ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 3, pp. 474–481. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © B.A. Demidchuk, V.S. Brovarets, A.N. Chernega, J.A.K. Howard, A.N. Vasilenko, A.V. Turov, B.S. Drach, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 3, pp. 510–517.

Reaction of 1-Aryl-1,3,4,4-tetrachloro-2-azabuta-1,3-dienes with Aminoazoles

B. A. Demidchuk[a], V. S. Brovarets[a], A. N. Chernega[b], J. A. K. Howard[c], A. N. Vasilenko[a], A. V. Turov[d], and B. S. Drach[a]

[a] *Institute of Bioorganic and Petroleum Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 1, Kiev, 02660 Ukraine*
e-mail: drach@bpci.kiev.ua

[b] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 5, Kiev, 02660 Ukraine*

[c] *Department of Chemistry, Durham University, Durham, United Kingdom*

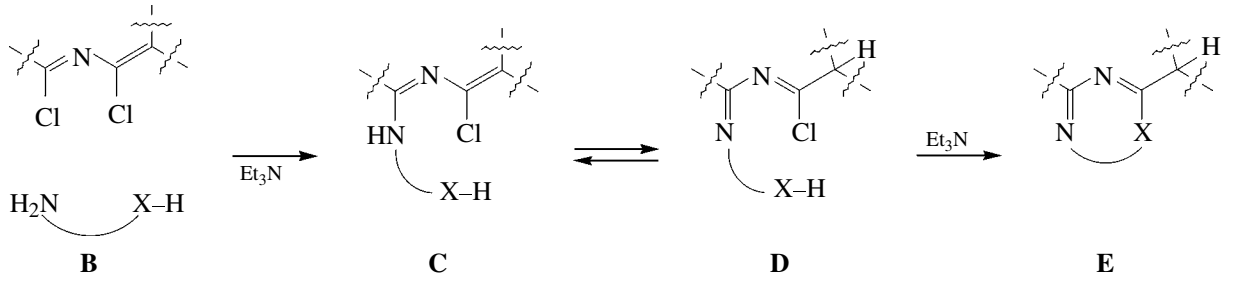
[d] *Taras Shevchenko Kiev University, Kiev, Ukraine*

Received July 25, 2006

Abstract — Reactions of polychlorinated 2-aza-1,3-dienes of the general formuls ArCCl=NCCl=CCl_2 with 3(5)-aminopyrazoles, 3(5)-amino-1,2,4-triazoles, and 5-aminotetrazole led to the formation of substituted pyrazolo[1,5-*a*][1,3,5]triazines, [1,2,4]triazolo[1,5-*a*][1,3,5]triazines, and 2-azido-1,3,5-triazine derivatives whose structure was reliably established by spectral methods and X-ray analysis.
DOI: 10.1134/S107036320703022X

We previously showed that chlorine-containing 2-aza-1,3-dienes having a structural fragment like **A** can be involved in regioselective cyclocondensations with some nitrogen-centered nucleophiles like **B** due to considerably different reactivities of the C^1 and C^3 electrophilic centers in system **A** [1–3]. As shown in Scheme 1, the initial step is the condensation at the most electrophilic C^1 center, and intermediates **C** thus formed are capable of undergoing prototropic isomerization with activation of the C^3 center and subsequent intramolecular cyclization **D** → **E**.

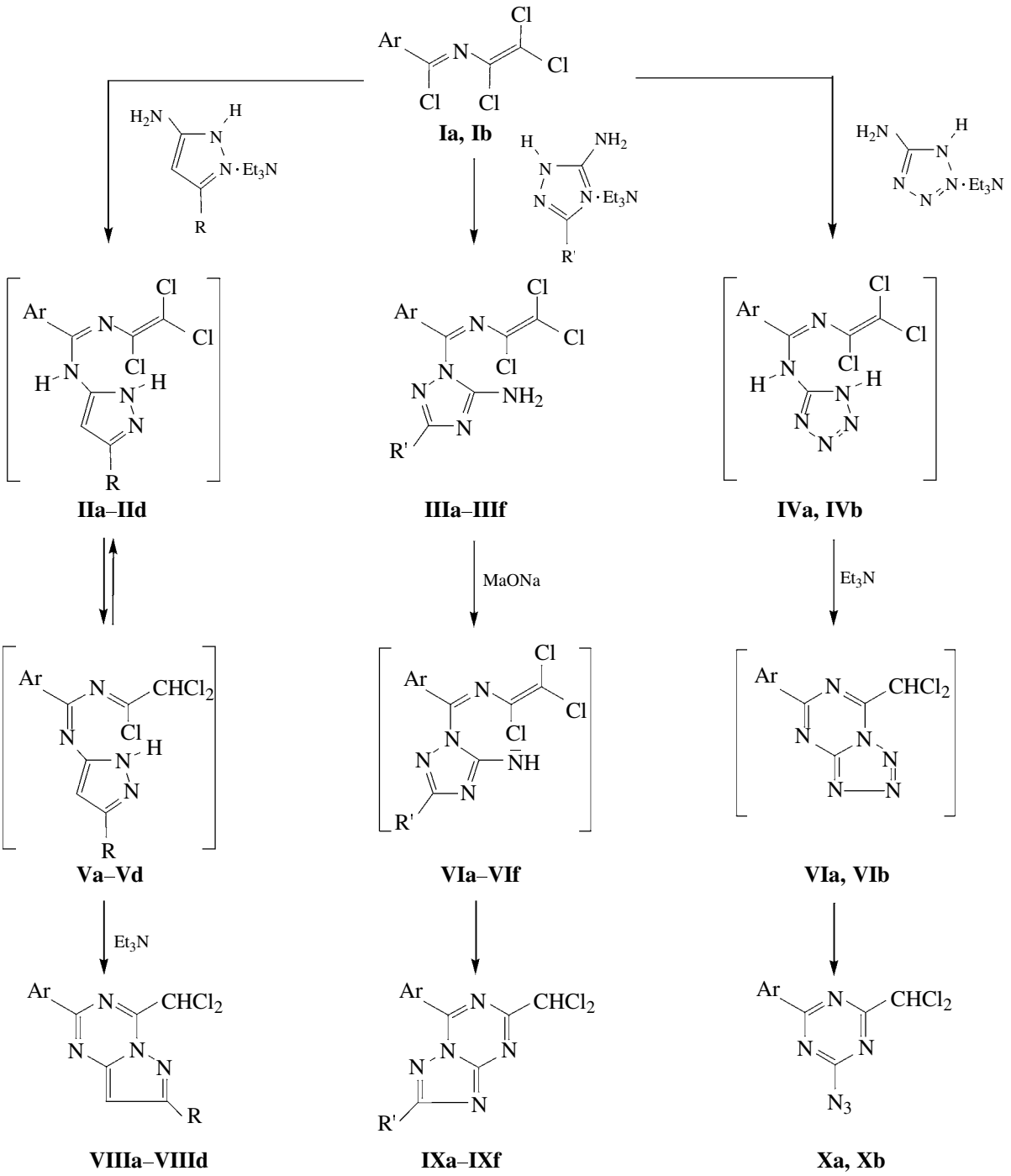
Scheme 1.



B **C** **D** **E**

Most frequently, such transformations were performed with accessible 1-aryl-1,3,4,4-tetrachloro-2-azabuta-1,3-dienes **I** that are readily obtained from the chloral adducts with aromatic amides [4]. Aromatic amines, hydrazine, arylhydrazines, hydroxylamine, and benzamidine and its analogs were used as nucleophiles **B** in these cyclizations [1–4]. In the present work we examined for the first time the condensation of compounds **I** with various aminoazoles having three labile hydrogen atoms. We found that the reactions follow a complicated pattern and that the expected transformation sequence shown in Scheme 1 is often accompanied by other processes (see structures **II**–**X** in Scheme 2 and Table 1).

Scheme 2.



Ar = C_6H_5 (**Ia–Xa, IIc, IIIb, IIIc; Vc, VIb, VIc; VIIIc, IXb, IXc**), 4-$CH_3C_6H_4$ (**Ib, IIb, IId; IIId–IIIf, IVb, Vb, Vd; VId–VIf, VIIb, VIId; IXd–IXf; Xb**); R = C_6H_5 (**IIa, IIb; Va, Vb; VIIIa, VIIIb**); 4-$CH_3C_6H_4$ (**IIc, IId; Vc, Vd; VIIIc, VIIId**); R' = C_6H_5 (**IIIa, IIId; VIa, VId; IXa, IXd**), F_3C (**IIIb, IIIe; VIb, VIe; IXb, IXe**), CH_3S (**IIIc, IIIf; VIc, VIf; IXc, IXf**).

In the reactions of compounds **I** with 3(5)-aminopyrazoles on prolonged heating in tetrahydrofuran in the presence of triethylamine, the transformation sequence **I** → **II** → **V** → **VIII** resulted in the formation of no more than 44% of the corresponding heterocyclization products, 2,7-diaryl-4-dichloromethylpyrazolo-[1,5-*a*][1,3,5]triazines. Even taking into account unavoidable loss of products **VIII** during their isola-

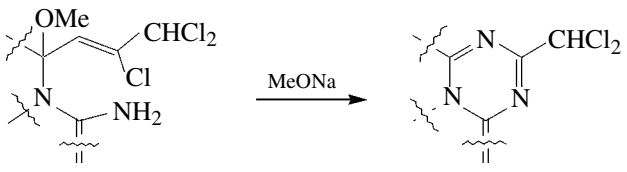
Table 1. Yields, melting points, and elemental analyses of compounds **III** and **VIII–X**

Comp. no	Yield,[a] %	mp, °C (solvent)	Found, %		Formula	Calculated, %	
			Cl	N		Cl	N
IIIa	49	193–194 (EtOH–DMF, 5 : 1)	26.89	17.51	$C_{17}H_{12}Cl_3N_5$	27.08	17.84
IIIb	46	172–173 (EtOH–DMF, 10 : 1)	26.05	17.61	$C_{12}H_7Cl_3N_5F_3$	27.66	18.21
IIIc	48	187–188 (EtOH–DMF, 5 : 1)	29.03	19.65	$C_{12}H_{10}Cl_3N_5S$[b]	29.33	19.31
IIId	52	198–199 (EtOH–DMF, 5 : 1)	26.07	17.13	$C_{18}H_{14}Cl_3N_5$	26.15	17.22
IIIe	41	183–184 (EtOH–DMF, 10 : 1)	27.69	16.72	$C_{13}H_9Cl_3N_5F_3$	26.68	17.57
IIIf	60	165–167 (EtOH–DMF, 5 : 1)	28.10	18.24	$C_{13}H_{12}Cl_3N_5S$[c]	28.23	18.59
VIIIa	42	229–230 (CH_3CN)	20.62	15.02	$C_{18}H_{12}Cl_2N_4$	19.96	15.77
VIIIb	46	227–228 (EtOH–DMF, 5 : 1)	20.02	15.56	$C_{19}H_{14}Cl_2N_4$	19.20	15.17
VIIIc	40	221–222 (EtOH–DMF, 5 : 1)	19.23	15.08	$C_{19}H_{14}Cl_2N_4$	19.20	15.17
VIIId	44	241–242 (EtOH–DMF, 5 : 1)	18.78	14.58	$C_{20}H_{16}Cl_2N_4$	18.50	14.62
IXa	92 (45)	199–200 (EtOH)	20.01	19.05	$C_{17}H_{11}Cl_2N_5$	19.91	19.66
IXb	87 (40)	185–186 (*i*-PrOH)	20.56	19.90	$C_{12}H_6Cl_2N_5F_3$	20.37	20.12
IXc	89 (43)	153–154 (*i*-PrOH)	21.77	21.40	$C_{12}H_9Cl_2N_5S$[d]	21.74	21.47
IXd	92 (48)	210–211 (MeOH)	19.03	18.56	$C_{18}H_{13}Cl_2N_5$	19.15	18.92
IXe	68 (35)	165–166 (MeOH)	19.25	19.38	$C_{13}H_8Cl_2N_5F_3$	19.58	19.34
IXf	88 (53)	197–198 (MeOH)	20.74	20.08	$C_{13}H_{11}Cl_2N_5S$[e]	20.84	20.58
Xa	58	155–156 (EtOH–DMF, 10 : 1)	24.81	29.79	$C_{10}H_6N_6Cl_2$	25.22	29.90
Xb	55	179–180 (EtOH)	24.27	28.31	$C_{11}H_8N_6Cl_2$	24.02	28.47

[a] In parentheses are given the yields of **IXa**–**IXf** calculated on the initial compounds **Ia** and **Ib**. [b] Found, %: S 8.85. Calculated, %: S 8.84. [c] Found, %: S 8.58. Calculated, %: S 8.51. [d] Found, %: S 9.84. Calculated, %: S 9.83. [e] Found, %: S 9.68. Calculated, %: S 9.42.

tion, it is obvious that the process is accompanied by other reactions involving the electrophilic C^1 center of I and endocyclic nitrogen atoms in the pyrazole ring rather than the primary amino group. In this case, intermediate condensation products (which we failed to isolate as individual substances) are unlikely to undergo intramolecular closure of triazine ring, for prototropic isomerization necessary for the activation of the C^3 center in the 2-aza-1,3-diene moiety is impossible. By special experiments including quantitative determination of the triethylamine hydrochloride formed by reaction of **I** (R = 4-$CH_3C_6H_4$) with 3(5)-amino-5(3)-phenylpyrazole and triethylamine at a molar ratio of 1 : 1 : 2 we found that the molar ratio of the condensation products at the amino group and N^1/N^2 is about 1 : 1, the conversion being 85–90%. In analogous reactions with 3(5)-amino-5(3)-phenyl-1,2,4-triazole and its derivatives, the contribution of the condensation involving the primary amino group was smaller, so that we succeeded in isolating N^1-imidoylation products **III** which failed to undergo cyclization by the action of triethylamine.

Treatment of compounds **III** with sodium methoxide in methanol gave 2-substituted 7-aryl-5-dichloromethyl[1,2,4]triazolo[1,5-*a*][1,3,5]triazines **IX**. Presumably, intermediate deprotonation of compounds **III** or addition of methanol to the electron-deficient 2-aza-1,3-diene moiety, leading to reactive structure **F**, are important here. Structure **F** is capable of undergoing cyclization to G by the action of sodium methoxide.



F **G**

The transformation **III** → **IX** is quite selective; however, the overall yield of **IX** calculated on the initial reagent **I** is 35–53%. Interestingly, the reactions of **I** with 5-aminotetrazole in the presence of triethylamine gave no appreciable amounts of products analogous to **III**, and the final products were substituted azidotriazines **X**. The latter are likely to be formed through intermediates **IV** that are capable for prototropic isomerization, fusion of tetrazole ring, and its subsequent opening. Structures **VII** and **X** illustrate an example of the azido–tetrazole tautomerism where the equilibrium is displaced toward the azido tautomer

Table 2. ^{1}H NMR and IR spectra of compounds **III** and **VIII–X**

Comp. no.	^{1}H NMR spectrum, δ, ppm
IIIa[a]	7.41 m ($3H_{arom}$), 7.56 m ($5H_{arom}$), 7.79 m ($2H_{arom}$), 8.02 br. s (2H, NH_2)
IIIb[a]	7.49–7.63 m (5H, C_6H_5), 8.29 br.s (2H, NH_2)
IIIc[a]	2.32 s (3H, CH_3), 7.40–7.60 m ($5H_{arom}$), 8.01 br.s (2H, NH_2)
IIId[a]	2.44 s (3H, CH_3), 7.36 m ($7H_{arom}$), 7.81 m ($2H_{arom}$), 7.93 s (2H, NH_2)
IIIe[a]	2.43 s (3H, CH_3), 7.34 s ($4H_{arom}$), 8.20 br. s (2H, NH_2)
IIIf[a]	2.34 s (3H, CH_3), 2.41 s (3H, CH_3), 7.31 m ($4H_{arom}$), 7.93 br.s (2H, NH_2)
VIIIa	7.41 s (1H, C^8–H), 7.75 m ($6H_{arom}$), 7.98 s (1H, $CHCl_2$), 8.13 m ($2H_{arom}$), 8.52 m ($2H_{arom}$)
VIIIb	2.43 s (3H, CH_3), 7.35 s (1H, C^8–H), 7.36 d ($2H_{arom}$), 7.51 m ($3H_{arom}$), 8.00 s (1H, $CHCl_2$), 8.13 m ($2H_{arom}$), 8.38 d ($2H_{arom}$)
VIIIc	2.39 s (3H, CH_3), 7.37 d ($2H_{arom}$), 7.47 s (1H, C^8–H), 7.63 m ($3H_{arom}$), 8.06 s (1H, $CHCl_2$), 8.09 d ($2H_{arom}$), 8.49 m ($2H_{arom}$)
VIIId	2.39 s (3H, CH_3), 2.42 s (3H, CH_3), 7.40 m ($4H_{arom}$), 7.42 s (1H, C^8–H), 8.04 s (1H, $CHCl_2$), 8.07 d ($2H_{arom}$), 8.37 d ($2H_{arom}$)
IXa	7.58 s (1H, $CHCl_2$), 7.63 m ($3H_{arom}$), 7.80 m ($3H_{arom}$), 8.34 m ($2H_{arom}$), 8.88 m ($2H_{arom}$)
IXb	7.53 s (1H, $CHCl_2$), 7.74 m ($2H_{arom}$), 7.85 m ($1H_{arom}$), 8.72 d ($2H_{arom}$)
IXc	2.76 s (3H, CH_3), 7.39 s (1H, $CHCl_2$), 7.69 m ($2H_{arom}$), 7.80 ($1H_{arom}$), 8.82 d ($2H_{arom}$)
IXd	2.51 s (3H, CH_3), 7.39 s (1H, $CHCl_2$), 7.51 d ($2H_{arom}$), 7.58 m ($3H_{arom}$), 8.32 m ($2H_{arom}$), 8.84 d ($2H_{arom}$)
IXe	2.52 s (3H, CH_3), 7.48 s (1H, $CHCl_2$), 7.54 d ($2H_{arom}$), 8.68 d ($2H_{arom}$)
IXf	2.49 s (3H, CH_3), 2.75 s (3H, CH_3), 7.36 s (1H, $CHCl_2$), 7.50 d ($2H_{arom}$), 8.72 d ($2H_{arom}$)
Xa[b]	7.26 s (1H, $CHCl_2$), 7.64 m ($3H_{arom}$), 8.45 d ($2H_{arom}$)
Xb[c]	2.45 s (3H, CH_3), 7.20 s (1H, $CHCl_2$), 7.40 d ($2H_{arom}$), 8.34 d ($2H_{arom}$)

[a] IR spectruma of **IIIa–IIIf**: $\nu(NH_{as})$ 3100–3400 cm^{-1}. [b] IR spectrum: $\nu(N_3)$ 2200 cm^{-1} (band with a shoulder). [c] IR spectrum: $\nu(N_3)$ 2175 cm^{-1} (band with a shoulder).

due to pronounced electron-deficient properties of the 1,3,5-triazine ring.

To conclude, it should be notes that the structure of compounds **VIII–X** was reliably established by IR and NMR spectroscopy and X-ray analysis (Tables 2–4). The IR and ^{1}H NMR spectra showed disappearance of the NH_2 group, N–H bond, and 2-aza-1,3-diene fragment during formation of cyclization products **VIII–X**. The presence of a dichloromethyl group in these compounds is consistent with the ^{1}H NMR spectra which contained a singlet at ~7.20–8.06 ppm. The structure of **IXf** (Ar = 4-$CH_3C_6H_4$, R^1 = CH_3S) was unambiguously proved by the X-ray diffraction data (Fig. 1). Molecule **IXf** is almost planar: the N^1–N^5 and C^1–C^4 atoms lie in one plane within 0.011 Å, and the dihedral angle between the five-membered $N^1N^2N^3C^1C^2$ ring and six-membered $N^3N^4N^5C^2C^3C^4$ ring is as small as 0.7°.

In addition, we recorded the ^{1}H–^{13}C heteronuclear correlation spectra (HMQC and HMBC techniques) for compound **IXf**. The principal correlations and signal assignments are shown in Fig. 2, and the complete list of correlations is given in Table 3. The C^7 nucleus (δ_C 154.53 ppm) resonates in a stronger field than C^5 (δ_C 163.72 ppm), which is very consistent with the X-ray diffraction data and general views on the electron density distribution in molecule **IXf**.

The structure of compounds **VIII** was determined on the basis of the ^{1}H and ^{13}C NMR spectra and HMBC heteronuclear correlation spectrum of **VIIIb** (Ar = 4-$CH_3C_6H_4$, R = C_6H_5). Figure 3 shows the principal correlations and signal assignments, and all the correlations found are listed in Table 4. The assignment of singlets from the $HCCl_2$ and 8-H protons in compound **VIIIb** is beyond doubt, for 8-H (δ 7.39 ppm) is coupled with C^7 (δ_C 158.61 ppm); on the other hand, the C^7 atom shows correlations with 2b-H and 6b-H (δ 8.14 ppm). Proton resonating at δ 8.0 ppm is coupled with a carbon atom whose signal appears at δ_C 64.29 ppm. Such an upfield signal may arise only from the $CHCl_2$ carbon atom. Taking into account that the *ortho*-proton in the *p*-tolyl fragment of **VIIIb** is coupled with a carbon nuclei having the largest chemical shift (C^2, δ_C 157.31 ppm), as well as the X-ray diffraction and spectral data for **IXf**, the structure of the isomer in which the dichloromethyl group is attached to C^2 can be ruled out.

Table 3. ^1H–^{13}C Correlations in the HMQC and HMBC spectra of compound **IXf**[a]

^1H, δ, ppm	^{13}C, δ_C, ppm	
	HMQC	HMBC
2.42 (CH_3)	22.12 (CH_3)	22.12 (CH_3), 145.96 (C^{4a}), 130.06 (C^{3a}, C^{5a})
2.72 (CCH_3)	14.17 (SCH_3)	14.17 (SCH_3), 171.55 (C^2)
7.44 ($C^{3a}H$,	130.06 (C^{3a}, C^{5a})	130.06 (C^{3a}, C^{5a}),
$C^{5a}H$)		22.12 (CH_3), 126.42 (C^{1a})
7.49 ($CHCl_2$)	71.26 ($CHCl_2$)	71.26 ($CHCl_2$), 163.72 (C^5)
8.64 ($C^{2a}H$,	131.87 (C^{2a}, C^{6a})	131.87 (C^{2a}, C^{6a}),
$C^{6a}H$)		145.96 (C^{4a}), 154.53 (C^7)

[a] For atom numbering, see Fig. 2.

Table 4. ^1H–^{13}C Correlations in the HMBC spectrum of compound **VIIIb**[a]

^1H, δ, ppm	^{13}C, δ_C, ppm
2.42 (CH_3)	21.09 (CH_3), 142.24 (C^{4a}), 129.57 (C^{3a}, C^{5a})
7.39 (C^8H)	94.34 (C^8), 151.01 (C^{8a}), 158.61 (C^7)
7.41 ($C^{3a}H$, $C^{5a}H$)	129.57 (C^{3a}, C^{5a}), 132.58 (C^{1a})
7.54 ($C^{4b}H$)	127.00 (C^{2b}, C^{6b})
7.56 ($C^{3b}H$, $C^{5b}H$)	128.98 (C^{3b}, C^{5b}), 131.44 (C^{1b})
8.00 ($CHCl_2$)	64·29 ($CHCl_2$), 152.05 (C^4)
8.14 ($C^{2b}H$, $C^{6b}H$)	127.00 (C^{2b}, C^{6b}), 130.16 (C^{4b}), 158.61 (C^7)
8.38 ($C^{2a}H$, $C^{6a}H$)	128.37 (C^{2a}, C^{6a}), 142.24 (C^{4a}), 157.31 (C^2)

[a] For atom numbering, see Fig. 3.

The presence of an azido group in molecule **Xa** was confirmed by both IR (Table 2) and X-ray diffraction data (Fig. 4). The benzene and triazine rings and the azido group in **Xa** lie almost in one plane. The dichloromethyl group is oriented gauche with respect to the triazine ring: the torsion angles $N^2C^2C^4Cl^1$ and $N^2C^2C^4Cl^2$ are –66.6(4) and 56.0(4)°, respectively.

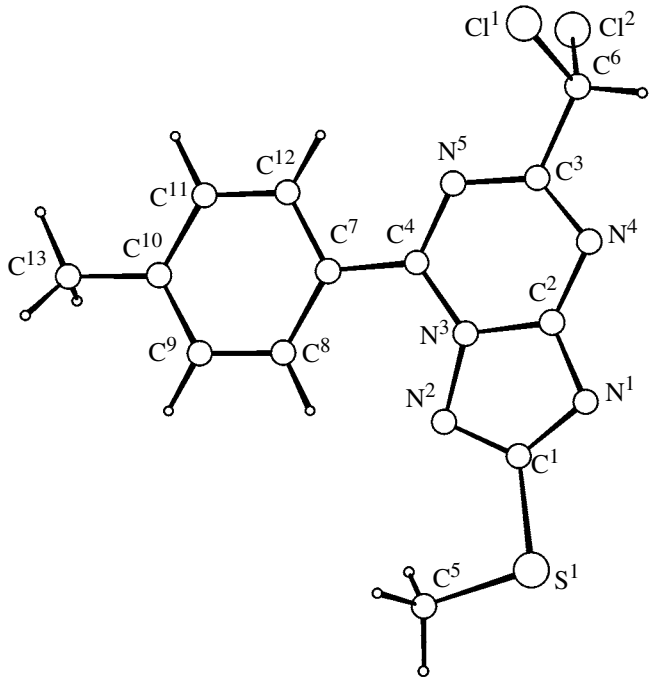


Fig. 1. Structure of the molecule of compound **IXf** according to the X-ray diffraction data; principal bond lengths (Å) and bond angles (deg): S^1–C^1 1.734(4), S^1–C^5 1.789(5), N^1–C^1 1.361(5), N^1–C^2 1.323(5), N^2–N^3 1.368(4), N^2–C^1 1.340(5), N^3–C^2 1.400(5), N^3–C^4 1.363(4), N^4–C^2 1.344(5), N^4–C^3 1.312(5), N^5–C^3 1.350(5), N^5–C^4 1.321(5); $C^1S^1C^5$ 99.6(2), $C^1N^1C^2$ 102.4(3), $N^3N^2C^1$ 100.7(3), $N^2N^3C^2$ 109.8(3), $C^2N^3C^4$ 121.3(3), $C^2N^4C^3$ 113.1(3), $C^3N^5C^4$ 118.6(3).

EXPERIMENTAL

The IR spectra were recorded in KBr on a Specord M-80 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Varian Mercury-400 instrument from solutions in DMSO-d_6 using tetramethylsilane as internal reference.

X-Ray diffraction data for compound IXf. A 0.10 × 0.16 × 0.20-mm single crystal of **IXf** was examined at 120 K using a Bruker-Apex CCD panoramic diffractometer (MoK_α irradiation). Total of 12117 reflections were measure, 4349 of which were symmetry-independent (R_{int} = 0.017). Monoclinic crystals with the following unit cell parameters: a = 6.7879(5), b = 11.5213(9), c = 19.230(1) Å; V = 1481.6(2) Å^3; M 593.8; Z = 4, d_{calc} = 1.53 g cm^{-3}; μ = 5.8 cm^{-1}; F(000) = 696.0; space group $P2_1/n$ (no. 14). The structure was solved by the direct method and was refined by the least-squares procedure in full-matrix anisotropic approximation using CRYSTALS software package [6]. The refinement was performed using 2556 reflections with $I > 4\sigma(I)$ (190 refined parameters, 13.4 reflections per parameters). About 50% of hydrogen atoms were revealed from the difference synthesis of electron density, and the positions of the other hydrogen atoms were cal-

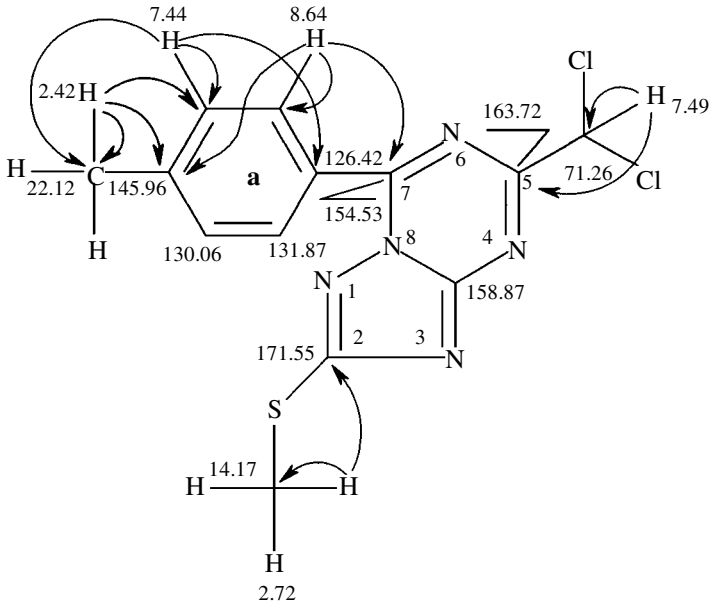


Fig. 2. Principal correlations (denoted with arrows) and signal assignment (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **IXf**.

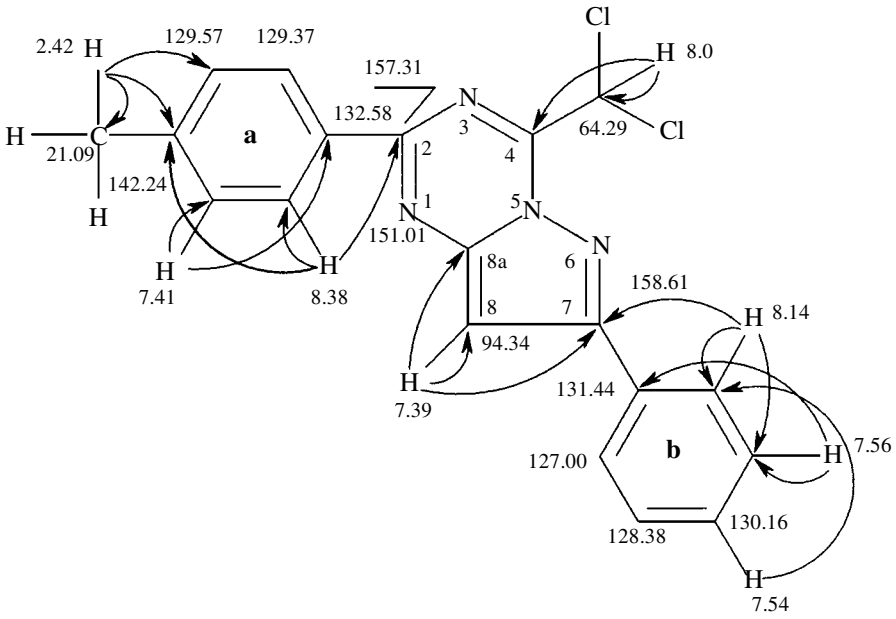


Fig. 3. Principal correlations (denoted with arrows) and signal assignment (ppm) in the ^{1}H and ^{13}C NMR spectra of compound **VIIIb**.

culated from the geometry considerations. All hydrogen atoms were included in the refinement process with fixed positional and thermal parameters. Chebyshev's weight scheme [7] was applied with the following three parameters: 2.15, 1.08, and 1.69. The final divergence factors were R = 0.088 and R_W = 0.068; goodness of fit 0.965. The complete set of crystallographic data for compound **IXf** was deposited to the Cambridge Crystallographic Data Center (entry no. CCDC 611295).

X-Ray diffraction data for compound Xa. A $0.40 \times 0.20 \times 0.12$ mm single crystal of **Xa** was examned at room temperature on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (λMoK_α irradiation, graphite monochromator, $\omega/2\theta$ scanning,

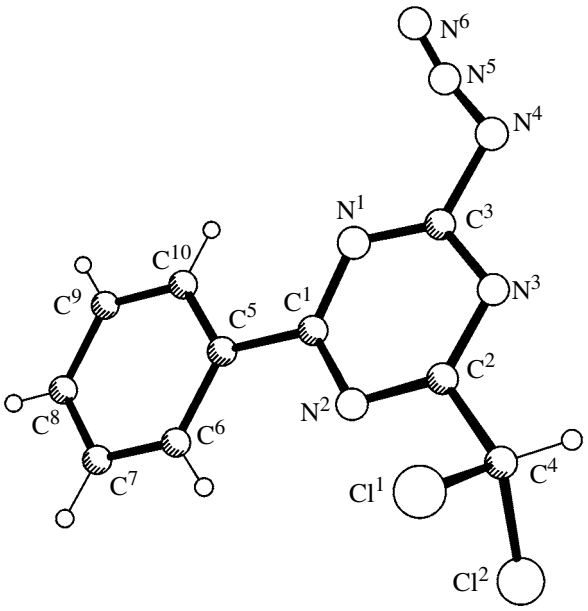


Fig. 4. Structure of the molecule of compound **Xa** according to the X-ray diffraction data; principal bond lengths (Å) and bond angles (deg): C^3–N^4 1.399(4), C^4–Cl^2 1.762(4), C^4–Cl^1 1.765(4), N^4–N^5 1.256(5), N^5–N^6 1.114(5) Å; $N^5N^4C^3$ 113.4(3), $N^6N^5N^4$ 171.5(4)°.

λ_{max} = 25.0°, spherical segment $0 \le h \le 7$, $-9 \le k \le 10$, $-13 \le l \le 13$). The unit cell parameters and crystal orientation matrix were determined from 22 reflections with $11.08 < \theta < 12.90°$. Total of 2344 reflections were measured, 2141 of which were independent (averaging R factor is 0.025). Triclinic crystals; a = 6.700(2), b = 18.665(3), c = 11.646(4) Å; α = 85.87(3), β = 77.16(3), γ = 67.47(3)°; V = 608.9(3) Å^{-}; Z = 2; d_{calc} = 1.352; μ = 0.081 mm^{-1}; $F(000)$ = 284; space group P-1 (no. 2). The structure was solved by the direct method and was refined by the least-squares procedure in full-matrix anisotropic approximation using SHELXS97 and SHELXL97 programs [8, 9]; 2141 reflections were used in the refinement [1320 reflections with $I > 2\sigma(I)$, 187 refined parameters, 11.45 reflections per parameter]. The weight scheme $\omega = 1/[\sigma^2(Fo^2) + (0.0313R)^2 + 0.5989R]$, where $R = (Fo^2 + 2Fc^2)/3$, was applied; the ratio of the maximal (average) shift to the deviation in the last iteration was 0.001 (0.000). A correction for anomalous scattering was introduced, and a semiempirical correction for absorption was made using the PSI scanning technique (T_{min} = 0.7817, T_{max} = 0.8971). All hydrogen atoms were visulized objectively from the Fourier difference series, and their positions were refined in isotropic approximation. The final divergence factors were $R_1(F)$ = 0.1014, $R_W(F^2)$ = 0.1193 (*GOF* 0.997; from all reflections) and $R_1(F)$ = 0.0540, $R_W(F^2)$ = 0.1000 [*GOF* 0.997; from reflections with $I > 2\sigma(I)$]. After the last iteration, the residual electron density in the Fourier difference series was 0.33 and –0.28 e Å^{-3}. The complete set of crystallographic data for compound **Xa** was deposited to the Cambridge Crystallographic Data Center (entry no. CCDC 611 296).

1-(5-Amino-3-R^1-1,2,4-triazol-1-yl)-1-aryl-3,4,4-trichloro-2-azabuta-1,3-dienes IIIa–IIIf *(general procedure).* A solution of 0.01 mol of compound **Ia** or **Ib** in 20 ml of THF and 0.022 mol of triethylamine were added to a suspension of 0.01 mol of the corresponding aminotriazole in 20 ml of THF. The mixture was heated for at least 84 h under reflux and cooled, the precipitate of triethylamine hydrochloride was filtered off, the filtrate was evaporated under reduced pressure, the residue was treated with water, and the precipitate was filtered off and purified by recrystallization.

2,7-Diaryl-4-dichloromethylpyrazolo[1,5-*a*]-[1,3,5]triazines VIIIa–VIIId were synthesized according to the procedure described above for compounds **IIIa–IIIf** using aza dienes **Ia** and **Ib** and the corresponding aminopyrazoles as starting compounds.

7-Aryl-2-R^1-5-dichloromethyl[1,2,4]triazolo[1,5-*a*][1,3,5]triazines IXa–IXf *(general procedure).* A solution of 0.011 mol of sodium methoxide in 2 ml of methanol was added to a suspension of 0.01 mol of compound **IIIa–IIIf** in 50 ml of anhydrous methanol. The mixture was stirred for at least 36 h at 20°C and diluted with 100 ml of water, and the precipitate was filtered off and purified by recrystallization.

6-Aryl-2-azido-4-dichloromethyl[1,3,5]triazines Xa and Xb *(general procedure).* A solution of 0.01 mol of compound **Ia** or **Ib** and 0.022 mol of triethylamine were added to a solution of 0.01 mol of 1*H*-tetrazol-5-amine in 20 ml of THF. The mixture was heated for 24 h under reflux, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, the residue was treated with 50 ml of water, and the precipitate was filtered off and purified by recrystallization.

ACKNOWLEDGMENTS

This study was performed under financial support by the Royal Society and by the Higher Research Society.

REFERENCES

1. Drach, B.S., Kovalev, V.A., and Kirsanov, A.V., *Zh. Org. Khim.,* 1976, vol. 12, no. 3, p. 673.
2. Drach, B.S. and Kovalev, V.A., *Zh. Org. Khim.,* 1976, vol. 12, no. 11, p. 2319.

3. Demidchuk, B.A., Brovarets', V.S., Chernega, O.M., and Drach, B.S., *Dopov. Nats. Akad. Nauk Ukrainy,* 2005, no. 12, p. 137.
4. Drach, B.S., Brovarets, V.S., and Smolii, O.B., *Sintezy azotsoderzhashchikh geterotsiklicheskikh soedinenii na osnove amidoalkiliruyushchikh agentov* (Syntheses of Nitrogen-Containing Heterocyclic Compounds on the Basis of Amidoalkylating Agents), Kiev: Naukova Dumka, 1992, p. 117.
5. Drach, B.S., Kovalev, V.A., and Kirsanov, A.V., *Zh. Org. Khim.,* 1975, vol. 11, no. 1, p. 122.
6. Watkin, D.J., Prout, C.K., Carruthers, J.R., and Betteridge, P.W., *CRYSTALS,* Issue 10, Chemical Crystallography Laboratory, Univ. of Oxford, 1996.
7. Carruthers, J.R. and Watkin, D.J., *Acta Crystallogr., Sect. A,* 1979, vol. 35, no. 3, p. 698.
8. Sheldrick, G.M., *SHELXS97. Program for the Solution of Crystal Structure,* Gottingen, Germany: Univ. of Gottingen.
9. Sheldrick, G.M., *SHELXL97. Program for the Refinement of Crystal Structures,* Gottingen, Germany: Univ. of Gottingen.