted derivatives. When there are several reaction centers in the compound, the direction of alkylation is determined both by its fine structure and the nature of the alkylating agent [4]; however, it is reasonable to assume that the reaction will be directed to the same position of the starting heterocyclic compound under virtually identical conditions both in the case of hydroxymethylation and in the case of aminomethylation [5].

The above-noted instability of IIa-c and IIIa-c in solutions does not make it possible to determine the site of substitution by chemical methods. The structures of these compounds were established by comparison of their spectral characteristics and the spectral characteristics of derivatives IV and V (Table 1). The IR spectra of IIa and IIIa are similar to the spectrum of 2-methyl derivative IV rather than to the spectrum of 3-methyl analog V, i.e., intense absorption at 1440-1510 cm^{-1}, which is absent in the IR spectrum of V, and a lower (than in the case of 3-substituted V) frequency of carbonyl absorption are characteristics for 2-substituted IIa, IIIa, and IV. The UV spectra of hydroxymethyl and aminomethyl derivatives IIa and IIIa are similar to the spectrum of IV (and to the spectrum of starting Ia), and this also constitutes evidence in favor of alkylation at the exocyclic nitrogen atom.

In the PMR spectrum of II, a broad signal of an NH proton lies at weaker field than in the case of 2-methyl IV, the reason for which may be the existence of an OH... NH hydrogen bond. The signal of an NH proton is not observed in the PMR spectrum of IIIa, while the signal of the 2-NH proton for 3-methyl compound V is narrow and intense, and this confirms, in our opinion, the 2-aminomethyl structure of IIIa.

Although model analogs have not been obtained for Ib,c, the similar character (with respect to that examined above) of the spectra of their hydroxymethyl and aminomethyl derivatives makes it possible to propose that these derivatives are also 2-substituted IIb,c and IIIb,c, respectively.

A detailed discussion of the PMR spectra and the fine structure of I-IV, including the tautomerism of I-IIIa and IV, will be the subject of our next communication.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in d_6-DMSO were recorded with a Perkin–Elmer R-12 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra were obtained with an IKS-29 spectrometer. The UV spectra of solutions of the compounds in ethanol (c 10^{-4} M, l = 1 cm) were recorded with an SF-16 spectrophotometer. The derivatograms were recorded with a derivatograph of the Paulik–Paulik–Erdey system; the sample weights ranged from 20 to 25 mg, the time for one revolution of the drum was 100 min, the DTA, DTG, and TG sensitivities were, respectively, 1/3, 1/30, and 50 mg, the heating rate was 8 deg/min, and the standard was Al_2O_3. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates [elution with acetone–hexane (1 : 2) and ethanol–chloroform (1 : 10)].

2-Imino-5-arylidenethiazolidin-4-ones (Ia-c) were obtained by a known method [6] and were recrystallized from acetic acid or ethanol.

2-Hydroxymethylimino-5-arylidenethiazolidin-4-ones (IIa-c). A mixture of 0.01 mole of I, 5 ml of formalin, and 100 ml of dioxane was stirred at 60°C until Ia-c dissolved completely, after which the mixture was poured into water (~700 ml), and the aqueous mixture was allowed to stand for 30 min. The precipitated IIa-c were removed by filtration. Starting Ia-c were isolated in attempts to recrystallize the products from dioxane or ethanol; in the case of IIa and IIc a precipitate was formed from boiling dioxane.

2-Piperidinomethylimino-5-arylidenethiazolidin-4-ones (IIIa-c). A mixture of 0.01 mole of I, 5 ml of formalin, 1.70 g (0.02 mole) of piperidine, and 100 ml of dioxane was stirred at 60°C until Ia-c dissolved completely, and the mixture was poured into water (~700 ml). The aqueous mixture was allowed to stand for 30 min, after which the precipitated IIIa-c were removed by filtration. The starting Ia-c were isolated in attempts to crystallize the products from dioxane or ethanol (IIIa), ethanol (IIIc), and dioxane–ethanol (4 : 1) (IIIb).

2-Methylimino-5-benzylidenethiazolidin-4-one (IV). A 6.20-g (0.05-mole) sample of a 25% aqueous solution of methylamine was added to 2.49 g (0.01 mole) of 2-theylthio-5-benzylidene-2-thiazolidin-4-one. After the starting compound had dissolved, the mixture was extracted with chloroform (three 15-ml portions), and the chloroform extract was dried with calcium chloride. The chloroform was evaporated, and the solid precipitate was crystallized from chloroform.

2-Imino-3-methyl-5-benzylidenethiazolidin-4-one (V). A mixture of 2.20 g (0.017 mole) of 2-imino-3-methylthiazolidin-4-one, 2.21 g (0.02 mole] of benzaldehyde, three to four drops of pyridine, and 30 ml of absolute ethanol was refluxed for 45 min, after which the undissolved starting compound was removed by filtration, and the filtrate was evaporated to precipitate the product, which was crystallized from ethanol.

LITERATURE CITED

1. I. I. Chizhevskaya and N. M. Yatsevits, Izv. Akad. Nauk Beloruss. SSR, Ser. Khim., No. 1, 85 (1971).
2. S. Kambe, T. Hayashi, H. Yasuda, and A. Sakurai, Nippon Kagaku Zasshi, 92, 867 (1971).
3. Yu. V. Svetkin, S. A. Vasil'eva, V. I. Pronima, and A. I. Dukaeva, Izv. Vyssh. Uchebn. Zaved. Ser. Khim., 18, 1061 (1975).
4. S. A. Shevelev, Usp. Khim., 39, 1773 (1970).
5. A. F. Halasa and G. E. P. Smith, J. Org. Chem., 36, 636 (1971).
6. R. Andreash, Monatsh., 24, 499 (1903).

SYNTHESIS AND STUDY OF THE PROPERTIES OF TETRAZOLES, AZIDES, TRIAZENES, AND AZO COMPOUNDS OF THE THIADIAZOLE SERIES

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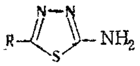
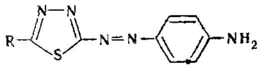
Azo compounds and bistriazenes were obtained by diazo coupling of diazotized 5-amino-2-R-1,3,4-thiadiazoles; tetrazolo[4,5-b]-1,3,4-thiadiazoles, to which azido−tetrazole tautomerism is peculiar, were obtained by replacement of the diazo group by an azido group. The structures of the products were confirmed by their IR and UV spectra.

Research on the synthesis of azides, tetrazoles, triazenes, and azo compounds on the basis of 5-amino-2-R-1,3,4-thiadiazoles with the general formula

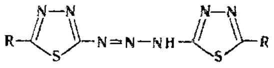


was carried out in order to search for efficient stabilizers of silver halide photographic emulsions, as well as new light-sensitive and photosemiconductor materials.

5-Amino-2-R-1,3,4-thiadiazoles have the properties of aromatic amines. Their diazotization can be realized in hydrochloric acid with an aqueous solution of sodium nitrite or in a mixture of concentrated propionic and acetic acids or in orthophosphoric acid with nitrosylsulfuric acid. The corresponding azo compounds Ia-e (Table 1) are formed by coupling the resulting diazonium salts with aniline hydrochloride in an aqueous medium (pH 4-5); diazotization in the presence of excess starting amine leads to the formation of triazenes IIa-e (Table 1):



I a-e



II a-e

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