ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 11, pp. 1622–1627. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.I. Potkin, S.K. Petkevich, P.V. Kurman, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 11, pp. 1626–1632.

Reactions of 1-Aryl-2-bromo-3,4,4-trichlorobut-3-en-1-ones with Some Nucleophilic Reagents

V. I. Potkin, S. K. Petkevich, and P. V. Kurman

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus,
ul. Surganova 13, Minsk, 220072 Belarus
e-mail: potkin@ifoch.bas-net.by

Received February 2, 2007

Abstract—Reactions of 2-bromo-1-phenyl- and 2-bromo-1-(4-methylphenyl)-3,4,4-trichlorobut-3-en-1-ones with morpholine and diethylamine are accompanied by prototropic allylic rearrangement, leading to 3-amino-1-aryl-2-bromo-4,4-dichlorobut-2-en-1-ones as mixtures of *E* and *Z* isomers. The title compounds react with hydrazine, hydroxylamine, and thiourea to give the corresponding 5-aroyl-4-methoxypyrazoles, 3-aryl-5-hydroxyiminomethyl-4-methoxyisoxazoles, and 2-amino-4-aryl-5-trichlorovinylthiazoles.

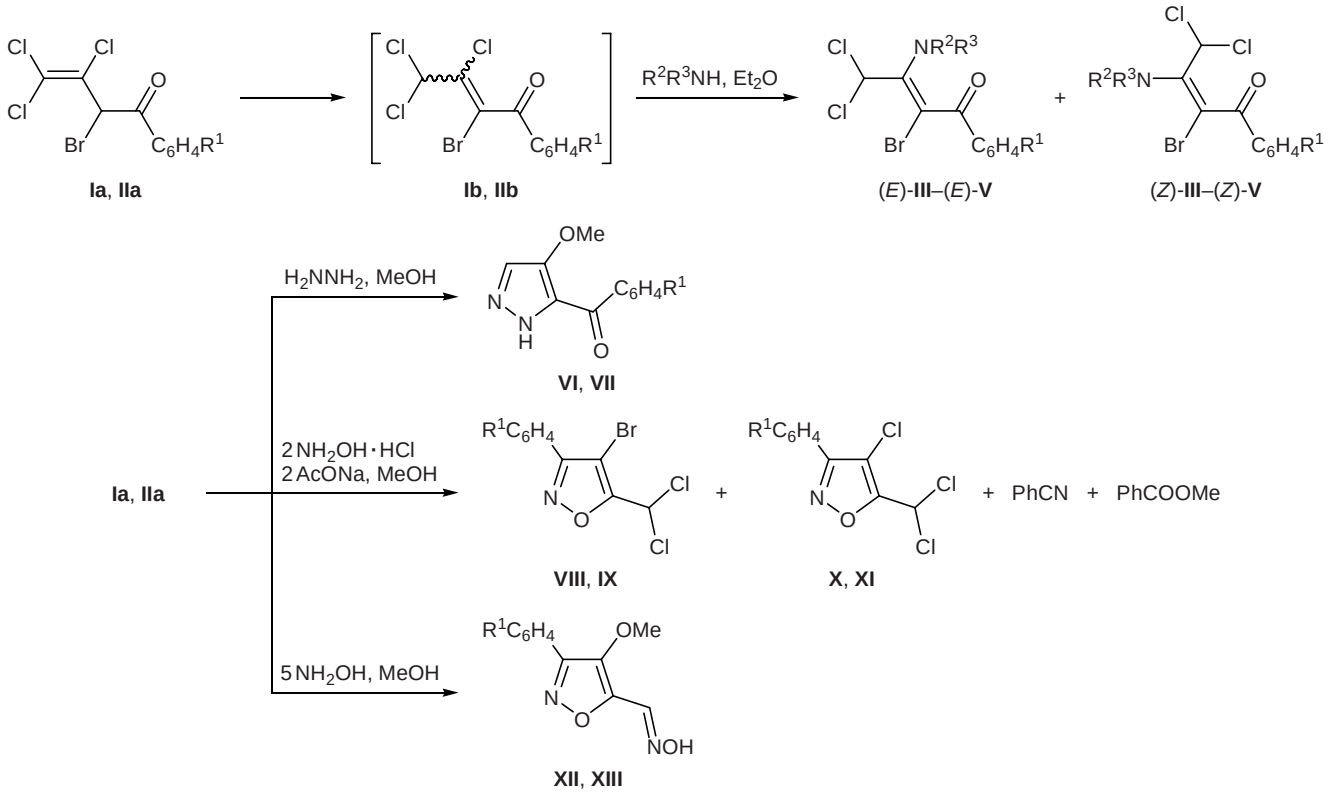
DOI: 10.1134/S1070428007110061

Halogen-substituted ketones are widely used in the synthesis of various practically important products [1–4]. Chlorovinyl ketones attract specific interest due to their high reactivity arising from mutual effect of the conjugated carbonyl and chlorovinyl groups; these compounds are convenient starting materials for building up heterocyclic systems [5]. We recently described a practical method for the synthesis of 1-aryl-2-bromo-3,4,4-trichlorobut-3-en-1-ones [6] from accessible aryl trichloroallyl ketones that are capable of readily undergoing prototropic allylic rearrangement into chlorovinyl ketones, namely 1-aryl-3,4,4-trichlorobut-2-en-1-ones [7]. It might be expected that 1-aryl-2-bromo-3,4,4-trichlorobut-3-en-1-ones could also undergo analogous rearrangement with formation of isomeric reactive bromochlorovinyl ketones, 1-aryl-2-bromo-3,4,4-trichlorobut-2-en-1-ones. The presence of a bromine atom in their molecules gives rise to a new reaction center, which could considerably extend their synthetic potential, as compared to their precursors, 1-aryl-3,4,4-trichlorobut-3-en-1-ones.

The present work was aimed at studying reactions of 1-aryl-2-bromo-3,4,4-trichlorobut-3-en-1-ones with mono- and difunctional nucleophiles (such as amines, hydrazine, hydroxylamine, and thiourea) and elucidating their potential for the synthesis of heterocyclic compounds. As substrates we used 2-bromo-3,4,4-trichloro-1-phenylbut-3-en-1-one (**Ia**) and 2-bromo-3,4,4-trichloro-1-(4-methylphenyl)but-3-en-1-one (**IIa**).

The reactions of **Ia** and **IIa** with secondary amines (morpholine and diethylamine) involved rearrangement of the initial ketones into isomeric conjugated bromochlorovinyl ketones **Ib** and **IIb**, followed by replacement of the chlorine atom in position *3* by amino group. As a result, the corresponding 3-amino-1-aryl-2-bromo-4,4-dichlorobut-2-en-1-ones **III**–**V** were formed in 74–97% yield (Scheme 1). The elemental analyses of the products unambiguously showed that just chlorine rather than bromine atom was replaced. The structure of **III**–**V** was assigned on the basis of their IR, ^{1}H and ^{13}C NMR, and mass spectra. The IR spectra of amino ketones **III**–**V** contained a strong absorption band at 1693–1703 cm^{-1} due to stretching vibrations of the carbonyl group, and vibrations of the C=C bond were characterized by absorption bands in the region 1576–1606 cm^{-1}. In the ^{1}H NMR spectra of **III**–**V** we observed signals from the Cl_2CH group and protons in the amine and aromatic fragments. However, the number of signals and their multiplicity suggested that amino ketones **III**–**V** are mixtures of *E* and *Z* isomers. For example, the spectrum contained two singlets at δ 6.6 and 7.2 ppm with an intensity ratio of about 2:1, which were assigned to the $CHCl_2$ proton. According to published ^{1}H NMR data for derivatives of β-amino-γ,γ-dichlorocrotonic acid, signal of the $CHCl_2$ proton in isomers with *cis* arrangement of the carbonyl and dichloromethyl groups with respect to the double C=C bond appears in a weaker field that the corresponding signal of the *trans* isomers due to formation of intramolecular hydrogen bond $Cl_2CH\cdots O{=}C$ in the former [8, 9]. Therefore, the signal at δ 7.2 ppm in the spectra of

Scheme 1.



I, **III**, **V**, **VI**, **VIII**, **X**, **XII**, R^1 = H; **II**, **IV**, **VII**, **IX**, **XI**, **XIII**, R^1 = 4-Me; **III**, **IV**, R^2R^3N = morpholino; **V**, $R^2 = R^3$ = Et.

amino ketones **III**–**V** was assigned to the $CHCl_2$ proton in the *Z* isomers, and that at δ 6.6 ppm, to the corresponding proton in the *E* isomer, i.e., *E* isomers of **III**–**V** predominate in the isomer mixture. We also recorded the ^{13}C NMR spectrum of morpholinovinyl ketone **III**. The spectrum contained two sets of signals, indicating the presence of two isomers. Using the DEPT sequence, the signals at δ_C 55.96 and 69.81 ppm with an intensity ratio of ~2:1 were assigned to the $CHCl_2$ carbon atom. As in the ^1H NMR spectrum, the minor signal appeared in a weaker field and was assigned to the *Z* isomer in which hydrogen bonding is possible between the C=O and Cl_2CH groups.

No molecular ion peaks were observed in the electron impact mass spectra of amino ketones **III**–**V**. Peaks with the maximal *m*/*z* value belong to the $[M - HCl]^+$ ions; the corresponding isotope ratio (76:100:24) indicates the presence of one chlorine and one bromine atoms in these ions [10, 11]. In addition, the mass spectra contained peaks of ions arising from elimination of aroyl, aryl, and amino groups and halogen atoms.

Compounds **Ia** and **IIa** reacted with difunctional nucleophiles in peculiar fashions, depending on the nucleophile nature (Scheme 1). As in the reactions with amines, the condensation of aryl bromotrichloroallyl ketones with hydrazine in methanol was accompanied by prototropic allylic rearrangement, and it resulted in the formation of pyrazole ring. However, the cyclization did not involve the carbonyl group but involved the dichloromethyl fragment which reacted with hydrazine with replacement of both chlorine atoms. The other reaction center in the ketone molecule, participating in the heterocyclization process, was the =CBr moiety. The bromine atom therein was replaced by the second nucleophilic nitrogen atom of hydrazine. In addition, the reaction was accompanied by replacement of the remaining chlorine atom by methoxy group from the solvent. The final products were 5-benzoyl-4-methoxy-1*H*-pyrazole (**VI**) and 4-methoxy-5-(4-methylbenzoyl)pyrazole (**VII**) from ketones **Ia** and **IIa**, respectively (yield 54 and 71%). Interestingly, the reaction of **Ia** and **IIa** with hydrazine in ethanol gave no expected ethoxypyrazoles but resulted in complete tarring of the reaction mixture.

Unlike hydrazine, ketones **Ia** and **IIa** reacted with hydroxylamine in methanol in a classical way, i.e., with participation of the C=O group of ketones **Ib** and

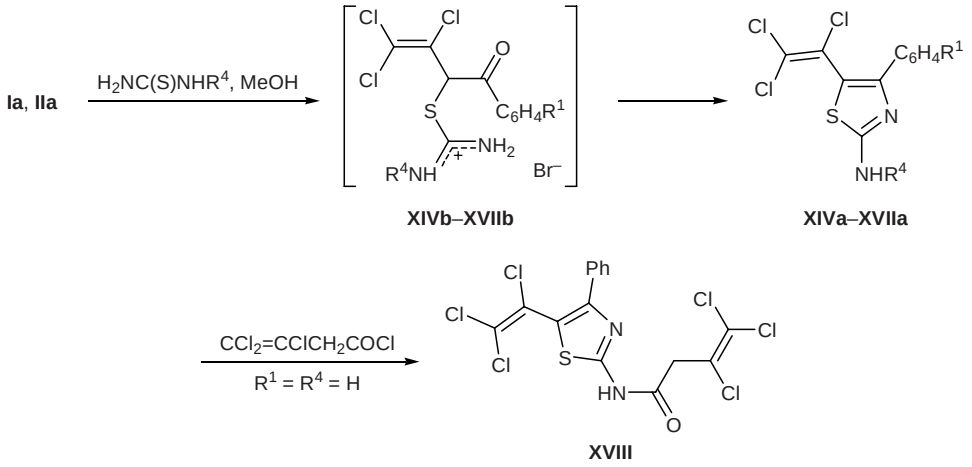
IIb formed by prototropic rearrangement of the initial ketones. The structure of the final products depends on the reactant ratio and reaction conditions. At a ketone-to-hydroxylamine ratio of 1 : 2 we obtained a complex mixture of products, among which we identified by GC–MS 3-aryl-4-bromo-5-dichloromethyl-1,2-oxazoles **VIII** and **IX**, 3-aryl-4-chloro-5-dichloromethylisoxazoles **X** and **XI**, benzonitrile, and methyl benzoate. The mass spectra of these compounds contained the corresponding molecular ion peaks and fragment ion peaks. The isotope ratios of the molecular ion clusters were 61 : 100 : 46 : 6.4 for compounds **VIII** and **IX** and 100 : 98 : 32 : 3.5 for **X** and **XI**, in keeping with the presence of one bromine and two chlorine atoms in molecules of the former and of three chlorine atoms in molecules of the latter [10, 11]. The reactions of ketones **Ia** and **IIa** with hydroxylamine were accompanied by strong tarring, and the yield of isoxazoles **VIII**–**XI** did not exceed 8–10%. Methyl benzoate and benzonitrile were likely to be formed as a result of cleavage of the (Br)C–C(O) bond in molecules of the initial ketone and ketone oxime, respectively. The formation of bromo-substituted isoxazoles **VIII** and **IX** might be expected, so that it requires no additional comments, whereas the formation of chloroisoxazoles **X** and **XI** was quite surprising. We believe that compounds **X** and **XI** arise from intramolecular halogen migration in isomeric ketones **Ib** and **IIb**. By carrying out the reactions of **Ia** and **IIa** with hydroxylamine hydrochloride in methanol in the presence of an equimolar (with respect to hydroxylamine) amount of sodium acetate we succeeded in minimizing tar formation and obtaining mixtures of 4-bromo- and 4-chloroisoxazoles **VIII**/**X** and **IX**/**XI** at a ratio of ~1 : 1 in an overall yield of 25%. Compounds **VIII**–**XI** were not isolated as individual substances, and their structure was confirmed, apart from the GC–MS data, by the ^{1}H NMR spectra of mixtures of 4-chloro and 4-bromo derivatives. The Cl_2CH groups therein gave rise to singlets at δ 6.36, 6.54 and 6.35, 6.37 ppm for **VIII**, **X** and **IX**, **XI**, respectively, and protons in the methyl groups attached to the benzene ring in **IX** and **XI** resonated as singlets at δ 2.41 and 2.45 ppm. When compounds **Ia** and **IIa** were treated with excess hydroxylamine as free base (ketone-to-hydroxylamine ratio 1 : 5) in methanol, the products were 3-aryl-5-hydroxyiminomethyl-4-methoxyisoxazoles **XII** and **XIII**, respectively (yield 35 and 45%).

It is known that chlorovinyl ketones are capable of reacting with thiourea to give thiazine or thiazole derivatives, depending on the conditions and ketone structure [12–14]. We found that bromotrichloroallyl ketones **Ia** and **IIa** react with thiourea in methanol in a selective fashion, yielding the corresponding substituted thiazoles. Unlike the reactions with hydrazine and hydroxylamine, the condensations of **Ia** and **IIa** with thiourea were not accompanied by rearrangements into isomeric structures **Ib** and **IIb**, presumably due to low basicity of thiourea. 2-Amino-4-aryl-5-trichlorovinyl-1,3-thiazoles **XIVa** and **XVa** were isolated in 87 and 92% yield, respectively. In the reactions of ketones **Ia** and **IIa** with *N*-acetylthiourea we obtained 2-acetylamino-4-aryl-5-trichlorovinylthiazoles **XVIa** and **XVIIa**, respectively, but their yield did not exceed 18% because of concomitant hydrolysis to thiazoles **XIVa** and **XVa**; the latter were isolated in 45–50% yield. Presumably, the reactions of ketones **Ia** and **IIa** with thiourea derivatives begin with nucleophilic attack by the sulfur atom of thiourea on the electrophilic CHBr carbon atom with formation of isothiuronium salts **XIVb**–**XVIIb**. The latter undergo intramolecular ring closure to give the corresponding 1,3-thiazoles as hydrobromides, and their treatment with sodium hydrogen carbonate yields thiazoles **XIVa**–**XVIIa** (Scheme 2). The proposed scheme is consistent with published data [15–17].

Acylaminothiazoles can be obtained in a higher yield by acylation of preliminarily prepared 2-aminothiazoles with carboxylic acid chlorides. For example, by treatment of aminothiazole **XIVa** with 3,4,4-trichlorobut-3-enoyl chloride (which is readily available starting from trichloroethylene dimer [18]) we synthesized 3,4,4-trichloro-*N*-[4-phenyl-5-trichlorovinyl-1,3-thiazol-2-yl]but-3-enamide (**XVIII**) in 87% yield.

The structure of heterocyclic compounds **VI**, **VII**, and **XIV**–**XVIII** was determined on the basis of their elemental compositions and IR, ^{1}H NMR, and mass spectra. The IR spectra of pyrazoles **VI** and **VII** contained a strong absorption band at 1730 cm^{-1} due to stretching vibrations of the ketone carbonyl group and bands in the region 1615–1620 cm^{-1} due to vibrations of the C=N bond. In the ^{1}H NMR spectra of **VI** and **VII** we observed a broadened singlet in the region δ 8.1–10.0 ppm from the NH proton, multiplet of aromatic protons, and singlets at δ 3.9 and 7.0 ppm from the methoxy group and CH proton in the pyrazole ring. The aromatic methyl protons in compound **VII** resonated as a singlet at δ 2.39 ppm. Pyrazoles **VI** and **VII** showed in the electron impact mass spectra the molecular ion peaks and fragment ion peaks corresponding to elimination of the aryl and methoxy groups and decomposition of the pyrazole ring.

Scheme 2.



I, **XIV**, **XV**, R^1 = H; **II**, **XV**, **XVII**, R^1 = 4-Me; **XIV**, **XV**, R^4 =H; **XVI**, **XVII**, R^4 = Ac.

Isoxazoles **XII** and **XIII** were characterized by IR absorption bands in the regions 1600–1640 (ν C=N) and 1514–1587 cm^{-1} (ν C=C). Their ^{1}H NMR spectra contained a singlet from the methoxy group at δ 3.40–3.45 ppm) and a multiplet belonging to aromatic protons. The exocyclic –CH=N group gave a singlet in the region δ 8.08–8.12 ppm, the aromatic methyl protons of compound **XIII** resonated as a singlet at δ 2.37 ppm, and a broadened singlet at δ 11.5–11.7 ppm was assigned to the oxime NOH proton.

Stretching vibrations of the endocyclic C=N bond in thiazoles **XIV**–**XVIII** had an IR frequency of 1604–1627 cm^{-1}, absorption bands in the region 1516–1600 cm^{-1} were assigned to the endo- and exocyclic C=C bonds, and the amide carbonyl groups in **XVI**–**XVIII** gave rise to absorption bands at 1622–1702 cm^{-1}. In the ^{1}H NMR spectra of **XIV**–**XVIII**, multiplets from aromatic protons were located in the region δ 7.2–7.7 ppm, the NH_2 protons in **XIV** and **XV** resonated as a broadened singlet at δ 5.5 ppm, and the amide NH protons in **XVI**–**XVIII** were characterized by chemical shifts δ of 10.6–11.6 ppm. The mass spectra of thiazoles **XIV**–**XVIII** contained the molecular ion clusters with isotope intensity ratios of 100:98:32:3.5 for compounds **XIV**–**XVII** and 51:100:82:35:8.7 for **XVIII**, indicating the presence of three chlorine atoms in molecules **XIV**–**XVII** and six chlorine atoms in molecule **XVIII** [10, 11].

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protege-460 spectrometer with Fourier transform. The ^{1}H NMR spectra were measured on a Tesla BS-567A instrument (100 MHz) from solutions in $CDCl_3$ (**III**–**XI**, **XIV**–**XVIII**) and acetone-d_6 (**XII**, **XIII**) using tetramethylsilane as internal reference. The ^{13}C NMR spectrum of a solution of compound **III** in $CDCl_3$ was obtained on a Bruker Avance-500 spectrometer; the chemical shifts were measured relative to the solvent signal (δ_C 77.0 ppm). The mass spectra (electron impact, 70 eV) were recorded on a Hewlett–Packard HP 5972 mass-selective detector coupled with an HP 5890 gas chromatograph (HP-5MS capillary column, 30 m × 0.25 mm, film thickness 0.25 μm, stationary phase 5% of phenylmethylsilicone, injector temperature 250°C).

3,4,4-Trichlorobut-3-enoyl chloride was synthesized from trichloroethylene dimer according to the procedure described in [18].

2-Bromo-4,4-dichloro-3-morpholino-1-phenylbut-2-en-1-one (III). A solution of 0.53 g (6 mmol) of morpholine in 10 ml of anhydrous diethyl ether was added dropwise at 15°C to a solution of 1.0 g (3 mmol) of ketone **Ia** in 30 ml of anhydrous diethyl ether. The mixture was stirred for 1 h, and the precipitate was filtered off, washed with water (3 × 30 ml), and dried under reduced pressure. Yield 1.08 g (94%), mp 112–113°C (decomp.). IR spectrum, ν, cm^{-1}: 928 ($CHCl_2$); 1580, 1593 (C=C); 1696 (C=O). ^{1}H NMR spectrum, δ, ppm (major *Z* isomer): 3.23 m (4H, CH_2N), 3.38 m (4H, CH_2O), 6.59 s (1H, $CHCl_2$), 7.45 m (3H, H_{arom}), 7.87 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm (major *Z* isomer): 50.61 (CH_2N), 55.96 ($CHCl_2$), 67.42 (CH_2O), 128.90 ($2CH_{arom}$), 129.77 ($2CH_{arom}$), 134.61 (CH_{arom}), 188.95 (C=O), 119.40, 134.90, 143.2. Found, %: C 44.52; H 3.99; Hlg 39.69; N 3.77. $[M - HCl]^+$ 341. $C_{14}H_{14}BrCl_2NO_2$. Calculated, %: C 44.36; H 3.72; Hlg 39.78; N 3.69. *M* 379.

Amino ketones **IV** and **V** were synthesized in a similar way from the corresponding ketone and amine.

2-Bromo-4,4-dichloro-1-(4-methylphenyl)-3-morpholinobut-2-en-1-one (IV). Yield 97%, mp 107–108°C (decomp.). IR spectrum, ν, cm^{-1}: 929 ($CHCl_2$); 1580, 1606 (C=C); 1693 (C=O). ^1H NMR spectrum, δ, ppm (major *Z* isomer): 2.44 s (3H, CH_3), 2.60 m (4H, CH_2N), 3.34 m (4H, CH_2O), 6.59 s (1H, $CHCl_2$), 7.27 d (2H, H_{arom}, ^3J = 8 Hz), 7.80 m (2H, H_{arom}, ^3J = 8 Hz). Found, %: C 45.62; H 3.79; Hlg 38.57; N 3.70. $[M - HCl]^+$ 355. $C_{15}H_{16}BrCl_2NO_2$. Calculated, %: C 45.83; H 4.10; Hlg 38.36; N 3.56. *M* 393.

2-Bromo-4,4-dichloro-3-diethylamino-1-phenylbut-2-en-1-one (V). Yield 74%, mp 72–73°C (decomp.). IR spectrum, ν, cm^{-1}: 923 ($CHCl_2$); 1576, 1593 (C=C); 1703 (C=O). ^1H NMR spectrum, δ, ppm (major *Z* isomer): 0.67 t (6H, CH_3), 2.91 q (4H, CH_2N), 6.60 s (1H, $CHCl_2$), 7.51 m (3H, H_{arom}), 7.85 m (2H, H_{arom}). Found, %: C 46.47; H 4.59; Hlg 40.99; N 3.92. $[M - HCl]^+$ 327. $C_{14}H_{16}BrCl_2NO$. Calculated, %: C 46.06; H 4.42; Hlg 41.31; N 3.84. *M* 365.

5-Aroyl-4-methoxy-1*H*-pyrazoles VI and VII (*general procedure*). A solution of 0.61 g (12.2 mmol) of hydrazine hydrate in 10 ml of methanol was added dropwise over a period of 30 min under vigorous stirring to a solution of 6 mmol of ketone **Ia** or **IIa** in 25 ml of methanol, maintaining the temperature at 10°C. The mixture was stirred for 1 h and poured into water. The oily material was extracted into methylene chloride, the extract was dried over $CaCl_2$ and concentrated to a volume of 10 ml under reduced pressure, and the product was isolated by precipitation with hexane at –5°C and dried under reduced pressure.

5-Benzoyl-4-methoxy-1*H*-pyrazole (VI). Yield 54%, mp 181–182°C (decomp.). IR spectrum, ν, cm^{-1}: 1492, 1560, 1590 (C=C); 1620 (C=N); 1731 (C=O); 3203 (N–H). ^1H NMR spectrum, δ, ppm: 3.85 s (3H, OCH_3), 7.05 s (1H, 3-H), 7.4 m (3H, H_{arom}), 7.7 m (2H, H_{arom}), 10.0 br.s (1H, NH). Found, %: C 65.39; H 4.93; N 13.76. $[M]^+$ 202. $C_{11}H_{10}N_2O_2$. Calculated, %: C 65.34; H 4.98; N 13.85. *M* 202.

4-Methoxy-5-(4-methylbenzoyl)pyrazole (VII). Yield 71%, mp 194–195°C (decomp.). IR spectrum, ν, cm^{-1}: 1509, 1560, 1580 (C=C); 1615 (C=N); 1729 (C=O); 3200 (N–H). ^1H NMR spectrum, δ, ppm: 2.39 s (3H, CH_3), 3.94 s (3H, OCH_3), 7.08 s (1H, =CH), 7.24 d (2H, H_{arom}, ^3J = 8 Hz), 7.63 d (2H, H_{arom}, ^3J = 8 Hz), 8.1 br.s (1H, NH). Found, %: C 66.47; H 5.99; N 12.79. $[M]^+$ 216. $C_{12}H_{12}N_2O_2$. Calculated, %: C 66.65; H 5.59; N 12.95. *M* 216.

3-Aryl-5-hydroxyiminomethyl-4-methoxyisoxazoles XII and XIII (*general procedure*). A solution of hydroxylamine, prepared from 2.08 g (30 mmol) of hydroxylamine hydrochloride and 3.04 g (30 mmol) of triethylamine in 30 ml of methanol, was added dropwise at 15°C to a solution of 6 mmol of ketone **Ia** or **IIa** in 30 ml of methanol. The mixture was heated to 45°C, stirred for 5 h at that temperature, evaporated to 1/3 of the initial volume, and poured into water. An oily material separated and was extracted into chloroform, the extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, and the residue was recrystallized from hexane–$CHCl_3$ (1:5).

4-Methoxy-3-phenylisoxazole-5-carbaldehyde oxime (XII). Yield 35%, mp 130–132°C. IR spectrum, ν, cm^{-1}: 1530, 1587 (C=C); 1600, 1618 (C=N); 3311 (O–H). ^1H NMR spectrum, δ, ppm: 3.40 s (3H, OCH_3), 7.3 m (3H, H_{arom}), 7.6 m (2H, H_{arom}), 8.12 s (1H, N=CH), 11.50 br.s (1H, OH). Found, %: C 60.82; H 5.01; N 12.77. $[M]^+$ 218. $C_{11}H_{10}N_2O_3$. Calculated, %: C 60.55; H 4.62; N 12.84. *M* 218.

4-Methoxy-3-(4-methylphenyl)isoxazole-5-carbaldehyde oxime (XIII). Yield 45%, mp 149–151°C. IR spectrum, ν, cm^{-1}: 1514, 1526 (C=C); 1613, 1640 (C=N); 3305 (O–H). ^1H NMR spectrum, δ, ppm: 2.37 s (3H, CH_3), 3.45 s (3H, OCH_3), 7.22 d (2H, H_{arom}, ^3J = 8 Hz), 7.46 d (2H, H_{arom}, ^3J = 8 Hz), 8.08 s (1H, =CH), 11.70 br.s (1H, OH). Found, %: C 62.21; H 5.19; N 12.45. $[M]^+$ 232. $C_{12}H_{12}N_2O_3$. Calculated, %: C 62.06; H 5.21; N 12.06. *M* 232.

2-Amino-4-aryl-5-trichlorovinyl-1,3-thiazoles XIVa and XVa (*general procedure*). A solution of 4 mmol of ketone **Ia** or **IIa** and 0.61 g (8 mmol) of thiourea in 30 ml of methanol was stirred for 3 h at 40°C. The mixture was poured into 200 ml of water and treated with sodium hydrogen carbonate to weakly alkaline reaction. The precipitate was filtered off, washed with water, and dried under reduced pressure at 60°C.

4-Phenyl-5-trichlorovinyl-1,3-thiazol-2-amine (XIVa). Yield 87%, mp 147–148°C (decomp.). IR spectrum, ν, cm^{-1}: 1520, 1600 (C=C); 1627 (C=N); 3266, 3464 (NH_2). ^1H NMR spectrum, δ, ppm: 5.50 br.s (2H, NH_2), 7.4 m (3H, H_{arom}), 7.6 m (2H, H_{arom}). Found, %: C 43.15; H 2.64; Cl 34.33; N 9.03; S 10.35. $[M]^+$ 304. $C_{11}H_7Cl_3N_2S$. Calculated, %: C 43.23; H 2.31; Cl 34.80; N 9.17; S 10.49. *M* 305.

4-(4-Methylphenyl)-5-trichlorovinyl-1,3-thiazol-2-amine (XVa). Yield 92%, mp 156–157°C (decomp.). IR spectrum, ν, cm^{-1}: 1516, 1537 (C=C); 1604 (C=N); 3241, 3468 (NH_2). ^1H NMR spectrum, δ, ppm: 2.39 s

(3H, CH_3), 5.50 br.s (2H, NH_2), 7.22 d (2H, H_{arom}, ^3J = 8 Hz), 7.50 d (2H, H_{arom}, ^3J = 8 Hz). Found, %: C 45.49; H 2.88; Cl 32.80; N 8.79; S 9.88. $[M]^+$ 318. $C_{12}H_9Cl_3N_2S$. Calculated, %: C 45.09; H 2.84; Cl 33.27; N 8.76; S 10.03. *M* 319.

***N*-[4-Aryl-5-trichlorovinyl-1,3-thiazol-2-yl)acetamides XVIa and XVIIa (*general procedure*).** A solution of 4 mmol of bromo ketone **Ia** or **IIa** and 0.95 g (8 mmol) of *N*-acetylthiourea in 30 ml of methanol was stirred for 3 h at 40°C. The mixture was poured into 200 ml of water, the precipitate was extracted into chloroform, the extract was dried over $CaCl_2$ and evaporated under reduced pressure to a volume of 20 ml, 20 ml of hexane was added, and the precipitate of aminothiazole **XIV** or **XV** was filtered off (after drying under reduced pressure, the yields were 45 and 50%, respectively). The filtrate was kept for 40 h at –5°C, and the precipitate of **XVIa** or **XVIIa** was filtered off, washed with hexane, and dried under reduced pressure.

***N*-(4-Phenyl-5-trichlorovinyl-1,3-thiazol-2-yl)-acetamide (XVIa).** Yield 18%, mp 222–224°C. IR spectrum, ν, cm^{-1}: 1525, 1600 (C=C); 1625 (C=N); 1678 (C=O); 3264, 3449 (N–H). ^{1}H NMR spectrum, δ, ppm: 1.56 s (3H, CH_3), 7.45 m (3H, H_{arom}), 7.7 m (2H, H_{arom}), 11.60 br.s (1H, NH). Found, %: C 44.83; H 2.82; Cl 30.55; N 8.03; S 9.20. $[M]^+$ 346. $C_{13}H_9Cl_3N_2OS$. Calculated, %: C 44.91; H 2.61; Cl 30.59; N 8.06; S 9.22. M 347.

***N*-[4-(4-Methylphenyl)-5-trichlorovinyl-1,3-thiazol-2-yl)acetamide (XVIIa).** Yield 10%, mp 188–190°C. IR spectrum, ν, cm^{-1}: 1523, 1590 (C=C); 1615 (C=N); 1622 (C=O); 3240 (NH). ^{1}H NMR spectrum, δ, ppm: 1.62 s (3H, CH_3), 2.41 s (3H, CH_3), 7.20 d (2H, H_{arom}, ^3J = 8 Hz), 7.55 d (2H, H_{arom}, ^3J = 8 Hz), 11.50 br.s (1H, NH). Found, %: C 46.83; H 3.15; Cl 29.38; N 7.35; S 8.55. $[M]^+$ 360. $C_{14}H_{11}Cl_3N_2OS$. Calculated, %: C 46.49; H 3.07; Cl 29.41; N 7.75; S 8.87. *M* 361.

3,4,4-Trichloro-*N*-(4-phenyl-5-trichlorovinyl-1,3-thiazol-2-yl)but-3-enamide (XVIII). A mixture of 0.83 g (3.99 mmol) of 3,4,4-trichlorobut-3-enoyl chloride and 2.44 g (7.98 mmol) of aminothiazole **XIVa** in 20 ml of anhydrous chloroform was stirred for 5 h at 50°C. The mixture was cooled, 30 ml of anhydrous diethyl ether was added, the precipitate of initial aminothiazole hydrochloride was filtered off, the filtrate was evaporated to dryness under reduced pressure, and the residue was recrystallized from hexane–chloroform (1:1). Yield 1.66 g (87%), mp 173–175°C. IR spectrum, ν, cm^{-1}: 1536, 1598, 1610 (C=C, C=N); 1702 (C=O); 3250 (N–H). ^{1}H NMR spectrum, δ, ppm: 3.16 s (2H, CH_2), 7.48 m (3H, H_{arom}), 7.66 m (2H, H_{arom}), 10.60 br.s (1H, NH). Found, %: C 37.51; H 1.76; Cl 44.34; N 5.61; S 6.68. $[M]^+$ 474. $C_{15}H_8Cl_6N_2OS$. Calculated, %: C 37.77; H 1.69; Cl 44.59; N 5.87; S 6.72. *M* 477.

This study was performed under financial support by the Byelorussian Foundation for Basic Research (project no. Kh07-050).

REFERENCES

1. Nenaidenko, V.G., Sanin, A.V., and Balenkova, E.S., *Usp. Khim.*, 1999, vol. 68, p. 483.
2. Moiseev, I.K., Zemtsova, M.N., and Makarova, N.V., *Khim. Geterotsikl. Soedin.*, 1994, p. 867.
3. Moiseev, I.K., Makarova, N.V., and Zemtsova, M.N., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 1685.
4. Rulev, A.Yu., *Usp. Khim.*, 1998, vol. 67, p. 317.
5. Kaberdin, R.V., Potkin, V.I., and Petkevich, S.K., *Vestsi Akad. Navuk Belarusi, Ser. Khim.*, 2006, no. 2, p. 99.
6. Potkin, V.I., Petkevich, S.K., Kaberdin, R.V., and Kurman, P.V., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 1617.
7. Potkin, V.I., Petkevich, S.K., Kaberdin, R.V., and Tychinskaya, L.Yu., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1271.
8. Roedig, A. and Ritschel, W., *Justus Liebigs Ann. Chem.*, 1983, no. 1, p. 13.
9. Roedig, A. and Ritschel, W., *Chem. Ber.*, 1983, vol. 116, p. 1595.
10. Takhistov, V.V., *Prakticheskaya mass-spektrometriya organicheskikh soedinenii* (Practical Mass Spectrometry of Organic Compounds), Leningrad: Leningr. Gos. Univ., 1977, p. 265.
11. Takhistov, V.V., Rodin, A.A., and Maksimov, B.N., *Usp. Khim.*, 1991, vol. 60, p. 2143.
12. Levkovskaya, G.G., Bozhenkov, G.V., Larina, L.I., Evstaf'eva, I.T., and Mirskova, A.N., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 644.
13. Mirskova, A.N., Levkovskaya, G.G., and Atavin, A.S., *Zh. Org. Khim.*, 1976, no. 12, p. 904.
14. Spitzner, R., Mielke, D., Schollz, D., Schroth, W., and Preiss, A., *Tetrahedron*, 1982, vol. 38, p. 927.
15. Spitzner, R., Menzel, M., and Schroth, W., *Synthesis*, 1982, no. 2, p. 206.
16. Schroth, W., Spitzner, R., Koch, B., Freitag, S., and Mielke, D., *Tetrahedron*, 1982, vol. 38, p. 937.
17. *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 3. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1983, vol. 5, p. 667.
18. Petkevich, S.K., Dikusar, E.A., Potkin, V.I., Kaberdin, R.V., Moiseichuk, K.L., Yuvchenko, A.P., and Kurman, P.V., *Russ. J. Gen. Chem.*, 2004, vol. 74, p. 586.