TABLE 1. ^{35}Cl NQR Frequencies at 77°K (ν^{77}) of 3(5)-Aryl-5(3)-chloro-1,2,4-triazoles

Compound	X	ν^{77}, MHz	Signal/noise
1	H	36,800	2
2	o-CH_3	36,642	2
3	m-CH_3	36,805	5
4	p-CH_3	36,389	2
5	o-Br	36,786	5
6	o-NO_2	37,117	10
7	m-NO_2	37,207	10
8	p-NO_2	38,084	10

EXPERIMENTAL

The ^{35}Cl NQR spectra at 77°K were obtained with an NQR pulse spectrometer of the ISSh-1-12 type. The synthesis of the chloro-1,2,4-triazoles was previously described in [3].

LITERATURE CITED

1. V. V. Makarskii, M. G. Voronkov, V. P. Feshin, V. A. Lopyrev, N. I. Berestennikov, E. F. Shibanova, and L. I. Volkova, Dokl. Akad. Nauk SSSR, 220, 101 (1975).
2. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry [in Russian], Izd. Rostovsk. Univ., Rostov-on-Don (1966), p. 315.
3. T. I. Yushmanova, E. N. Medvedeva, L. I. Volkova, V. V. Makarskii, V. A. Lopyrev, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 3, 421 (1976).

SYNTHESIS AND REACTIONS OF AZIDES OF HETEROCYCLIC COMPOUNDS

5.* SYNTHESIS AND INVESTIGATION OF 1,2,3-TRIAZOL-2-INES THAT CONTAIN BENZOTHIAZOLE RESIDUES

I. A. Ol'shevskaya

UDC 547.789.6'791.6'26'467.2.07 : 542.943.543.422

The reaction of 2-methyl-5- and 2-methyl-6-azidobenzothiazoles with alkyl acrylates was used to synthesize 1,2,3-triazol-2-ines, which are cleaved in the presence of bases to give the corresponding diazopropanoic acid esters. Oxidation of the triazolines leads to the corresponding triazoles.

It is known that aromatic azides and benzyl azide add to α,β-unsaturated esters of carboxylic acids to give the corresponding 1,2,3-triazol-2-ines [2]. It seemed of interest to study the same reactions of benzothiazole azides.

For the investigation we selected 5-azido-2-methyl- (I) and 6-azido-2-methylbenzothiazoles (II), which were previously described in [3] and react with methyl and ethyl acrylates to give colorless crystalline 1-benzothiazolyl-1,2,3-triazol-2-ines (III-VI).

Vibrations at 2080-2200 cm^{-1} (N_3) are absent in the IR spectra of III-VI, while bands are present at 1230-1250 cm^{-1} ($-\underset{|}{N}-N=N-$) and 1740-1750 cm^{-1} (COOR). The PMR spectra of triazolines III-VI contain a quartet at ~5.25 ppm (4-H), a multiplet centered at ~4.0 ppm (5-H), and a singlet at 2.8 ppm (2'-CH_3).

---

*See [1] for Communication 4.

T. G. Shevchenko Kiev State University, Kiev 252017. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 839-841, June, 1982. Original article submitted September 16, 1981.

0009-3122/82/1806-0638$07.50

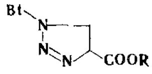
TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	UV spectrum, λ_{max}, nm ($\log \varepsilon \cdot 10^4$)	IR spectrum, cm^{-1}	N found, %	Empirical formula	N calc., %	Yield, %
III	105—106 (dec.)	240 (2,10), 305 (1,53)	1750, 1200, 1250	20,3	$C_{12}H_{12}N_4O_2S$	20,5	52
IV	110—112 (dec.)	240 (1,60), 305 (1,24)	1740, 1230, 1250	19,5	$C_{13}H_{14}N_4O_2S$	19,3	53
V	106—107 (dec.)	225 (1,48), 245 (1,20), 310 (1,58), 320* (1,44)	1750, 1220, 1250	20,3	$C_{12}H_{12}N_4O_2S$	20,5	55
VI	101—102 (dec.)	225 (1,28), 245 (1,05), 307 (1,41), 320* (1,26)	1750, 1230, 1250	19,2	$C_{13}H_{14}N_4O_2S$	19,3	46
VII	85—86 (dec.)	237 (3,20), 255 (2,32), 325 (0,36)	1710, 2090, 3430	20,3	$C_{12}H_{12}N_4O_2S$	20,5	75
VIII	78—80 (dec.)	237 (3,04), 255 (2,22), 330 (0,34)	1700, 2090, 3430	19,5	$C_{13}H_{14}N_4O_2S$	19,3	80
IX	81—83 (dec.)	225 (2,82), 252 (1,80), 295 (1,20)	1710, 2090, 3400	20,3	$C_{12}H_{12}N_4O_2S$	20,5	80
X	Oil	225 (2,96), 252 (1,96), 295 (1,18)	1700, 2090, 3400	19,2	$C_{13}H_{14}N_4O_2S$	19,3	95
XI	179	240 (3,18)	1720, 1270, 1280, 880	20,5	$C_{12}H_{10}N_4O_2S$	20,4	88
XII	184—186	237 (3,06)	1720, 1290, 895	19,2	$C_{13}H_{12}N_4O_2S$	19,4	68
XIII	198	270 (1,69)	1720, 1295, 880	20,4	$C_{12}H_{10}N_4O_2S$	20,4	88
XIV	170—172	275 (1,88)	1720, 1300, 870	19,8	$C_{13}H_{12}N_4O_2S$	19,4	67
XV	188—189	237 (2,60)	1710, 1280, 880	21,6	$C_{11}H_8N_4O_2S$	21,5	45
XVI	161	275 (1,84)	1695, 1295, 890	21,6	$C_{11}H_8N_4O_2S$	21,5	23

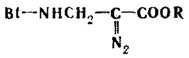
*Inflection.

The PMR spectra of triazolines III and V contain yet another singlet at ~3.90 ppm ($COOCH_3$), while the PMR spectra of IV and VI contain a quartet at 4.31 ppm and a triplet at ~1.40 ppm ($COOC_2H_5$).

The triazolines obtained melt with decomposition. Colorless solutions of these compounds turn yellow rapidly when they are heated in light and in the presence of bases. The behavior of the triazolines obtained in the presence of organic bases (a 5% benzene solution of triethylamine in the dark at room temperature for 24 h) was investigated in detail; the triazolines underwent complete conversion to 3-benzothiazolylamino-2-diazopropanoic acid esters (VII-X).

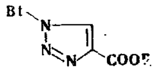


III-VI



$\mathrm{Bt{-}NHCH_2{-}\underset{\underset{N_2}{\|}}{C}{-}COOR}$

VII-X



XI-XIV

III, IV, VII, VIII, XI, XII Bt—5-; V, VI, IX, X, XIII, XIV Bt—6-; III, V, VII, IX, XI, XIII R=CH_3; IV, VI, VIII, X, XII, XIV R=C_2H_5; Bt– 2-methylbenzothiazolyl

The IR spectra of the esters contain bands at 2090-2100 ($-C=N=N$) and 3400-3430 cm^{-1} (NH). When the triazoline ring is opened, the bands of the carbonyl group are shifted 40 cm^{-1} to the low-frequency side (see Table 1); this is explained by conjugation of the carbonyl group with the diazo group and confirms the structures of the diazo esters and starting triazolines III-VI.

The kinetics of conversion of methyl esters III and V to diazopropanoic acid esters VII and IX in the case of catalysis by triethylamine in benzene at room temperature show that it is a first-order reaction. The triazoline and diazo ester concentrations in solution were determined from the change in the peak intensities of the carbonyl groups at 1700 and 1740 cm^{-1} with time.

The corresponding 1,2,3-triazoles XI-XIV were obtained by oxidation of triazolines III-VI with potassium permanganate at room temperature (see Table 1). As compared with starting triazoles III-VI, a 20-30 cm^{-1} shift of the band of the carbonyl group to the low-frequency side due to its conjugation with the aromatic ring of the triazole [4] is observed in the IR spectra of triazoles XI-XIV.

Triazolecarboxylic acid esters XI-XIV were subjected to alkaline hydrolysis to the corresponding acids XV and XVI, the IR spectra of which are in agreement with the literature data [5].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer. The UV spectra of solutions of the compounds in ethanol were recorded with an SF-4 spectrophotometer. The PMR spectra of solutions in deuterochloroform were obtained with a ZKR-60 spectrometer with tetramethylsilane as the internal standard. The constants and yields of the compounds obtained are presented in Table 1.

Methyl 1-(2'-Methyl-5'-benzothiazolyl)-1,2,3-triazoline-4-carboxylate (III). A 1.9-g (0.01 mole) sample of 2-methyl-5-azidobenzothiazole (I) was dissolved in 3.44 g (0.04 mole) of methyl acrylate, and the mixture was allowed to stand in a sealed flask at room temperature in the dark. After 5 days, the precipitated triazoline was removed by filtration, washed with alcohol, and crystallized from alcohol to give colorless acicular crystals.

Triazolines IV-VI were similarly obtained after 4 days in the case of V and after 6 days in the case of IV and VI.

Methyl 3-(2'-Methyl-5'-benzothiazolyl)amino-2-diazopropanoate (VII). A 1.38 g (0.005 mole) sample of triazoline III was dissolved in 10 ml of a 5% solution of triethylamine in benzene, and the solution was allowed to stand at room temperature. After 24 h, the benzene was removed by vacuum distillation. The resulting diazo ester was a yellow powder.

Compounds VIII-X were similarly obtained.

Methyl 1-(2'-Methyl-5'-benzothiazolyl)-1,2,3-triazole-4-carboxylate (XI). A solution of 2.37 g (0.015 mole) of potassium permanganate in acetone was added slowly to a solution of 1.38 g (0.005 mole) of ester VII in 80 ml of acetone. The first portions of the oxidizing agent were consumed rapidly. The mixture was allowed to stand for 0.5 h, after which a small amount of methanol was added, and the mixture was refluxed. The manganese dioxide was removed by filtration, and the solvent was evaporated in vacuo. The resulting triazole was crystallized from aqueous alcohol with activated charcoal.

Triazoles XII-XIV were similarly obtained.

1-(2'-Methyl-5'-benzothiazolyl)-1,2,3-triazole-4-carboxylic Acid (XV). A 1.37-g (0.005 mole) sample of ester XI or XII was added with heating to a solution of 0.6 g (0.015 mole) of sodium hydroxide in 50 ml of water, and the mixture was refluxed for another 30 min after the ester had dissolved completely. The triazolecarboxylic acid was liberated by acidifying the solution with dilute (1 :4) hydrochloric acid. The triazolecarboxylic acid was removed by filtration, washed with water, and crystallized from alcohol.

1-(2'-Methyl-6'-benzothiazolyl)-1,2,3-triazole-4-carboxylic Acid (XVI). This compound was obtained in the same way as acid XV from XIII or XIV by saponification in an alkaline solution and was crystallized from methanol.

LITERATURE CITED

1. I. A. Ol'shevskaya, V. Ya. Pochinok, V. V. Kolibaba, and V. I. Rafal'skaya, Vestn. Kievsk. Univ., No. 20, 51 (1979).
2. R. Huisgen, G. Szeimies, and L. Möbius, Chem. Ber., 99, 475 (1966).
3. I. A. Ol'shevskaya, V. Ya. Pochinok, and L. F. Avramenko, Khim. Geterostikl. Soedin., No. 5, 898 (1968).
4. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
5. L. A. Kazitsina and N. B. Kuplet-skaya, Application of UV, IR, and PMR Spectroscopy in Organic Chemistry [in Russian], Vysshaya Shkola, Moscow (1971), p. 37.