Reaction of 1-aryl-2-alkenyldiazene 1-oxides with hydrogen chloride. Novel approach to the synthesis of functionally substituted arylhydrazones

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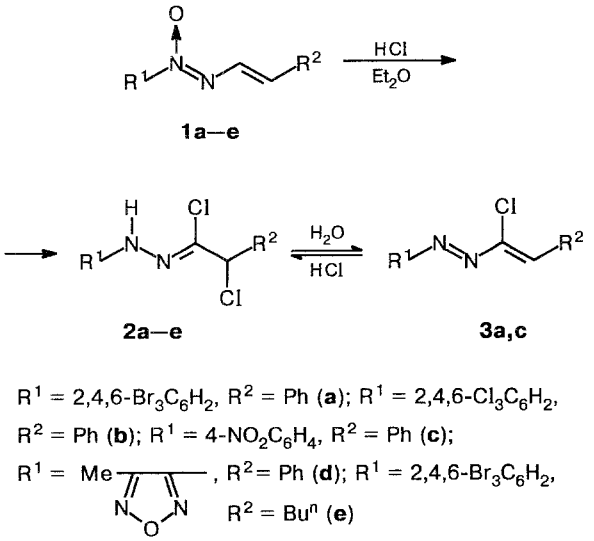
The reaction of 1-aryl-2-alkenyldiazene 1-oxides with HCl yields arylhydrazones of α-chloroacyl chlorides, which eliminate HCl to give 1-aryl-2-(1-chloroalken-1-yl)diazenes. The latter add amines, alcohols, and carboxylic acids to give arylhydrazone chlorides with α-functional groups.

Key words: chlorohydrazones, diazene oxides, azoxyalkanes, azoolefins.

In the previous paper[1] we suggested a convenient method for the synthesis of 1-aryl-2-alkenyldiazene 1-oxides (**1**) by the reaction of 1-aryl-2-bromodiazene 1-oxides with olefins followed by treatment of the intermediate 1-aryl-2-(β-bromoalkyl)diazene 1-oxides with triethylamine. Some representatives of aliphatic azoxyolefins of this type are known,[2] although, their chemical properties have not been studied. Therefore, it is of interest, most of all, to study the possibility of electrophilic addition to the C=C bond of compounds **1** with retention of the diazene oxide moiety. However, compounds **1** are almost entirely converted into chlorohydrazones **2**, when treated with an ethereal solution of HCl (Scheme 1, Table 1).

Scheme 1



R^1 = 2,4,6-$Br_3C_6H_2$, R^2 = Ph (**a**); R^1 = 2,4,6-$Cl_3C_6H_2$, R^2 = Ph (**b**); R^1 = 4-$NO_2C_6H_4$, R^2 = Ph (**c**); R^1 = Me–(1,2,5-oxadiazole), R^2 = Ph (**d**); R^1 = 2,4,6-$Br_3C_6H_2$, R^2 = Bu^n (**e**)

One may assume that the first step of this reaction is 1,5-addition of HCl to azoxy olefin **1** to give intermediate adduct **4** (Scheme 2). Then H_2O is eliminated *via* protonation of the OH group, and cation **5** adds the Cl^- anion to yield azo compound **6**. Chlorohydrazone **2** probably results from the migration of the active α-H proton. A similar cleavage of the N—O bond has been observed by us previously[3] in the decomposition of 1-aryl-2-(2-bromo-2-phenylethyl)diazene 1-oxides to give formaldehyde bromohydrazone and benzaldehyde. Recently it has been shown[4] that diazene oxides containing an active methylene fragment are converted into chlorohydrazones through the action of HCl. The reaction apparently occurs *via* type **4** enol form.

The structure of hydrazones **2** was determined on the basis of spectral data (^1H NMR, ^{13}C NMR, and IR spectroscopy and mass spectrometry). The presence of the hydrazone fragment was confirmed by the INEPT ^{15}N NMR spectra, which exhibit a signal for the ^{15}N atom bound to one proton ($\delta \sim -250$, $^1J_{^{15}N-^1H} \approx 90$ Hz).

Chlorohydrazones **2a** and **2c** are readily converted into chlorovinyldiazenes **3** (see Scheme 1): the H and Cl atoms are eliminated from positions 1 and 4, when water is added to a solution of compound **2** in MeCN. Compounds **3a,c** precipitate as crystals. This reaction is

Table 1. Preparation of chlorohydrazones **2** (see Scheme 1)

Hydrazone	Duration of the reaction/h	Yield (%)	M.p./°C
2a	1	100	84—87 (dec.)
2b	1	100	72—74
2c	3	95	95—96
2d	1	95	100—108 (dec.)
2e	1	100	Oil

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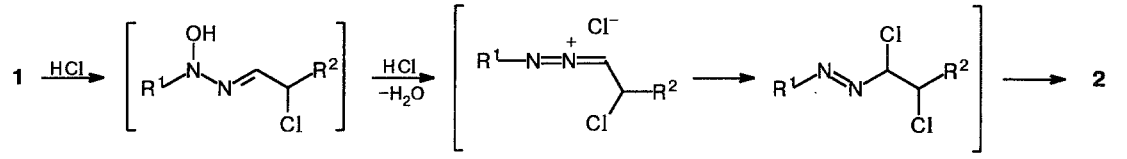
Scheme 2



4 **5** **6**

reversible, and treatment with a dry ethereal solution of HCl leads to the **3** → **2** conversion.

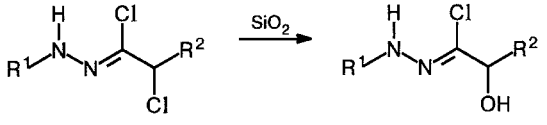
Unlike chlorohydrazones **2a,c**, compounds **2b,d,e** when treated with water in acetonitrile solutions yield oils that are mixtures of hydrazones **2** and azoolefins **3**, according to NMR spectroscopy. The structures of compounds **3b,d,e** were confirmed by ^{1}H NMR spectra. Attempts to bind HCl by the addition of bases (Et_3N, pyridine, collidine, Al_2O_3, NaF, and Na_2CO_3) in order to obtain analytically pure samples of compounds **3b,d,e** were unsuccessful. Silica gel also cannot be used for the abstraction of HCl from compounds **2**, since in this case, hydrolysis occurs. For example, chlorohydrazone **2e** is converted on silica gel into compound **7e** in a 58 % yield (Scheme 3).

Azoolefin **3a** is formed as a mixture of *E* and *Z* isomers (the ^{1}H and ^{13}C NMR spectra exhibit two sets of signals) in which the thermodynamically less favorable isomer predominates. On heating it is converted into the more stable isomer. Compound **3c** was obtained as one thermodynamically favorable isomer, which may be due to its easy isomerization caused by the presence of the electronegative R^1 substituent. The *trans*-arrangement of the bulky Ph and Cl substituents suggested by us was confirmed by MM2 calculations of the energies of the isomers.

It should be noted that no general methods for the synthesis of azochloroolefins are known. Only some representatives of this class have been reported,[5] and their properties have not yet been studied.

We showed that azoolefins **3** readily react with amines (Scheme 4). The rate of 1,4-addition of morpholine to

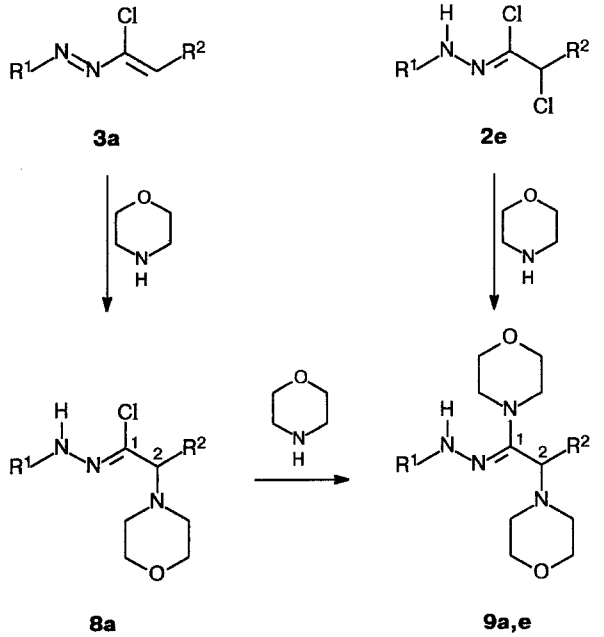
Scheme 3



2e **7e**

R^1 = 2,4,6-$Br_3C_6H_2$, R^2 = Bu^n

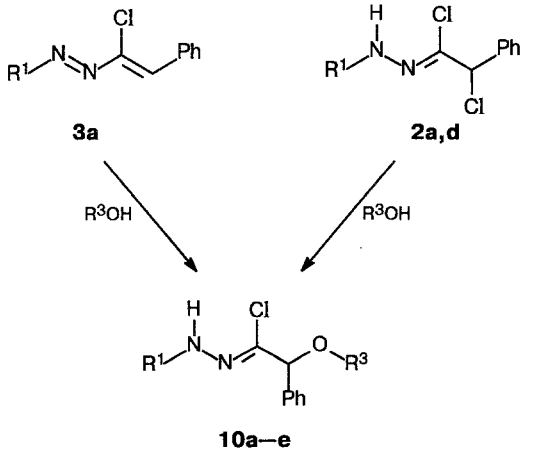
Scheme 4



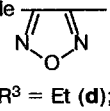
3a **2e** **8a** **9a,e**

R^1 = 2,4,6-$Br_3C_6H_2$; R^2 = Ph (**a**), Bu^n (**e**)

Scheme 5



3a **2a,d** **10a–e**

10: R^1 = 2,4,6-$Br_3C_6H_2$, R^3 = Me (**a**); R^1 = 2,4,6-$Br_3C_6H_2$, R^3 = Et (**b**); R^1 =  , R^3 = Me (**c**);

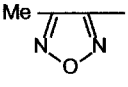
R^1 =  , R^3 = Et (**d**); R^1 = 2,4,6-$Br_3C_6H_2$, R^3 = Ac (**e**)

Table 2. Preparation of chlorohydrazones **10** (see Scheme 3)

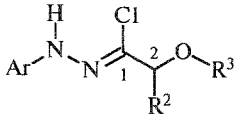
Starting compound	Reagent	Hydrazone	Duration of the reaction/h	Yield (%)	M.p. /°C
2a	MeOH	**10a**	0.5	90	81—82
3a	MeOH	**10a**	2.5	95	80—82
2a	EtOH	**10b**	4	95	79—80
3a	EtOH	**10b**	1	95	79—80
2d	MeOH	**10c**	4	90	136—138
2d	EtOH	**10d**	24	90	85—86
3a	AcOH	**10e**	1	89	78—79

compound **3a** is greater than the rate of substitution of chlorine, and hydrazone **8a** can be isolated in 55 % yield. Treatment with an excess of amine results in the replacement of the Cl atom to give amidrazone **9a**. In those cases where pure azochloroolefin cannot be isolated, amidrazone is readily obtained by treatment of chlorohydrazone **2** with an excess of amine. For example, compound **9e** is produced from chlorohydrazone **2e** in 72 % yield.

Azochloroolefins readily add alcohols or carboxylic acids (Scheme 5). For example, compound **3a** reacts with methanol to give hydrazone **10a** in 90 % yield. Compounds **10** can be obtained directly from chlorohydrazones **2** in one step (Table 2). The structures of compounds **10** have been confirmed by spectroscopy data (Tables 3—5).

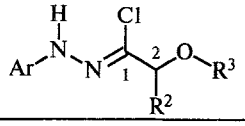
Experimental

^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13, 75.5, 21.5, and 30.42 MHz, respectively); the chemical shifts were referred to tetramethylsilane (for ^1H and ^{13}C NMR) or $MeNO_2$ (for ^{14}N and ^{15}N, an external standard). To observe the ^{15}N signals, the

Table 3. Data of ^1H, ^{14}N, and ^{15}N (INEPT) NMR spectroscopy for compounds **2,3** and  (R^2 = Ph or $\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$)

Compound	^1H NMR, δ			^{14}N and ^{15}N NMR, δ (*J*/Hz)
	C(2)H	NH (br)	Other signals	
2a	5.90	7.9	7.33—7.40 (m, H_m, H_p, R^2); 7.54 (dd, H_o, R^2); 7.63 (H_m, Ar)	−246.80 (^{15}NH, ^1J = 89); −66.55 (^{15}N=C, ^2J = 4.7)
2b	5.86	7.9	7.24 (H_m, Ar); 7.30—7.40 (m, H_m, H_p, R^2); 7.50 (dd, H_o, R^2)	−67.09 (^{15}N=C, ^2J = 4.7); −253.15 (^{15}NH, ^1J = 90)
2c	5.95	8.4	7.08 (d, H_o, Ar); 7.35—7.45 (m, H_m, H_p, R^2); 7.54 (dd, H_o, R^2); 8.13 (d, H_m, Ar)	−241.97 (^{15}NH, ^1J = 95); −16 ($^{14}NO_2$, $\Delta\nu_{1/2} \approx 1000$)
2d	5.83	8.7	2.26 (s, Ar); 7.3—7.5 (m, H_o, H_m, H_p, R^2)	−262.94 (^{15}NH, ^1J = 94)
2e	4.69 (t)	7.9	0.92 (t, HC(6), R^2); 1.30—1.48 (m, HC(4)—HC(5), R^2); 1.98—2.20 (m, HC(3), R^2); 7.68 (H_m, Ar)	−51 (^{14}N=C, $\Delta\nu_{1/2} \approx 250$)
3a[a]	7.57	—	7.32—7.38 (m, H_m, H_p, R^2); 7.78 (H_m, Ar); 7.86 (dd, H_o, R^2)	
3a[b]	8.01	—	7.46—7.50 (m, H_m, H_p, R^2); 7.77 (H_m, Ar); 8.04 (dd, H_o, R^2)	
3c	8.05	—	7.45—7.55 (m, H_p, H_m, R^2); 7.98 (d, H_o, Ar); 8.05 (dd, H_o, R^2); 8.36 (d, H_m, Ar)	−14 ($^{14}NO_2$, $\Delta\nu_{1/2} \approx 400$)
7e	4.40 (dt)	8.0	0.89 (t, HC(6), R^2); 1.30—1.50 (m, HC(4)—HC(5), R^2); 1.75—1.85 (m, HC(3), R^2); 4.73 (d, R^3); 7.86 (H_m, Ar)	
10a	5.14	7.9	3.47 (R^3); 7.30—7.40 (m, H_m, H_p, R^2); 7.46 (dd, H_o, R^2); 7.66 (H_m, Ar)	−247.35 (^{15}NH, ^1J = 88.2)
10b	5.26	7.9	1.31 (t, 3 H, CH_3, R^3); 3.58 (dq, 1 H, CH_2, R^3); 3.71 (dq, 1 H, CH_2, R^3); 7.26—7.38 (m, H_m, H_p, R^2); 7.48 (dd, H_o, R^2); 7.65 (H_m, Ar)	−247.47 (^{15}NH, ^1J = 88)
10c	5.11	8.5	2.38 (s, Me, Ar); 3.48 (R^3); 7.30—7.50 (m, H_m, H_p, H_o, R^2)	
10d	5.22	8.5	1.31 (t, 3 H, CH_3, R^3); 2.36 (s, Me, Ar); 3.55—3.72 (m, 2 H, CH_2, R^3); 7.30—7.50 (m, H_o, H_m, H_p, R^2)	
10e	6.53	7.9	2.16 (Me, R^3); 7.30—7.40 (m, H_m, H_p, R^2); 7.46 (dd, H_o, R^2); 7.60 (H_m, Ar)	−246.85 (^{15}NH, ^1J = 88.5)

[a] The major isomer, the ratio between the isomers is ~2 : 1. [b] The minor isomer.

Table 4. Data of ^{13}C NMR spectroscopy for compounds **2**, **3** and  (R^2 = Ph or $^{3}CH_2{}^{4}CH_2{}^{5}CH_2{}^{6}CH_3$)

Compound	^{13}C NMR, δ										
	Ar				R^2				C(1)	C(2)	R^3
	CNH	C_o	C_m	C_p	CCH or C(3)	C_o or C(4)	C_m or C(5)	C_p or C(6)			
2a[a]	137.75	116.04	135.16	116.71	135.84	127.69	128.49	128.88	128.35	63.95	—
2b	135.22	126.46	128.86	128.70	135.76	127.59	128.35	128.86	128.50	63.85	—
2c	147.92	112.91	125.69	141.50	135.64	127.73	128.61	129.14	129.28	64.17	—
2d[b]	—	—	—	—	144.58	127.72	128.65	129.19	128.35	63.70	—
2e	138.04	116.29	135.35	116.90	35.70	28.50 and 21.97		13.64	129.11	62.99	—
3a[c]		111.97	131.23	117.82		128.01	124.64	126.48		136.86	—
3a[d]		112.09	131.12	117.42		127.25	124.71	127.09		140.94	—
3c[e]		123.76	124.78			131.37	128.91	131.22	133.10	144.81	—
7e	140.20	118.30	136.02	117.73	35.06	28.18 and 23.08		14.28	134.48	74.86	—
10a	138.29	116.53	135.10	116.80	137.00	126.44	128.29	128.19	130.71	84.40	56.98 (CH_3)
10b	138.35	116.37	135.10	116.65	137.39	126.48	128.25	128.08	131.34	82.60	15.10 (CH_3); 64.79 (CH_2)
10c[f]	—	—	—	—	136.54	126.60	128.51	128.60	133.39	84.68	57.26 (CH_3)
10d[g]	—	—	—	—	137.05	126.68	128.48	128.48	133.89	83.00	65.21 (CH_2); 15.09 (CH_3)
10e	137.91	115.71	135.04	116.35	135.14	127.16	128.47	128.78	127.20	76.21	20.81 (CH_3); 169.05 (C=O)

[a] $J_{^1H-^{13}C}$/Hz: C(2), ^1J = 155, ^3J = 4.9; C_o(Ar), ^2J = 3.8, $^3J = {}^4J$ = 2.7; C_p(Ar), ^3J = 4.3; C_o(R^2), ^1J = 161.0; C(1), ^2J = 4.8, ^3J = 7.6; C_m(R^2), ^1J = 161.8; C_p(R^2), ^1J = 161.0, ^3J = 7.5; C_m(Ar), ^1J = 173.6, ^3J = 6.2; CCH(R^2), ^3J = 7.5, ^2J = 4.8; CNH (Ar), ^3J = 7.1, ^2J = 4.9. [b] δ: 9.62 (CH_3); 153.94 (CMe); 161.96 (C=N). [c] The major isomer, δ: 129.32, 136.57, 144.74 (C(1), CNH from Ar, CCH from Ph). [d] The minor isomer, δ: 128.69, 137.61, 144.30 (C(1), CNH from Ar, CCH from Ph). [e] δ: 142.66, 148.76, 155.15 (C_p from Ar, CNH from Ar, CCH from Ph). [f] δ: 9.60 (CH_3); 144.43 (CMe); 154.06 (CNH). [g] δ: 9.60 (CH_3); 144.52 (CMe); 154.19 (CNH).

INEPT and SPT procedures were used. The spectra of compound **7e** were obtained in acetone-d_6; those of other compounds were recorded in $CDCl_3$. To assign the ^1H and ^{13}C NMR signals the following procedures were used: accumulation of the ^{13}C signals without proton decoupling, selective transfer of the $^1H-^{13}C$ polarization, recording of the ^{13}C NMR spectra with selective proton decoupling, and $^1H-^1H$ and $^1H-^{13}C$ correlations. IR spectra were recorded on a UR-20 instrument. Mass spectra were measured on a Varian MAT CH-6 mass spectrometer.

Arylhydrazones of α-chloroacyl chlorides (2) (general procedure). A 1 *M* ethereal solution of HCl (15 mL) (prepared by passing dry HCl through ether dried with NaOH) was added to a stirred solution of azoxyolefin **1** (1 mmol) in 15 mL of CH_2Cl_2. The duration of the reaction at 24 °C is given in Table 1. The solvent was evaporated *in vacuo*, and the solid products were recrystallized from hexane.

1-Aryldiazenyl-1-chloro-2-phenylethylenes (3a,c) (general procedure). Water (50 mL) was added with stirring to a solution of chlorohydrazone **2** (0.5 mmol) in 10 mL of MeCN, and the crystals precipitated were filtered off, washed with water, and dried in a desiccator over NaOH. The yield of compound **3** was 95—100 %; the melting point of **3a** was 111—116 °C (a mixture of two isomers); after heating in MeCN (80 °C, 15 h), m.p. 126—128 °C (one isomer). The melting point of **3c** was 165—167 °C. After addition of water, compounds **3b,d,e** precipitated as oils, which were extracted with CH_2Cl_2, and the solutions were dried with $MgSO_4$ and concentrated under reduced pressure. The mixtures were analyzed by ^1H NMR spectroscopy. The ratios between the products were determined to be the following: **3b** : **2b** = 1 : 1, **3d** : **2d** = 1 : 2, **3e** : **2e** = 4 : 1. ^1H NMR, δ: **3b**: 8.05 (=CH); **3d**: 2.58 (CH_3); **3e**: 0.98 (t, CH_3); 1.45—1.65 (m, CH_2CH_2); 2.68 (q, =CHCH_2); 7.24 (t, =CH); 7.77 (CH, Ar).

2-Hydroxy-2-butylacetyl chloride 2,4,6-tribromophenylhydrazone (7e). A solution of chlorohydrazone **2e** (0.2 g, 0.4 mmol) in 30 mL of $CHCl_3$ was deposited onto silica gel, after 2 h the products were washed with methylene chloride, and the solvent was evaporated *in vacuo*. Purification by column chromatography (silica gel; hexane—chloroform, 5 : 1, as the eluent) gave 0.11 g of compound **7e** (yield 58 %), m.p. 115—116 °C.

2-Morpholino-2-phenylacetyl chloride 2,4,6-tribromophenylhydrazone (8a). A solution of morpholine (0.058 mL, 0.67 mmol) in 6 mL of 1,4-dioxane was added dropwise over a period of 1 h to a stirred solution of azochloroolefin **3a** (0.3 g, 0.63 mmol) in 5 mL of dioxane. The reaction mixture was kept for 1 h, and the solvent was evaporated in a vacuum of an oil pump. Acetone extraction (5 mL) of impurities from the solid residue afforded 0.19 g of compound **8a** (yield 55 %), m.p. 144.5—146 °C. ^1H NMR, δ: 2.45—2.55 (m, 4 H, CH_2N); 3.70—3.80 (m, 4 H, CH_2O); 4.30 (1 H, C(2)H);

Table 5. Data of elemental analysis and IR and mass spectra of compounds synthesized

Compound	IR,[a] ν/cm^{-1}	MS[b]	Found / Calculated (%)				Molecular formula
			C	H	N	Cl+Br	
2a	3315 (N—H)	512 $[M]^+$	32.73 32.56	1.78 1.74	5.35 5.43	60.30 60.27	$C_{14}H_9N_2Br_3Cl_2$
2b	3325 (N—H)	380 $[M]^+$	43.76 43.92	2.33 2.35	7.30 7.32	46.38 46.41	$C_{14}H_9N_2Cl_5$
2c	3330 (N—H)	323 $[M]^+$	51.61 51.85	3.36 3.40	13.01 12.96	21.99 21.91	$C_{14}H_{11}N_3O_2Cl_2$
2d	3200,3230 (N—H)	284 $[M]^+$	46.66 46.32	3.70 3.51	19.90 19.65	25.04 24.91	$C_{11}H_{10}N_4OCl_2$
2e	3300 (br, N—H)	456 $[M-HCl]^+$	29.27 29.03	2.51 2.62	5.83 5.65	62.85 62.70	$C_{12}H_{13}N_2Br_3Cl_2$
3a	1550(N=N); 1620(C=C)	476 $[M]^+$	35.29 35.04	1.62 1.67	5.89 5.84	57.51 57.46	$C_{14}H_8N_2Br_3Cl$
3c	1522(N=N); 1595(C=C)	287 $[M]^+$	58.21 58.43	3.40 3.48	14.69 14.61	12.38 12.35	$C_{14}H_{10}N_3O_2Cl$
7e	3325 (N—H); 3400 (O—H)	474 $[M]^+$	30.28 30.16	2.97 2.93	5.75 5.86	57.55 57.70	$C_{12}H_{14}N_2OBr_3Cl$
8a	3310, 3320 (N—H)	563 $[M]^+$	38.30 38.13	3.08 3.00	7.45 7.41	48.70 48.63	$C_{18}H_{17}N_3OBr_3Cl$
9a	3270, 3430 (br, N—H)	614 $[M]^+$	42.83 42.79	4.09 4.05	9.11 9.08	38.95 38.90	$C_{22}H_{25}N_4O_2Br_3$
9e	3180 (br, N—H)	594 $[M]^+$	40.45 40.20	4.79 4.86	9.30 9.38	40.28 40.20	$C_{20}H_{29}N_4O_2Br_3$
10a	3300 (N—H)	508 $[M]^+$	35.43 35.19	2.37 2.35	5.51 5.47	53.80 53.86	$C_{15}H_{12}N_2OBr_3Cl$
10b	3310 (N—H)	522 $[M]^+$	36.30 36.54	2.73 2.66	5.41 5.33	52.60 52.43	$C_{16}H_{14}N_2OBr_3Cl$
10c	3215, 3240 (N—H)	280 $[M]^+$	51.41 51.34	4.71 4.63	20.07 19.96	12.78 12.66	$C_{12}H_{13}N_4O_2Cl$
10d	3200, 3230 (N—H)	294 $[M]^+$	52.88 52.97	5.15 5.09	19.08 19.02	12.18 12.05	$C_{13}H_{15}N_4O_2Cl$
10e	3305 (N—H)	536 $[M]^+$	35.77 35.59	2.29 2.22	5.05 5.19	51.19 51.07	$C_{16}H_{12}N_2O_2Br_3Cl$

[a] IR spectra were recorded for samples pressed with KBr; the spectrum of compound **2e** was recorded in a thin film (NaCl glasses). [b] The molecular ion is given for the ^{35}Cl and ^{79}Br isotopes.

7.30—7.40 (m, 3 H, H_m, H_p, Ph); 7.51 (dd, 2 H, H_o, Ph); 7.68 (s, 2 H, Ar); 7.9 (br.s, 1 H, NH). ^{13}C NMR, δ: 51.65 (CH_2N); 66.95 (CH_2O); 76.20 (C(2)H); 116.41 (C_o, Ar); 116.64 (C_p, Ar); 128.30 (C_p, Ph); 128.51 and 128.95 (C_o and C_m, Ph); 130.93 (C(1)); 135.19 (C_m, Ar); 136.30 (CCH, Ph); 138.56 (CNH, Ar).

2-Morpholino-2-phenylacetomorpholide 2,4,6-tribromophenylhydrazone (9a). Morpholine (0.3 mL, 3.4 mmol) was added to a solution of azochloroolefin **3a** (0.3 g, 0.63 mmol) in 19 mL of ether, and the mixture was kept for 30 min at 20 °C, evaporated to half its initial volume, and kept for an additional 30 min. The solution was washed with water (5×50 mL), and the solvent was evaporated to give 0.4 g of compound **9a** (yield 90 %), m.p. 78—80 °C. ^1H NMR, δ: 2.4—2.5 (m, 2 H, CH_2N); 2.62—2.72 (m, 2 H, CH_2N); 2.83—2.91 (m, 2 H, CH_2N); 2.91—3.00 (m, 2 H, CH_2N); 3.65—3.75 (m, 8 H, CH_2O); 4.33 (s, 1 H, C(2)H); 7.24—7.38 (m, 3 H, H_m and H_p, Ph); 7.41 (dd, 2 H, H_o, Ph); 7.64 (s, 2 H, Ar); 8.0 (br.s, 1 H, NH). ^{13}C NMR, δ: 47.33 and 51.33 (CH_2N); 67.09 and 67.24 (CH_2O); 70.74 (C(2)); 114.66 (C_p, Ar); 115.75 (C_o, Ar); 127.98 (C_p, Ph); 128.11 and 130.15 (C_o and C_m, Ph); 134.88 (C_m, Ar); 135.31, 141.67, 147.89 (CN from Ar, CCH from Ph, C(1)). ^{15}N NMR (INEPT), δ: −249.39 (NH, ^1J = 81.8 Hz).

2-Morpholino-2-butylacetomorpholide 2,4,6-tribromophenylhydrazone (9e). Morpholine (0.31 mL, 3.5 mmol) was added to a solution of 2-chloro-2-butylacetyl chloride 2,4,6-tribromophenylhydrazone (**2e**) (0.35 g, 0.7 mmol) in 5 mL of CH_2Cl_2, the precipitate of morpholine hydrochloride was filtered off, and the filtrate was evaporated. Purification by column chromatography (silica gel; chloroform followed by ether) gave 0.3 g of compound **9e** (yield 72 %), m.p. 190—192 °C. ^1H NMR, δ: 0.90 (t, 3 H, CH_3); 1.30—1.50 (m, 4 H, CH_2CH_2); 1.65—1.80 (m, 1 H, CH_2CH); 2.25—2.40 (m, 1 H, CH_2CH); 2.45—2.75 (m, 4 H, CH_2N); 3.15—3.30 (m, 4 H, CH_2N); 3.75—3.95 (m, 9 H, C(2)H and OCH_2);

7.57 (s, 2 H, Ar); 9.6 (br.s, 1 H, NH). ^{13}C NMR, δ: 13.91 (CH_3); 22.64 and 25.78 (CH_2CH_2); 28.48 ($\underline{C}H_2CH$); 48.12 (CH_2N); 51.6 (br, CH_2N); 64.98 (C(2)H); 66.43 and 66.77 (CH_2O); 111.41 (C_p); 112.79 (C_o); 134.79 (C_m); 141.62 and 151.76 (C(1) and CN from Ar).

Synthesis of 2-alkoxyacyl chloride arylhydrazones (10) from chlorohydrazones 2 (general procedure). Alcohol R^3OH (10 mL) was added to a solution of chlorohydrazone **2** (1 mmol) in 5 mL of CH_2Cl_2 (the duration of the reaction at 24 °C is given in Table 2). The solvents were evaporated in a vacuum of an oil pump, and the product was purified on a short chromatographic column (h = 1 cm, silica gel, chloroform) and recrystallized from hexane.

Synthesis of 2-alkoxyacyl chloride arylhydrazones (10) from azochloroolefins 3 (general procedure). Azochloroolefin **3** (0.7 mmol) was boiled with reflux in 20 mL of alcohol (the duration of the reaction is given in Table 2). Excess alcohol was evaporated *in vacuo*, and the product was purified on a short chromatographic column (h = 1 cm, silica gel, chloroform) and recrystallized from hexane.

2-*O*-Acetyl-2-phenylacetyl chloride 2,4,6-tribromophenylhydrazone (10e). Azochloroolefin **3a** (0.2 g, 0.42 mmol) was dissolved in 10 mL of $MeCO_2H$, and the solution was heated on a water bath for 1 h at 90 °C. Excess acid was evaporated in a vacuum of an oil pump, the resulting oil was dissolved in 10 mL of CH_2Cl_2, washed with water to pH 7, and dried with $CaCl_2$, and the solvent was evaporated. The product was purified on a short chromatographic column (h = 1 cm, silica gel, chloroform). Evaporation of the solvent gave 0.2 g of compound **10e** (yield 89 %) as a slowly crystallizing oil.

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References

1. A. M. Churakov, A. Yu. Tyurin, E. L. Goncharova, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 924 [*Russ. Chem. Bull.*, 1995, **44**, 897 (Engl. Transl.)].
2. B. T. Gillis and J. D. Hagarty, *J. Org. Chem.*, 1967, **32**, 95.
3. (a) A. M. Churakov, A. Yu. Tyurin, E. L. Goncharova, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 917 [*Russ. Chem. Bull.*, 1995, **44**, 890 (Engl. Transl.)]; (b) A. M. Churakov, E. L. Goncharova, A. Yu. Tyurin, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Mendeleev Commun.*, 1991, 141.
4. O. A. Luk'yanov, Yu. B. Salamonov, A. G. Bass, Yu. A. Strelenko, and N. F. Karpenko, *Izv. Akad. Nauk SSSR, Ser. Khim*, 1990, 352 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 294 (Engl. Transl.)].
5. R. Helwig and M. Hanack, *Chem. Ber.*, 1985, **118**, 1008.

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