ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 10, pp. 1412–1421. © Pleiades Publishing, Ltd., 2014.
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Synthesis of Functional Derivatives of Aryl Trichlorovinyl (Trichloroallyl) Ketones via Consecutive Transformations of the Carbonyl Group

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Received April 23, 2014

Abstract—An efficient procedure have been developed for the selective reduction of the carbonyl group in phenyl trichlorovinyl ketone and aryl trichloroallyl ketones by the action of $NaBH_4$ in propan-2-ol to obtain the corresponding alcohols. The hydroxy group in the latter was converted into amino by the Ritter reaction. Treatment of the alcohols and amines with 5-phenylisoxazole-3-carbonyl chloride and 4,5-dichloroisothiazole-3-carbonyl chloride gave the corresponding esters and amides, and condensation of the amines with aromatic aldehydes afforded Schiff bases.

DOI: 10.1134/S1070428014100042

Unsaturated chlorinated ketones, especially chlorovinyl ketones (chloroenones), are widely used in organic synthesis due to their high synthetic potential which is determined by the presence in their molecules of several reactive fragments, carbonyl group, chlorine atoms, and C=C double bond [1–3]. Preparative procedures for the synthesis of various useful compounds, including biologically active substances, have been developed on the basis of reactions of such ketones [4, 5]. An important problem related to efficient use of accessible chloroenones consists of selective modification of different reactive centers in their molecules in order to ensure desired transformations and avoid side processes. Convenient methods for the synthesis of unsaturated chloro ketones from accessible lower chloroalkenes have been developed at the Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, and Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences [2, 6–8].

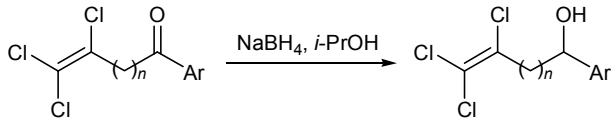
The goal of the present work was to find rational synthetic approaches to chlorinated unsaturated alcohols, amines, and Schiff bases via successive transformations of the carbonyl group in aryl trichlorovinyl and aryl trichloroallyl ketones with retention of the other reaction centers. The products of these reactions attract interest as substrates for further transformations, as well as for biological testing. As starting compounds we used 2,3,3-trichloro-1-phenylprop-2-en-1-one (**I**) and 1-aryl-3,4,4-trichlorobut-3-en-1-ones **II**–**V** which were prepared as described in [2, 6].

In the first step of our study we tried to develop an efficient procedure for the selective reduction of the carbonyl group, not involving chlorine atoms and C=C bond. Various reagents and reagent systems have been proposed for the reduction of carbonyl group, e.g., metallic sodium in alcohol, $LiAlH_4$, $NaBH(AcO)_3$, $NaBH_4$, and others. In our case, neither metallic sodium in alcohol nor sodium tetrahydridoborate can be used because of concurrent reactions involving the chlorine atoms and C=C double bond, which lead to complex mixtures of products. The reaction with sodium triacetoxyhydridoborate in anhydrous benzene in the presence of acetic acid was relatively slow, and the target alcohols were formed in low yield.

The optimal procedure for the reduction of ketones **I**–**V** was their treatment with a slight excess of $NaBH_4$ in propan-2-ol. In this case, the reaction involved

exclusively the carbonyl group and was complete in 4 h, and the desired chlorinated alcohols **VI**–**X** were obtained in high yield (91–94%; Scheme 1). The IR spectra of **VI**–**X** lacked carbonyl absorption bands, but a broadened band was present in the region 3374–3384 cm^{-1} due to stretching vibrations of the hydroxy group. In the ^1H NMR spectra of **VI**–**X**, the hydroxy proton resonated as a broadened singlet at δ 2.38–3.57 ppm. Signals from the CH and CH_2 protons in the spectra of **VII**–**X** appeared as multiplets since these alcohols were formed as racemic mixtures. The isotope ratios of the molecular ion clusters in the mass spectra of **VI**–**X** indicated the presence of three chlorine atoms (and one bromine atom in **X**) [9].

Scheme 1.

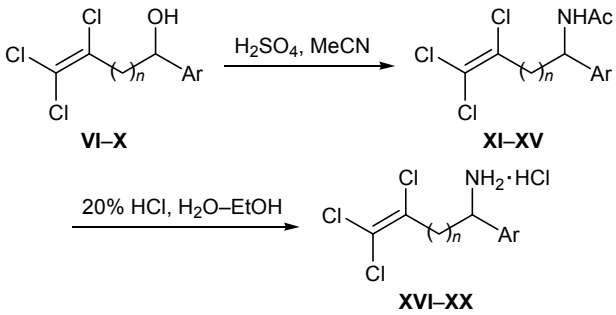


I–**V** **VI**–**X**

I, **VI**, n = 0, Ar = Ph; **II**, **VII**, n = 1, Ar = Ph; **III**, **VIII**, n = 1, Ar = 4-MeC_6H_4; **IV**, **IX**, n = 1, Ar = 2,5-$Me_2C_6H_3$; **V**, **X**, n = 1, Ar = 4-BrC_6H_4.

The hydroxy group in alcohols **VI**–**X** was converted into amino according to the approach based on the Ritter reaction [10]. The reaction of **VI**–**X** with acetonitrile in the presence of concentrated sulfuric acid gave the corresponding acetamides **XI**–**XV** whose hydrolysis with HCl in aqueous ethanol produced 2,3,3-trichloro-1-phenylprop-2-en-1-amine (**XVI**) and 1-aryl-3,4,4-trichlorobut-3-en-1-amine hydrochlorides **XVII**–**XX** (Scheme 2). The formation of amines as hydrochlorides hampered further reactions with participation of chlorine atoms in the aliphatic residue. The structure of amides **XI**–**XV** and amines **XVI**–**XX** was

Scheme 2.



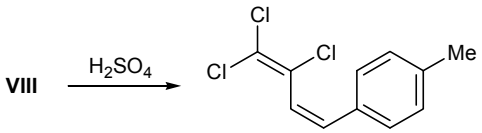
VI–**X** **XI**–**XV** **XVI**–**XX**

VI, **XI**, **XVI**, n = 0, Ar = Ph; **VII**–**X**, **XII**–**XV**, **XVII**–**XX**, n = 1; **VII**, **XII**, **XVII**, Ar = Ph; **VIII**, **XIII**, **XVIII**, Ar = 4-MeC_6H_4; **IX**, **XIV**, **XIX**, Ar = 2,5-$Me_2C_6H_3$; **X**, **XV**, **XX**, Ar = 4-BrC_6H_4.

determined on the basis of their elemental analyses and IR and ^1H and ^{13}C NMR spectra. Like the initial alcohols, compounds **XII**–**XV** and **XVII**–**XX** were racemates, and the CH_2 protons gave rise to multiplet signals in the ^1H NMR spectra.

Alcohols **VII**–**X** underwent dehydration by the action of sulfuric acid in the absence of acetonitrile. By treatment of 3,4,4-trichloro-1-(4-methylphenyl)but-3-en-1-ol (**VIII**) with H_2SO_4 we obtained 87% of 3,4,4-trichloro-1-(4-methylphenyl)buta-1,3-diene (**XXI**) which was identified by the IR and ^1H NMR spectra (Scheme 3). Diene **XXI** was formed as *Z* isomer, as followed from the coupling constants of the CH=CH protons (^3J = 7.1 Hz) [11].

Scheme 3.



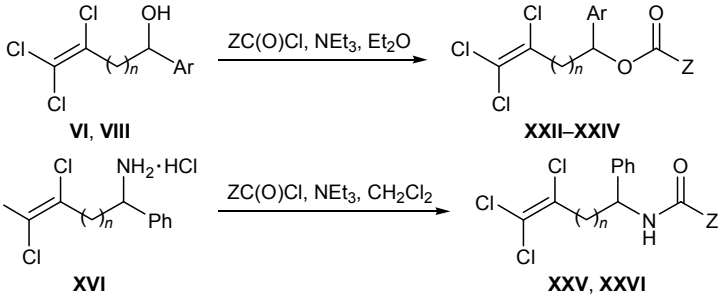
XXI

Further modification of the synthesized alcohols and amines involved introduction into their molecules of pharmacophoric isoxazole and isothiazole fragments with a view to obtaining biologically active compounds. There are numerous published data indicating a broad spectrum of biological activity of isothiazole and isoxazole derivatives [12, 13]. Moreover, we found previously that esters and amides derived from 4,5-dichloroisothiazole-3-carboxylic acid show synergistic effect in compositions with pyrethroid and neonicotinoid insecticides against potato beetle larvae and that some derivatives enhance the effect of cypermethrin against fleas [14, 15].

By acylation of alcohols **VI** and **VIII** and amine **XVI** with 5-phenylisoxazole-3-carbonyl chloride and 4,5-dichloroisothiazole-3-carbonyl chloride in the presence of triethylamine we synthesized the corresponding esters **XXII**–**XXIV** and amides **XXV** and **XXVI** (Scheme 4) which were identified by IR and NMR spectroscopy. The products are now being tested as cypermethrin synergists against the oriental rat flea *Xenopsylla cheopis* (carriers of plague and other diseases) at the Irkutsk Research Anti-plague Institute (Russian Federal Service for Surveillance on Consumer Rights Protection and Human Wellbeing).

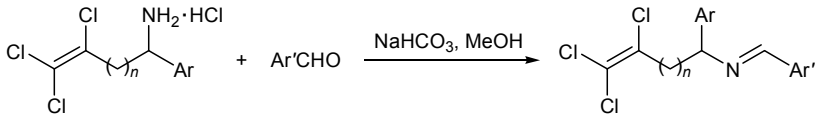
Amine hydrochlorides **XVI**–**XX** were also brought into condensation with substituted benzaldehydes in anhydrous ethanol in the presence of sodium hydrogen carbonate to obtain the corresponding Schiff bases. As

Scheme 4.



VI, **XXII**, **XXV**, **XXVI**, n = 0, Ar = Ph; **VIII**, **XXIII**, **XXIV**, n = 1, Ar = 4-MeC_6H_4; **XXII**, **XXIII**, **XXV**, Z = 5-phenyl-1,2-oxazole-3-yl; **XXIV**, **XXVI**, Z = 4,5-dichloro-1,2-thiazol-3-yl.

Scheme 5.



XVI, **XXVII**–**XXX**, n = 0, Ar = Ph; **XXVII**, Ar′ = 4-$MeOC_6H_4$; **XXVIII**, Ar′ = 4-HOC_6H_4; **XXIX**, Ar′ = 3-MeO-4-HOC_6H_3; **XXX**, Ar′ = 3-HO-4-$MeOC_6H_3$; **XVII**, **XXXI**–**XXXIV**, n = 1, Ar = Ph; **XVIII**, **XXXV**–**XXXVII**, n = 1, Ar = 4-MeC_6H_4; **XIX**, **XXXVIII**, **XXXIX**, n = 1, Ar = 2,5-$Me_2C_6H_3$; **XX**, **XL**, **XLI**, n = 1, Ar = 4-BrC_6H_4; **XXXI**, **XXXV**, **XXXVIII**, **XL**, Ar′ = 4-$MeOC_6H_4$; **XXXII**, **XXXVI**, Ar′ = 4-HOC_6H_4; **XXXIII**, **XXXVII**, **XXXIX**, **XLI**, Ar′ = 3-MeO-4-HOC_6H_3; **XXXIV**, Ar′ = 3-HO-4-$MeOC_6H_3$.

aldehyde components we used 4-hydroxybenzaldehyde, 4-methoxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde (vanillin), and 3-hydroxy-4-methoxybenzaldehyde (isovanillin) (Scheme 5). Schiff bases attract persistent interest and are widely used in organic synthesis due to their high synthetic potential. In addition, they possess a variety of useful properties, including a broad spectrum of biological activity [16]. Schiff bases derived from vanillin attract particular interest since some vanillin derivatives were found to inhibit DNA protein kinase and regulate repair of DNA damage according to the NHEJ (non-homologous DNA end-joining) mechanism; they also showed synergistic effect on the activity of neonicotinoid insecticide imidacloprid [14, 17].

Schiff bases **XXVII**–**XLI** were identified on the basis of their elemental analyses and IR and ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra of **XXVII**–**XLI**, the HC=N proton resonated as a singlet at δ 8.16–8.38 ppm, which is typical of *E* configuration of the azomethine fragment; the corresponding signal of *Z* isomers is usually located in a weaker field due to deshielding by the benzene ring [18].

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Protege-460 spectrometer with Fourier transform from samples prepared as KBr pellets (**XI**–**XXII**, **XXV**, **XXVI**, **XXXII**, **XXXVI**–**XXXVIII**) or thin films (**VI**–**X**, **XXIII**, **XXIV**, **XXVII**–**XXXI**, **XXXIII**–**XXXV**, **XXXIX**–**XLI**). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-500 spectrometer from solutions in $CDCl_3$ (**VI**–**XV**, **XXI**–**XXIV**, **XXVII**–**XXXV**, **XXXVII**–**XLI**), acetone-d_6 (**XXV**, **XXVI**, **XXXVI**), or DMSO-d_6 (**XVI**–**XX**); the chemical shifts were determined relative to to the residual proton and carbon signals of the deuterated solvent ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.2 ppm; acetone-d_5, δ 2.05 ppm; δ_C 30.2 ppm; DMSO-d_5, δ 2.50 ppm, δ_C 40.1 ppm). The mass spectra of alcohols **VI**–**X** (electron impact, 70 eV) were obtained using a Hewlett Packard HP 5890/5972 GC/MS system (HP-5MS capillary column, 30 m × 0.25 mm, film thickness 0.25 μm; injector temperature 250°C).

Reduction of ketones I–V (*general procedure*). Ketone **I**–**V**, 10 mmol, was dissolved in 50 mL of anhydrous propan-2-ol, 10 mmol of sodium tetrahydridoborate was added, and the mixture was stirred for 4 h at room temperature and poured into 300 mL of water. The product was extracted into chloroform, the extract was dried over sodium sulfate, and the solvent was removed under reduced pressure. Alcohols **VI**–**X** thus isolated required no additional purification.

2,3,3-Trichloro-1-phenylprop-2-en-1-ol (VI). Yield 94%, oily substance. IR spectrum, ν, cm^{-1}: 3374 (OH), 3064, 3032, 2924, 2851 (C–H), 1592, 1495,

1452 (C=C), 1108, 1046 (C–O), 921, 846 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.57 br.s (1H, OH), 6.12 s (1H, CH), 7.41 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 71.88 (CH), 125.79 (2C, CH_{arom}), 128.68 (2C, CH_{arom}), 128.52 (CH_{arom}), 119.77, 134.61, 138.88. Found, %: C 45.65; H 2.88; Cl 44.64. Mass spectrum: *m*/*z* 236 $[M]^+$. $C_9H_7Cl_3O$. Calculated, %: C 45.51; H 2.97; Cl 44.78. *M* 237.51.

3,4,4-Trichloro-1-phenylbut-3-en-1-ol (VII). Yield 94%, oily substance. IR spectrum, ν, cm^{-1}: 3383 (OH), 3087, 3064, 2971, 2916, 2868 (C–H), 1603, 1494, 1454, 1430 (C=C), 1193, 1046 (C–O), 923, 769 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.72 br.s (1H, OH), 2.72–3.15 m (2H, CH_2), 5.02 m (1H, CH), 7.37 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 45.52 (CH_2), 71.94 (CH), 125.85 (2C, CH_{arom}), 128.23 (CH_{arom}), 128.68 (2C, CH_{arom}), 119.77, 121.87, 142.60. Found, %: C 47.88; H 3.55; Cl 42.08. Mass spectrum: *m*/*z* 250 $[M]^+$. $C_{10}H_9Cl_3O$. Calculated, %: C 47.75; H 3.61; Cl 42.28. *M* 251.54.

3,4,4-Trichloro-1-(4-methylphenyl)but-3-en-1-ol (VIII). Yield 94%, oily substance. IR spectrum, ν, cm^{-1}: 3382 (OH), 3050, 3024, 2971, 2922, 2862 (C–H), 1612, 1514, 1430 (C=C), 1180, 1044 (C–O), 921, 818 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.42 s (3H, Me), 2.69 br.s (1H, OH), 2.69–3.17 m (2H, CH_2), 5.02 m (1H, CH), 7.22 d and 7.30 d (2H each, H_{arom}, ^3J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.25 (Me), 45.45 (CH_2), 71.80 (CH), 125.81 (2C, CH_{arom}), 129.33 (2C, CH_{arom}), 119.61, 121.69, 137.92, 139.69. Found, %: C 49.79; H 4.25; Cl 39.94. Mass spectrum: *m*/*z* 264 $[M]^+$. $C_{11}H_{11}Cl_3O$. Calculated, %: C 49.75; H 4.18; Cl 40.05. *M* 265.56.

3,4,4-Trichloro-1-(2,5-dimethylphenyl)but-3-en-1-ol (IX). Yield 91%, oily substance. IR spectrum, ν, cm^{-1}: 3381 (OH), 3044, 3020, 2970, 2923, 2869 (C–H), 1619, 1502, 1446 (C=C), 1204, 1045 (C–O), 923, 812 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.32 s and 2.35 s (3H each, Me), 2.38 br.s (1H, OH), 2.70–3.18 m (2H, CH_2), 5.28 m (1H, CH), 7.06 m (2H, H_{arom}), 7.38 s (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 18.56 (Me), 21.20 (Me), 44.65 (CH_2), 68.55 (CH), 125.94 (CH_{arom}), 128.60 (CH_{arom}), 130.59 (CH_{arom}), 119.61, 121.73, 131.24, 136.05, 140.71. Found, %: C 51.43; H 4.60; Cl 38.08. Mass spectrum: *m*/*z* 278 $[M]^+$. $C_{12}H_{13}Cl_3O$. Calculated, %: C 51.55; H 4.69; Cl 38.04. *M* 279.59.

1-(4-Bromophenyl)-3,4,4-trichlorobut-3-en-1-ol (X). Yield 91%, oily substance. IR spectrum, ν, cm^{-1}: 3384 (OH), 3050, 3030, 2971, 2916, 2854 (C–H), 1593, 1487, 1427 (C=C), 1191, 1050 (C–O), 922, 825 (C–Cl), 546 (C–Br). ^{1}H NMR spectrum, δ, ppm: 2.67 br.s (1H, OH), 2.77–3.09 m (2H, CH_2), 5.97 m (1H, CH), 7.22 d and 7.47 d (2H each, H_{arom}, ^3J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 45.48 (CH_2), 71.36 (CHOH), 127.59 (2C, CH_{arom}), 131.80 (2C, CH_{arom}), 120.13, 122.07, 128.86, 141.57. Found, %: C 36.28; H 2.51; Hlg 56.40. Mass spectrum: *m*/*z* 328 $[M]^+$. $C_{10}H_8BrCl_3O$. Calculated, %: C 36.35; H 2.44; Hlg 56.37. *M* 330.43.

Acetamides XI–XV (*general procedure*). Alcohol **VI–X**, 100 mol, was dissolved in 25 mL of anhydrous acetonitrile, 1 mL of concentrated sulfuric acid was added, and the mixture was stirred for 5 h at 20°C and poured into 250 mL of water. The product was extracted into chloroform, the extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, and the residue was recrystallized from 70% aqueous methanol (**XII**, **XIII**, **XV**) or hexane–chloroform (2:1) (**XI**, **XIV**).

***N*-(2,3,3-Trichloro-1-phenylprop-2-en-1-yl)acetamide (XI).** Yield 63%, mp 141–143°C. IR spectrum, ν, cm^{-1}: 3261 (N–H), 3032, 2948, 2926 (C–H), 1650 (C=O), 1595, 1537, 1496, 1453 (C=C, δN–H), 916, 837 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.03 s (3H, Me), 6.55 d (1H, CH, ^3J = 8.3 Hz), 6.81 d (1H, NH, ^3J = 8.3 Hz), 7.34 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.95 (Me), 54.31 (CH), 126.47 (2C, CH_{arom}), 128.46 (CH_{arom}), 128.98 (2C, CH_{arom}), 120.77, 131.91, 136.64, 169.79 (C=O). Found, %: C 47.40; H 3.77; Cl 38.05; N 5.05. $C_{11}H_{10}Cl_3NO$. Calculated, %: C 47.43; H 3.62; Cl 38.18; N 5.03.

***N*-(3,4,4-Trichloro-1-phenylbut-3-en-1-yl)acetamide (XII).** Yield 78%, mp 93–96°C. IR spectrum, ν, cm^{-1}: 3287 (N–H), 3065, 2986, 2926, 2853 (C–H), 1650 (C=O), 1601, 1542, 14983, 1445, 1425 (C=C, δN–H), 926, 867 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.94 s (3H, Me), 2.98–3.09 m (2H, CH_2), 5.36 m (1H, CH), 6.91 d (1H, NH, ^3J = 8.2 Hz), 7.28 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 23.28 (Me), 42.49 (CH_2), 51.78 (CH), 126.60 (2C, CH_{arom}), 127.99 (CH_{arom}), 128.79 (2C, CH_{arom}), 119.63, 129.34, 140.22, 169.86 (C=O). Found, %: C 49.19; H 4.22; Cl 36.09; N 4.78. $C_{12}H_{12}Cl_3NO$. Calculated, %: C 49.26; H 4.13; Cl 36.35; N 4.79.

***N*-[3,4,4-Trichloro-1-(4-methylphenyl)but-3-en-1-yl]acetamide (XIII).** Yield 65%, mp 129–132°C. IR spectrum, ν, cm^{-1}: 3272 (N–H), 3086, 2972, 2922, 2856 (C–H), 1650 (C=O), 1600, 1558, 1517, 1440, 1423 (C=C, δN–H), 933, 818 (C–Cl). ^{1}H NMR spec-

trum, δ, ppm: 1.96 s (3H, Me), 2.33 s (3H, Me), 2.98–3.13 m (2H, CH_2), 5.35 m (1H, CH), 6.41 d (1H, NH, ^3J = 8 Hz), 7.14 d and 7.20 d (2H each, H_{arom}, ^3J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.23 (Me), 23.41 (Me), 42.42 (CH_2), 51.59 (CH), 126.53 (2C, CH_{arom}), 129.55 (2C, CH_{arom}), 119.56, 129.51, 137.17, 137.81, 169.58 (C=O). Found, %: C 50.88; H 4.72; Cl 34.44; N 4.50. $C_{13}H_{14}Cl_3NO$. Calculated, %: C 50.92; H 4.60; Cl 34.69; N 4.57.

***N*-[3,4,4-Trichloro-1-(2,5-dimethylphenyl)but-3-en-1-yl]acetamide (XIV).** Yield 75%, mp 132–135°C. IR spectrum, ν, cm^{-1}: 3265 (N–H), 3079, 2946, 2923, 2856 (C–H), 1650 (C=O), 1563, 1504, 1427 (C=C, δN–H), 925, 814 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.96 s (3H, Me), 2.32 s (6H, Me), 2.92–3.15 m (2H, CH_2), 5.63 m (1H, CH), 6.09 d (1H, NH, ^3J = 7.9 Hz), 7.0 m (1H, H_{arom}), 7.06 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 18.94 (Me), 21.23 (Me), 23.38 (Me), 41.84 (CH_2), 48.00 (CH), 125.99 (CH_{arom}), 128.70 (CH_{arom}), 130.95 (CH_{arom}), 119.43, 129.66, 132.87, 135.93, 138.19, 169.35 (C=O). Found, %: C 52.64; H 5.00; Cl 33.00; N 4.33. $C_{14}H_{16}Cl_3NO$. Calculated, %: C 52.44; H 5.03; Cl 33.17; N 4.37.

***N*-[1-(4-Bromophenyl)-3,4,4-trichlorobut-3-en-1-yl]acetamide (XV).** Yield 65%, mp 141–144°C. IR spectrum, ν, cm^{-1}: 3228 (N–H), 3065, 2926, 2851 (CH), 1652 (C=O), 1603, 1541, 1488, 1433 (C=C, δN–H), 924, 823 (C–Cl), 554 (C–Br). ^1H NMR spectrum, δ, ppm (racemic mixture): 1.96 s (3H, Me), 2.95–3.08 m (2H, CH_2), 5.31 m (1H, CH), 6.50 d (1H, NH, ^3J = 7.9 Hz), 7.17 d and 7.44 d (2H each, H_{arom}, ^3J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.39 (Me), 42.24 (CH_2), 51.41 (CH), 128.35 (2C, CH_{arom}), 132.01 (2C, CH_{arom}), 120.11, 122.00, 128.90, 139.29, 169.73 (C=O). Found, %: C 38.66; H 3.08; Hlg 50.33; N 3.72. $C_{12}H_{11}BrCl_3NO$. Calculated, %: C 38.80; H 2.98; Hlg 50.14; N 3.77.

Amines XVI–XX (*general procedure*). A mixture of 10 mmol of acetamide **XI–XV**, 90 mL of 20% aqueous HCl, and 10 mL of ethanol was heated for 10 h under reflux. After cooling, the aqueous layer was separated, ethanol and water were removed under reduced pressure, and the residue was dried in a vacuum over P_2O_5.

2,3,3-Trichloro-1-phenylprop-2-en-1-amine hydrochloride (XVI). Yield 98%, mp 186–188°C (decomp.). IR spectrum, ν, cm^{-1}: 3177–2586 (NH_3^+), 3048, 3036, 2924 (C–H), 1589, 1519, 1499, 1456 (C=C, δN–H), 921, 818 (C–Cl). ^1H NMR spectrum, δ, ppm: 5.81 s (1H, CH), 7.46 m (3H, H_{arom}), 7.56 m (2H, H_{arom}), 9.64 br.s (3H, NH_3^+). ^{13}C NMR spectrum, δ_C, ppm: 54.96 (CH), 127.49 (2C, CH_{arom}), 129.59 (2C, CH_{arom}), 129.95 (CH_{arom}), 122.54, 129.80, 133.87. Found, %: C 39.55; H 3.40; Cl 52.02; N 5.10. $C_9H_9Cl_4N$. Calculated, %: C 39.60; H 3.32; Cl 51.95; N 5.13.

3,4,4-Trichloro-1-phenylbut-3-en-1-amine hydrochloride (XVII). Yield 82%, mp 191–193°C (decomp.). IR spectrum, ν, cm^{-1}: 3178–2626 (NH_3^+), 3038, 2888 (CH), 1595, 1515, 1497, 1459, 1435 (C=C, δN–H), 920, 769 (C–Cl). ^1H NMR spectrum, δ, ppm: 3.24–3.59 m (2H, CH_2), 4.47 m (1H, CH), 7.40 m (3H, H_{arom}), 7.59 m (2H, H_{arom}), 9.13 br.s (3H, NH_3^+). ^{13}C NMR spectrum, δ_C, ppm: 40.53 (CH_2), 53.04 (CH), 128.41 (2C, CH_{arom}), 129.19 (2C, CH_{arom}), 129.72 (CH_{arom}), 120.10, 128.73, 136.08. Found, %: C 41.69; H 3.93; Cl 49.33; N 4.90. $C_{10}H_{11}Cl_4N$. Calculated, %: C 41.85; H 3.86; Cl 49.41; N 4.88.

3,4,4-Trichloro-1-(4-methylphenyl)but-3-en-1-amine hydrochloride (XVIII). Yield 67%, mp 193–195°C (decomp.). IR spectrum, ν, cm^{-1}: 3188–2596 (NH_3^+), 3033, 2922 (C–H), 1603, 1518, 1500, 1435 (C=C, δN–H), 918, 817 (C–Cl). ^1H NMR spectrum, δ, ppm: 2.30 s (3H, Me), 3.21–3.56 m (2H, CH_2), 4.43 m (1H, CH), 7.22 d and 7.45 d (2H each, H_{arom}, ^3J = 8.1 Hz), 9.02 br.s (3H, NH_3^+). ^{13}C NMR spectrum, δ_C, ppm: 21.43 (Me), 40.36 (CH_2), 52.76 (CH), 128.31 (2C, CH_{arom}), 129.61 (2C, CH_{arom}), 119.95, 128.04, 133.05, 139.06. Found, %: C 43.92; H 4.48; Cl 47.03; N 4.62. $C_{11}H_{13}Cl_4N$. Calculated, %: C 43.89; H 4.35; Cl 47.11; N 4.65.

3,4,4-Trichloro-1-(2,5-dimethylphenyl)but-3-en-1-amine hydrochloride (XIX). Yield 67%, mp 195–197°C (decomp.). IR spectrum, ν, cm^{-1}: 3180–2610 (NH_3^+), 3005, 2923 (C–H), 1601, 1509, 1477 (C=C, δN–H), 919, 813 (C–Cl). ^1H NMR spectrum, δ, ppm: 2.28 s (3H, Me), 2.30 s (3H, Me), 3.28–3.54 m (2H, CH_2), 4.51 m (1H, CH), 7.09 m (2H, H_{arom}), 7.66 s (1H, H_{arom}), 8.99 br.s (3H, NH_3^+). ^{13}C NMR spectrum, δ_C, ppm: 19.18 (Me), 21.34 (Me), 40.26 (CH_2), 48.24 (CH), 126.38 (CH_{arom}), 128.35 (CH_{arom}), 130.98 (CH_{arom}), 119.99, 128.78, 133.29, 134.20, 136.00. Found, %: C 45.89; H 4.78; Cl 45.21; N 4.41. $C_{12}H_{15}Cl_4N$. Calculated, %: C 45.75; H 4.80; Cl 45.01; N 4.45.

1-(4-Bromophenyl)-3,4,4-trichlorobut-3-en-1-amine hydrochloride (XX). Yield 65%, mp 191–193°C (decomp.). IR spectrum, ν, cm^{-1}: 3089–2602 (NH_3^+), 3043, 3026, 2920, 2856 (C–H), 1594, 1512, 1493, 1417 (C=C, δN–H), 920, 824 (C–Cl), 540

(C–Br). ^{1}H NMR spectrum, δ, ppm: 3.21–3.55 m (2H, CH_2), 4.51 m (1H, CH), 7.56 d and 7.63 d (2H each, H_{arom}, ^3J = 8.1 Hz), 9.09 br.s (3H, NH_3^+). ^{13}C NMR spectrum, δ_C, ppm: 40.28 (CH_2), 52.32 (CH), 130.68 (2C, CH_{arom}), 132.09 (2C, CH_{arom}), 120.24, 123.01, 128.46, 135.46. Found, %: C 32.95; H 2.88; Hlg 60.48; N 3.79. $C_{10}H_{10}BrCl_4N$. Calculated, %: C 32.82; H 2.75; Hlg 60.60; N 3.83.

3,4,4-Trichloro-1-(4-methylphenyl)buta-1,3-diene (XXI). Yield 87%, mp 66–67°C. IR spectrum, ν, cm^{-1}: 3048, 3023, 2920, 2855 (C–H), 1604, 1513, 1496 (C=C), 1167, 1072, 960 (C–C), 928, 802 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.39 s (3H, CH_3), 7.13 d (3H, CH=CH, H_{arom}), 7.19 d (1H, CH=CH, ^3J = 7.1 Hz), 7.38 d (2H, H_{arom}, ^3J = 8.1 Hz).

Esters XXII–XXIV (*general procedure*). A solution of 5 mmol of triethylamine in 5 mL of anhydrous diethyl ether was slowly added dropwise to a solution of 5 mmol of 5-phenylisoxazole-3-carbonyl chloride or 4,5-dichloroisothiazole-3-carbonyl chloride and 5 mmol of alcohol **VI** or **VII** in 40 mL of anhydrous diethyl ether. The mixture was stirred for 4 h at 20°C and treated with water, and the organic layer was separated, dried over sodium sulfate, and evaporated. Oily products **XXIII** and **XXIV** were dried under reduced pressure, and crystalline compound **XXII** was recrystallized from hexane.

2,3,3-Trichloro-1-phenylprop-2-en-1-yl 5-phenyl-1,2-oxazole-3-carboxylate (XXII). Yield 76%, mp 102–104°C. IR spectrum, ν, cm^{-1}: 3151 (C–H_{isox}), 3079, 3062, 3041, 3013, 2967, 2925, 2856 (C–H), 1741 (C=O), 1611, 1591, 1572, 1497, 1455, 1443, 1422 (C=C), 1228, 1145 (C–O), 918, 806, 765 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 7.00 s (1H, CH), 7.31 s (1H, 4-H), 7.44 m (3H, H_{arom}), 7.50 m (3H, H_{arom}), 7.58 m (2H, H_{arom}), 7.83 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 74.05 (CH), 100.10 (C^4), 126.04 (2C, CH_{arom}), 126.39 (2C, CH_{arom}), 128.93 (2C, CH_{arom}), 129.28 (2C, CH_{arom}), 129.30 (CH_{arom}), 131.07 (CH_{arom}), 122.64, 126.50, 130.21, 134.79, 156.13, 158.54, 172.20 (C=O).

3,4,4-Trichloro-1-(4-methylphenyl)but-3-en-1-yl 5-phenyl-1,2-oxazole-3-carboxylate (XXIII). Yield 79%, oily substance. IR spectrum, ν, cm^{-1}: 3133 (C–H_{isox}), 3093, 3057, 3027, 2977, 2952, 2923, 2865 (C–H), 1738 (C=O), 1612, 1593, 1572, 1515, 1446, 1422 (C=C), 1239, 1138 (C–O), 923, 817, 765 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.36 s (3H, Me), 3.16–3.50 m (2H, CH_2), 6.35 m (1H, CH), 6.92 s (1H, 4-H), 7.18 d and 7.41 d (2H each, H_{arom}, ^3J = 8 Hz), 7.48 m (3H, H_{arom}), 7.80 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.21 (CH_3), 42.73 (CH_2), 74.86 (CH), 100.04 (C^4), 125.96 (2C, CH_{arom}), 126.63 (2C, CH_{arom}), 129.19 (2C, CH_{arom}), 129.51 (2C, CH_{arom}), 130.91 (CH_{arom}), 120.72, 123.17, 127.85, 134.73, 138.90, 156.59, 159.00, 171.83 (C=O).

3,4,4-Trichloro-1-(4-methylphenyl)but-3-en-1-yl 4,5-dichloro-1,2-thiazole-3-carboxylate (XXIV). Yield 84%, oily substance. IR spectrum, ν, cm^{-1}: 3098, 3053, 3026, 2977, 2951, 2923, 2863 (C–H), 1738 (C=O), 1607, 1515, 1483, 1403 (C=C), 1216, 1082 (C–O), 923, 883, 817, 761 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, Me), 3.15–3.49 m (2H, CH_2), 6.34 m (1H, CH), 7.16 d and 7.40 d (2H each, H_{arom}, ^3J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.19 (Me), 42.51 (CH_2), 75.08 (CH), 126.70 (2C, CH_{arom}), 129.43 (2C, CH_{arom}), 120.62, 123.10, 127.79, 134.58, 138.83, 150.60, 153.84, 157.98 (C=O).

Amides XXV and XXVI (*general procedure*). 5-Phenylisoxazole-3-carbonyl chloride or 4,5-dichloroisothiazole-3-carbonyl chloride, 3 mmol, was added to a suspension of 3 mmol of hydrochloride **XVI** in 25 mL of anhydrous methylene chloride, and 6.2 mmol of triethylamine was then added dropwise. The mixture was stirred for 4 h at 20°C and treated with water, the organic layer was separated and dried over calcium chloride, the solvent was distilled off under reduced pressure, and the residue was recrystallized from hexane– methylene chloride (2 : 1).

5-Phenyl-*N*-(2,3,3-trichloro-1-phenylprop-2-en-1-yl)-1,2-oxazole-3-carboxamide (XXV). Yield 81%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 3337 (N–H), 3154 (C–H_{isox}), 3085, 3060, 3026, 2977, 2943, 2856 (C–H), 1677 (C=O), 1613, 1599, 1591, 1574, 1523, 1494, 1450, 1425 (C=C), 932, 820, 764 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 6.75 m (1H, CH), 7.26 s (1H, 4-H), 7.41 t (1H, H_{arom}, ^3J = 7.4 Hz), 7.46 t (2H, H_{arom}, ^3J = 7.4 Hz), 7.55 m (5H, H_{arom}), 7.94 d (2H, H_{arom}, ^3J = 7.8, ^4J = 1.9 Hz), 8.39 d (1H, NH, ^3J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 55.86 (CH), 100.61 (C^4), 127.08 (2C, CH_{arom}), 127.95 (2C, CH_{arom}), 129.80 (CH_{arom}), 130.19 (2C, CH_{arom}), 130.49 (2C, CH_{arom}), 132.07 (CH_{arom}), 121.49, 133.50, 137.33, 159.63, 159.70, 160.11, 172.64 (C=O).

4,5-Dichloro-*N*-(2,3,3-trichloro-1-phenylprop-2-en-1-yl)-1,2-thiazole-3-carboxamide (XXVI). Yield 76%, mp 103–104°C. IR spectrum, ν, cm^{-1}: 3410 (N–H), 3092, 3058, 3032, 2955, 2926, 2856 (C–H), 1697 (C=O), 1600, 1595, 1586, 1504, 1493, 1476, 1449 (C=C), 919, 894, 827, 773 (C–Cl). ^{1}H NMR

spectrum, δ, ppm: 6.71 m (1H, CH), 7.39 t (1H, H_{arom}, ^3J = 7.4 Hz), 7.45 t (2H, H_{arom}, ^3J = 7.4 Hz), 7.51 d (2H, H_{arom}, ^3J = 7.4 Hz), 8.47 d (1H, NH, ^3J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 55.58 (CH), 127.78 (2C, CH_{arom}), 129.77 (CH_{arom}), 130.17 (2C, CH_{arom}), 121.49, 125.17, 133.40, 137.31, 151.42, 158.10, 159.78 (C=O).

Schiff bases XXVII–XLI (*general procedure*). A mixture of 1 mmol of amine hydrochloride **XVI–XX**, 1 mmol of aromatic aldehyde, and 1.1 mmol of sodium hydrogen carbonate in 20 mL of anhydrous methanol was heated for 10 h under reflux. The mixture was filtered, the solvent was removed from the filtrate under reduced pressure, the residue was dissolved in 5 mL of diethyl ether, the solution was filtered through a filter paper, the filtrate was evaporated under reduced pressure on a rotary evaporator, and the residue was dried at 35–40°C under reduced pressure.

(*E*)-2,3,3-Trichloro-*N*-(4-methoxybenzylidene)-1-phenylprop-2-en-1-amine (XXVII). Yield 80%, oily substance. IR spectrum, ν, cm^{-1}: 3088, 3063, 3031, 3002, 2955, 2935, 2908, 2835 (C–H), 1638 (C=N), 1606, 1578, 1512, 1494, 1466, 1451, 1422 (C=C), 1251, 1031 (C–O), 983, 919 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.86 s (3H, OCH_3), 6.06 s (1H, CH), 6.98 d (2H, H_{arom}, ^3J = 8.8 Hz), 7.40 m (3H, H_{arom}), 7.50 m (2H, H_{arom}), 7.85 d (2H, H_{arom}, ^3J = 8.8 Hz), 8.38 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 55.44 (OCH_3), 72.63 (CH), 114.14 (2C, CH_{arom}), 127.34 (2C, CH_{arom}), 127.95 (CH_{arom}), 128.56 (2C, CH_{arom}), 130.44 (2C, CH_{arom}), 162.77 (C=N), 119.30, 128.77, 134.60, 139.66, 162.32. Found, %: C 57.76; H 4.06; Cl 28.63; N 3.80. $C_{17}H_{14}Cl_3NO$. Calculated, %: C 57.57; H 3.98; Cl 29.99; N 3.95.

(*E*)-4-[(2,3,3-Trichloro-1-phenylprop-2-en-1-ylimino)methyl]phenol (XXVIII). Yield 78%, oily substance. IR spectrum, ν, cm^{-1}: 3346 (OH), 3087, 3062, 3028, 2977, 2945, 2877 (CH), 1637 (C=N), 1606, 1585, 1515, 1494, 1450 (C=C), 1278, 1028 (C–O), 982, 920 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 5.55 s (1H, OH), 6.07 s (1H, CH), 6.83 d (2H, H_{arom}, ^3J = 8.6 Hz), 7.40 m (3H, H_{arom}), 7.47 m (2H, H_{arom}), 7.73 d (2H, H_{arom}, ^3J = 8.6 Hz), 8.35 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 72.60 (CH), 115.97 (2C, CH_{arom}), 127.42 (2C, CH_{arom}), 128.64 (2C, CH_{arom}), 128.84 (CH_{arom}), 130.82 (2C, CH_{arom}), 163.67 (C=N), 119.69, 127.74, 134.25, 139.33, 159.83. Found, %: C 56.78; H 3.62; Cl 30.91; N 3.86. $C_{16}H_{12}Cl_3NO$. Calculated, %: C 56.42; H 3.55; Cl 31.22; N 4.11.

(*E*)-2-Methoxy-4-[(2,3,3-trichloro-1-phenylprop-2-en-1-ylimino)methyl]phenol (XXIX). Yield 82%, oily substance. IR spectrum, ν, cm^{-1}: 3407 (OH), 3084, 3063, 3028, 3008, 2973, 2938, 2857 (CH), 1638 (C=N), 1602, 1593, 1512, 1495, 1464, 1452, 1431 (C=C), 1285, 1160, 1021 (C–O), 979, 920 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.96 s (3H, OCH_3), 5.54 s (1H, OH), 6.07 s (1H, CH), 6.98 d (1H, H_{arom}, ^3J = 8.1 Hz), 7.24 d.d (1H, H_{arom}, ^3J = 8.1, ^4J = 1.8 Hz), 7.41 m (3H, H_{arom}), 7.48 m (2H, H_{arom}), 7.59 d (1H, H_{arom}, ^4J = 1.8 Hz), 8.33 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 56.15 (OCH_3), 72.53 (CH), 108.92 (CH_{arom}), 114.34 (CH_{arom}), 124.78 (CH_{arom}), 127.38 (2C, CH_{arom}), 128.00 (CH_{arom}), 128.60 (2C, CH_{arom}), 163.24 (C=N), 119.55, 128.55, 134.46, 139.53, 147.18, 149.14. Found, %: C 55.34; H 3.90; Cl 28.46; N 3.58. $C_{17}H_{14}Cl_3NO_2$. Calculated, %: C 55.09; H 3.81; Cl 28.69; N 3.78.

(*E*)-2-Methoxy-5-[(2,3,3-trichloro-1-phenylprop-2-en-1-ylimino)methyl]phenol (XXX). Yield 75%, oily substance. IR spectrum, ν, cm^{-1}: 3364 (OH), 3085, 3062, 3028, 3004, 2958, 2936, 2907, 2841 (C–H), 1639 (C=N), 1614, 1584, 1511, 1495, 1453, 1441 (C=C), 1275, 1162, 1030 (C–O), 979, 919 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.91 s (3H, OCH_3), 5.54 s (1H, OH), 6.05 s (1H, CH), 6.89 d (1H, H_{arom}, ^3J = 8.3 Hz), 7.30 d.d (1H, H_{arom}, ^3J = 8.3, ^4J = 1.9 Hz), 7.39 m (3H, H_{arom}), 7.48 m (2H, H_{arom}), 7.58 d (1H, H_{arom}, ^4J = 1.9 Hz), 8.32 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 56.04 (OCH_3), 72.52 (CH), 110.33 (CH_{arom}), 113.78 (CH_{arom}), 122.38 (CH_{arom}), 127.36 (2C, CH_{arom}), 127.94 (CH_{arom}), 128.54 (2C, CH_{arom}), 162.87 (C=N), 119.28, 129.57, 134.57, 139.64, 146.04, 149.67. Found, %: C 55.37; H 3.94; Cl 28.26; N 3.52. $C_{17}H_{14}Cl_3NO_2$. Calculated, %: C 55.09; H 3.81; Cl 28.69; N 3.78.

(*E*)-3,4,4-Trichloro-*N*-(4-methoxybenzylidene)-1-phenylbut-3-en-1-amine (XXXI). Yield 74%, oily substance. IR spectrum, ν, cm^{-1}: 3085, 3063, 3029, 3005, 2958, 2932, 2918, 2838 (C–H), 1642 (C=N), 1606, 1578, 1512, 1494, 1454, 1422 (C=C), 1252, 1030 (C–O), 924, 832 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.04–3.36 m (2H, CH_2), 3.85 s (3H, OCH_3), 4.71 m (1H, CH), 6.95 d (2H, H_{arom}, ^3J = 8.8 Hz), 7.39 m (3H, H_{arom}), 7.53 m (2H, H_{arom}), 7.77 d (2H, H_{arom}, ^3J = 8.8 Hz), 8.27 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 45.50 (CH_2), 55.42 (OCH_3), 72.20 (CH), 114.04 (2C, CH_{arom}), 127.08 (2C, CH_{arom}), 127.55 (CH_{arom}), 128.64 (2C, CH_{arom}), 130.11 (2C, CH_{arom}), 160.21 (C=N), 119.70, 129.19, 129.87, 142.63, 161.86. Found, %: C 58.95; H 4.47; Cl 28.61; N 3.54. $C_{18}H_{16}Cl_3NO$. Calculated, %: C 58.64; H 4.37; Cl 28.85; N 3.80.

(*E*)-4-[(3,4,4-Trichloro-1-phenylbut-3-en-1-ylimino)methyl]phenol (XXXII). Yield 68%, mp 188–189°C. IR spectrum, ν, cm^{-1}: 3415 (OH), 3077, 3062, 3030, 3008, 2961, 2925, 2865 (C–H), 1629 (C=N), 1607, 1594, 1518, 1495, 1443 (C=C), 1285, 1046 (C–O), 927, 833 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.03–3.30 m (2H, CH_2), 4.66 m (1H, CH), 5.33 s (1H, OH), 6.80 d (2H, H_{arom}, ^3J = 8.6 Hz), 7.36 m (3H, H_{arom}), 7.47 m (2H, H_{arom}), 7.63 d (2H, H_{arom}, ^3J = 8.6 Hz), 8.21 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 42.41 (CH_2), 72.26 (CH), 115.83 (2C, CH_{arom}), 126.61 (2C, CH_{arom}), 128.32 (2C, CH_{arom}), 129.06 (2C, CH_{arom}), 130.40 (CH_{arom}), 160.70 (C=N), 119.67, 129.25, 130.13, 142.61, 169.92. Found, %: C 57.40; H 4.06; Cl 29.50; N 3.48. $C_{17}H_{14}Cl_3NO$. Calculated, %: C 57.57; H 3.98; Cl 29.99; N 3.95.

(*E*)-2-Methoxy-4-[(3,4,4-trichloro-1-phenylbut-3-en-1-ylimino)methyl]phenol (XXXIII). Yield 71%, oily substance. IR spectrum, ν, cm^{-1}: 3357 (OH), 3085, 3063, 3029, 3005, 2969, 2936, 2853 (C–H), 1640 (C=N), 1602, 1589, 1513, 1495, 1465, 1453, 1430 (C=C), 1284, 1160, 1032 (C–O), 923, 818 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.09–3.39 m (2H, CH_2), 3.84 s (3H, OCH_3), 4.73 m (1H, CH), 6.90 d (1H, H_{arom}, ^3J = 8.1 Hz), 7.14 d.d (1H, H_{arom}, ^3J = 8.1, ^4J = 1.6 Hz), 7.38 m (3H, H_{arom}), 7.41 (1H, OH), 7.53 m (3H, H_{arom}), 8.22 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 45.11 (CH_2), 55.74 (OCH_3), 71.95 (CH), 109.06 (CH_{arom}), 114.70 (CH_{arom}), 124.13 (CH_{arom}), 126.21 (CH_{arom}), 127.07 (2C, CH_{arom}), 128.57 (2C, CH_{arom}), 160.76 (C=N), 119.56, 128.38, 129.88, 142.32, 147.43, 149.19. Found, %: C 56.48; H 4.35; Cl 27.09; N 3.26. $C_{18}H_{16}Cl_3NO_2$. Calculated, %: C 56.20; H 4.19; Cl 27.56; N 3.64.

(*E*)-2-Methoxy-5-[(3,4,4-trichloro-1-phenylbut-3-en-1-ylimino)methyl]phenol (XXXIV). Yield 72%, oily substance. IR spectrum, ν, cm^{-1}: 3358 (OH), 3084, 3063, 3029, 3003, 2956, 2935, 2839 (C–H), 1641 (C=N), 1602, 1586, 1512, 1495, 1454, 1441 (C=C), 1277, 1130, 1029 (C–O), 923, 802 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.03–3.32 m (2H, CH_2), 3.82 s (3H, OCH_3), 4.69 m (1H, CH), 5.35 s (1H, OH), 6.83 d (1H, H_{arom}, ^3J = 8.3 Hz), 7.22 d.d (1H, H_{arom}, ^3J = 8.3, ^4J = 1.7 Hz), 7.36 m (3H, H_{arom}), 7.50 m (3H, H_{arom}), 8.19 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 45.23 (CH_2), 55.78 (OCH_3), 72.01 (CH), 110.29 (CH_{arom}), 113.86 (CH_{arom}), 121.72 (CH_{arom}), 126.97 (2C, CH_{arom}), 127.42 (CH_{arom}), 128.49 (2C, CH_{arom}), 160.36 (C=N), 119.54, 129.74, 131.23, 142.40, 146.01, 149.42. Found, %: C 57.56; H 4.70; Cl 26.33; N 3.35. $C_{19}H_{18}Cl_3NO_2$. Calculated, %: C 57.24; H 4.55; Cl 26.68; N 3.51.

(*E*)-3,4,4-Trichloro-*N*-(4-methoxybenzylidene)-1-(4-methylphenyl)but-3-en-1-amine (XXXV). Yield 75%, oily substance. IR spectrum, ν, cm^{-1}: 3073, 3050, 3023, 3008, 2958, 2932, 2838 (C–H), 1641 (C=N), 1606, 1578, 1512, 1463, 1441, 1422 (C=C), 1253, 1033 (C–O), 923, 832 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, CH_3), 3.07–3.40 m (2H, CH_2), 3.84 s (3H, OCH_3), 4.72 m (1H, CH), 6.97 d (2H, H_{arom}, ^3J = 8.8 Hz), 7.23 d (2H, H_{arom}, ^3J = 8.0 Hz), 7.45 d (2H, H_{arom}, ^3J = 8.0 Hz), 7.80 d (2H, H_{arom}, ^3J = 8.8 Hz), 8.29 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 21.16 (CH_3), 45.32 (CH_2), 55.28 (OCH_3), 71.88 (CH), 113.94 (2C, CH_{arom}), 126.90 (2C, CH_{arom}), 129.25 (2C, CH_{arom}), 130.02 (2C, CH_{arom}), 159.98 (C=N), 119.48, 121.16, 129.14, 137.03, 139.55, 161.76. Found, %: C 60.02; H 4.88; Cl 27.39; N 3.40. $C_{19}H_{18}Cl_3NO$. Calculated, %: C 59.63; H 4.74; Cl 27.79; N 3.66.

(*E*)-4-{[3,4,4-Trichloro-1-(4-methylphenyl)but-3-en-1-ylimino]methyl}phenol (XXXVI). Yield 65%, mp 177–178°C. IR spectrum, ν, cm^{-1}: 3423 (OH), 3063, 3027, 3008, 2922, 2882, 2855 (C–H), 1637 (C=N), 1610, 1574, 1514, 1450 (C=C), 1241, 1032 (C–O), 922, 830 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, CH_3), 3.00–3.32 m (2H, CH_2), 4.68 m (1H, CH), 6.91 d (2H, H_{arom}, ^3J = 8.3 Hz), 7.16 d (2H, H_{arom}, ^3J = 7.8 Hz), 7.39 d (2H, H_{arom}, ^3J = 7.8 Hz), 7.70 d (2H, H_{arom}, ^3J = 8.3 Hz), 8.28 s (1H, CH=N), 8.94 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 21.46 (CH_3), 46.26 (CH_2), 72.90 (CH), 116.59 (2C, CH_{arom}), 128.06 (2C, CH_{arom}), 130.20 (2C, CH_{arom}), 131.27 (2C, CH_{arom}), 161.23 (C=N), 119.92, 129.01, 129.49, 131.67, 137.89, 141.10. Found, %: C 58.96; H 4.53; Cl 28.31; N 3.44. $C_{18}H_{16}Cl_3NO$. Calculated, %: C 58.64; H 4.37; Cl 28.85; N 3.80.

(*E*)-2-Methoxy-4-{[3,4,4-trichloro-1-(4-methylphenyl)but-3-en-1-ylimino]methyl}phenol (XXXVII). Yield 71%, mp 119–121°C. IR spectrum, ν, cm^{-1}: 3342 (OH), 3068, 3024, 3008, 2973, 2936, 2852 (C–H), 1640 (C=N), 1601, 1593, 1514, 1464, 1453, 1431 (C=C), 1287, 1158, 1032 (C–O), 921, 818 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, CH_3), 3.05–3.36 m (2H, CH_2), 3.87 s (3H, OCH_3), 4.69 m (1H, CH), 6.91 d (1H, H_{arom}, ^3J = 8.1 Hz), 7.13 d.d (1H, H_{arom}, ^3J = 8.1, ^4J = 1.6 Hz), 7.17 d (2H, H_{arom}, ^3J = 7.9 Hz), 7.37 d (2H, H_{arom}, ^3J = 7.9 Hz), 7.49 d (2H, H_{arom}, ^4J = 1.6 Hz), 8.19 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 21.20 (CH_3), 44.87 (CH_2), 55.94 (OCH_3), 71.66 (CH), 109.08 (CH_{arom}), 114.33 (CH_{arom}),

124.29 (CH_{arom}), 127.04 (2C, CH_{arom}), 129.33 (2C, CH_{arom}), 160.82 (C=N), 119.56, 128.65, 129.99, 137.25, 139.13, 147.19, 148.82. Found, %: C 57.48; H 4.72; Cl 26.10; N 3.29. $C_{19}H_{18}Cl_3NO_2$. Calculated, %: C 57.24; H 4.55; Cl 26.68; N 3.51.

(*E*)-3,4,4-Trichloro-1-(2,5-dimethylphenyl)-*N*-(4-methoxybenzylidene)but-3-en-1-amine (XXXVIII). Yield 74%, mp 90–91°C. IR spectrum, ν, cm^{-1}: 3067, 3040, 3016, 2957, 2921, 2838 (C–H), 1641 (C=N), 1608, 1579, 1511, 1443, 1423 (C=C), 1251, 1031 (C–O), 925, 812 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.41 s (3H, CH_3), 2.48 s (3H, CH_3), 2.90–3.47 m (2H, CH_2), 3.87 s (3H, OCH_3), 4.96 m (1H, CH), 6.99 d (2H, H_{arom}, ^3J = 8.8 Hz), 7.05 d (1H, H_{arom}, ^3J = 7.7, ^4J = 1.1 Hz), 7.12 d (1H, H_{arom}, ^3J = 7.7 Hz), 7.62 s (1H, H_{arom}), 7.80 d (2H, H_{arom}, ^3J = 8.8 Hz), 8.27 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 19.06 (CH_3), 21.28 (CH_3), 44.47 (CH_2), 55.39 (OCH_3), 68.56 (CH), 114.01 (2C, CH_{arom}), 127.96 (CH_{arom}), 128.01 (CH_{arom}), 130.11 (2C, CH_{arom}), 130.64 (CH_{arom}), 159.91 (C=N), 119.57, 121.25, 129.37, 131.63, 135.87, 140.61, 161.81. Found, %: C 60.92; H 5.14; Cl 26.38; N 3.26. $C_{20}H_{20}Cl_3NO$. Calculated, %: C 60.55; H 5.08; Cl 26.81; N 3.53.

(*E*)-2-Methoxy-4-{[3,4,4-trichloro-1-(2,5-dimethylphenyl)but-3-en-1-ylimino]methyl}phenol (XXXIX). Yield 73%, oily substance. IR spectrum, ν, cm^{-1}: 3417 (OH), 3074, 3046, 3005, 2958, 2924, 2855 (C–H), 1632 (C=N), 1598, 1515, 1463, 1430 (C=C), 1284, 1167, 1035 (C–O), 925, 814 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, CH_3), 2.41 s (3H, CH_3), 2.89–3.43 m (2H, CH_2), 3.90 s (3H, OCH_3), 4.94 m (1H, CH), 6.92 d (1H, H_{arom}, ^3J = 8 Hz), 7.02 s (1H, OH), 7.07 d (1H, H_{arom}, ^3J = 8 Hz), 7.14 d.d (2H, H_{arom}, ^3J = 8, ^4J = 1.1 Hz), 7.40 s (1H, H_{arom}), 7.50 d (2H, H_{arom}, ^4J = 1.1 Hz), 8.16 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 19.06 (CH_3), 21.23 (CH_3), 44.14 (CH_2), 56.06 (OCH_3), 68.05 (CH), 109.22 (CH_{arom}), 114.34 (CH_{arom}), 124.17 (CH_{arom}), 127.96 (CH_{arom}), 128.05 (CH_{arom}), 130.65 (CH_{arom}), 160.55 (C=N), 119.53, 121.44, 128.84, 131.84, 135.88, 140.10, 147.16, 148.75. Found, %: C 58.61; H 5.07; Cl 25.19; N 3.04. $C_{20}H_{20}Cl_3NO_2$. Calculated, %: C 58.20; H 4.88; Cl 25.77; N 3.39.

(*E*)-1-(4-Bromophenyl)-3,4,4-trichloro-*N*-(4-methoxybenzylidene)but-3-en-1-amine (XL). Yield 75%, oily substance. IR spectrum, ν, cm^{-1}: 3066, 3031, 3005, 2958, 2933, 2838 (C–H), 1642 (C=N), 1605, 1578, 1512, 1486, 1463, 1422 (C=C), 1254, 1032 (C–O), 923, 829 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.99–3.26 m (2H, CH_2), 3.80 s (3H, OCH_3), 4.64 m (1H, CH), 6.93 d (2H, H_{arom}, ^3J = 8.7 Hz), 7.39 d (2H, H_{arom}, ^3J = 8.4 Hz), 7.49 d (2H, H_{arom}, ^3J = 8.4 Hz), 7.75 d (2H, H_{arom}, ^3J = 8.7 Hz), 8.23 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 45.26 (CH_2), 55.29 (OCH_3), 71.35 (CH), 113.99 (2C, CH_{arom}), 128.73 (2C, CH_{arom}), 130.05 (2C, CH_{arom}), 131.57 (2C, CH_{arom}), 160.44 (C=N), 119.85, 121.23, 128.76, 129.35, 141.49, 161.88. Found, %: C 48.67; H 3.54; Hlg 41.18; N 2.80. $C_{18}H_{15}BrCl_3NO$. Calculated, %: C 46.64; H 3.26; Hlg 41.61; N 3.13.

(*E*)-4-{[1-(4-Bromophenyl)-3,4,4-trichlorobut-3-en-1-ylimino]methyl}-2-methoxyphenol (XLI). Yield 88%, oily substance. IR spectrum, ν, cm^{-1}: 3358 (OH), 3070, 3026, 3006, 2973, 2934, 2856 (C–H), 1640 (C=N), 1601, 1594, 1513, 1487, 1464, 1430 (C=C), 1284, 1160, 1033 (C–O), 922, 822 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.01–3.27 m (2H, CH_2), 3.86 s (3H, OCH_3), 4.64 m (1H, CH), 6.90 d (1H, H_{arom}, ^3J = 7.8 Hz), 7.13 d (1H, H_{arom}, ^3J = 7.8 Hz), 7.31 d (1H, H_{arom}, ^3J = 7.8 Hz), 7.36 d (2H, H_{arom}, ^3J = 7.1 Hz), 7.46 m (3H, 2H, H_{arom}, OH), 8.18 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 45.03 (CH_2), 55.91 (OCH_3), 71.29 (CH), 109.03 (CH_{arom}), 114.44 (CH_{arom}), 124.28 (CH_{arom}), 128.85 (2C, CH_{arom}), 131.66 (2C, CH_{arom}), 161.07 (C=N), 119.92, 121.38, 128.46, 129.42, 141.28, 147.22, 148.92. Found, %: C 46.55; H 3.35; Hlg 40.00; N 3.16. $C_{18}H_{15}BrCl_3NO_2$. Calculated, %: C 46.64; H 3.26; Hlg 40.18; N 3.02.

This study was performed under financial support by the Belarusian Republican Foundation for Basic Research (project no. Kh12SO-012) and by the Siberian Branch, Russian Academy of Sciences (project no. 21).

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