Synthesis of Azomethylene Derivatives of 4-Chloro-5*H*-1,2,3-dithiazole

Vladimir N. Yarovenko*, Andrey A. Es´kov, George V. Zatonsky, Igor V. Zavarzin, Mikhail M. Krayushkin, Boris B. Averkiev†, Mikhail Yu. Antipin†.

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russia
†A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russia
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Previously unknown azomethylene derivatives of 4-chloro-5*H*-1,2,3-dithiazole **5**-**7** were synthesized by the reaction of the Appel salt **1** with *N*-monosubstituted hydrazones **2**-**4**. It was shown that they could be transformed into heterocyclic compounds **8**-**10**.

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Introduction.

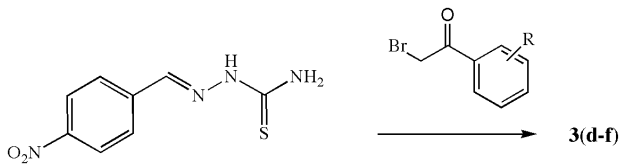
4,5-Dichloro-1,2,3-dithiazolium chloride [1] (Appel salt) **1** is widely used in syntheses of diverse biologically active substances [1,2]. The reaction of the Appel salt with amines affording 5-imino derivatives of 1,2,3-dithiazole has been studied in more detail. The reactions with water, hydrogen sulfide, hydrazines, and compounds containing the active methylene group were also described. A few examples for the reaction of the Appel salt with phenols are known [1]. Further modifications of the synthesized compounds afford various products, including heterocyclic compounds [3-16]. Thus, synthetic and practical aspects of 1,2,3-dithiazole derivatives stimulate further development of the chemistry of this class of compounds.

Results and Discussion.

In this work, we describe a method for the synthesis of earlier unknown azomethylene derivatives of 1,2,3-dithiazole **5-7** using the reaction of the Appel salt with N-monosubstituted aldehyde hydrazones **2**-**4** (Scheme 2). We also show that the new derivatives can be used for the synthesis of related heterocyclic compounds **8**-**10** (Schemes 3-5). A series of hydrazones **2-4** containing the nitro group, aryl, or hetaryl rings at the imide carbon atom were used in the reaction (Table 1).

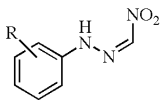
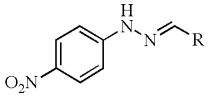
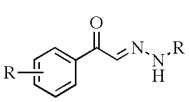
Compounds **2a-f** were synthesized by the reaction of aryldiazonium salts with nitromethane. Compounds **3a-c** and **4a-b** were prepared from the corresponding aldehydes. Compounds **3d-f** were synthesized by the reaction of thiosemicarbazide hydrazone with bromoketones (Scheme 1).

Scheme 1



The structure of the initial hydrazones should have influence on the reaction with the Appel salt. It is known that hydrazones containing one mobile hydrogen atom at the

Table 1
Hydrazones **2**-**4**

Compounds		R	R[1]
2		**a** 2-CN	
		b 2-F	
		c 2-NO_2	
		d 2-MeO	
		e 2-MeS	
		f 2-N_3	
3		**a** 2-$NO_2C_6H_4$-	
		b 3-$NO_2C_6H_4$-	
		c 5-nitrofuran-2-	
		d 5-(4-ClC_6H_4)-1,3-thiazole-2-	
		e 5-(4-BrC_6H_4)-1,3-thiazole-2-	
		f 5-(2,4-diClC_6H_3)-1,3-thiazole-2-	
4		**a** 4-F	2,4-$(NO_2)_2C_6H_3$-
		b 3-CH_3	2,4-$(NO_2)_2C_6H_3$-

α-C atom (with respect to the azomethine group) can exist as two prototropic tautomers **a** and **b** [17,18] (Figure 1).

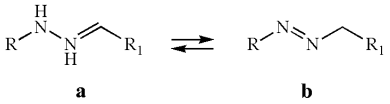


Figure 1

Based on the data of ^{1}H NMR spectroscopy and 2D correlation H-C (HSQC) and NOESY spectra, we can conclude that nitrohydrazones obtained by us exist only in the hydrazone form **a**.

For example, the proton spectrum of nitrohydrazone **2a** contains two singlets at 8.70 and 11.90 ppm. The singlet at 8.70 ppm exhibits a correlation peak in the HSQC spectrum at 8.70/143 ppm, which allows it to be assigned to the methine carbon. Correspondingly, the broadened singlet at 11.90 ppm can be assigned as the NH proton because it has not the corresponding correlation peak in the HSQC spectrum and is broadened, probably, due to exchange processes.

Analysis of the NOESY spectrum confirms the conclusion about the structure of the condensation product. The spectrum contains an intense cross peak between the NH and CH protons (11.90/8.70 ppm) and a lower-intensity cross peak between the NH and CH-a protons of the benzene ring.

Summarizing the data of the NOESY and heteronuclear correlation spectra, we can ascribe the structure of hydrazone tautomer **2a'** or **2a''** to compound **2a** (Figure 2).

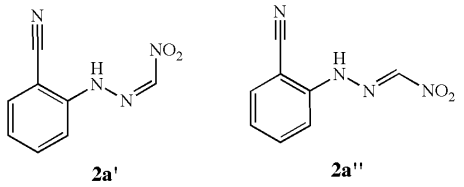


Figure 2

In all cases, the reaction of the Appel salt with hydrazones **2-4** in the presence of bases afforded the corresponding azomethylene derivatives of 1,2,3-dithiazole (Table 2).

We also studied the influence of the nature of the base, reaction duration, and order of mixing reactants on the reaction course. It was established that the corresponding azo derivatives of 1,2,3-dithiazole **5a-f** were formed in the reaction of the Appel salt with nitroformaldehyde hydrazones **2a-f** in the presence of pyridine. The best results were obtained when a twofold excess of pyridine was added to a mixture of nitrohydrazone and Appel salt in dichloromethane at room temperature. Solvents have a substantial effect on the reaction. For example, when the reaction is carried out in THF, azo derivatives are not formed or their yield decreases dramatically, likely, due to a decrease in the electrophilicity of the Appel salt in this more polar (than dichloromethane) solvent. It is noteworthy that substituents in the benzene ring of nitrohydrazones have no substantial effect on the process. The yields of the products obtained from hydrazones containing benzene rings with electron-withdrawing or electron-donating substituents are comparable.

The replacement of the nitro group in nitrohydrazones by the aryl or hetaryl fragment decreases the mobility of the imide hydrogen atom. Therefore, the corresponding azo derivatives of 1,2,3-dithiazole were obtained from compounds **3a-f** only with the use of collidine, which is more basic than pyridine. In this case, the best results were obtained when the Appel salt was added to a mixture of hydrazone and collidine.

It turned out that the introduction of the carbonyl group between the phenyl ring and aldehyde group in hydrazones **4a-b** did not favor the reaction. Therefore, in order to perform the process, as in the case of hydrazones **3a-f**, collidine should be used along with the order of mixing reactants described in the preceding method. Perhaps, the electron-withdrawing effect of the carbonyl group is aligned by the unfavorable configuration of compounds **4a-b** compared to hydrazones **2a-f**. This configuration prevents the electrophilic attack of the bulky Appel salt.

In order to support the structure of the formed azomethylene derivatives of dithiazole, we performed X-ray diffraction analysis of compound **5a**. The data of X-ray analysis shows (Figure 3) that the molecule lies in one

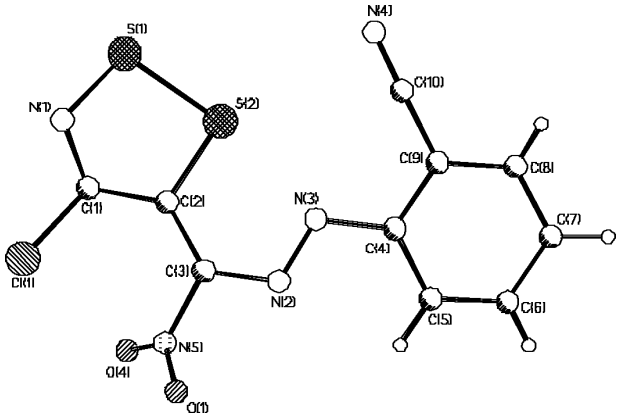


Figure 3. X-ray structure of compound **5a**, selected bond lengths (Å): S(1)-S(2) 2.096(1), S(1)-N(1) 1.622(3), S(2)-C(2) 1.726(3), N(1)-C(1) 1.293(4), C(1)-C(2) 1.447(4), C(1)-Cl(1) 1.725(3), C(2)-C(3) 1.390(4), C(3)-N(2) 1.350(4).

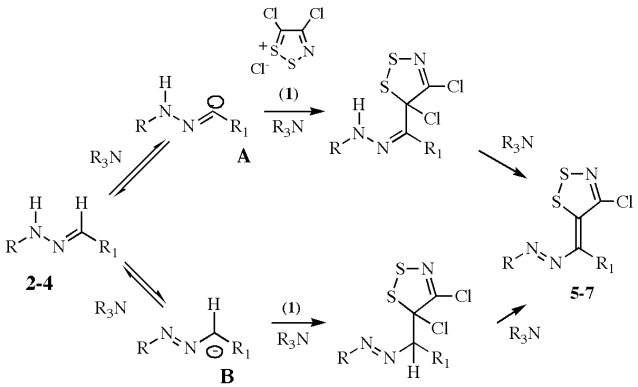
plane and is a *trans*-isomer in which the benzene and heterocyclic rings are in the *trans*-configuration relatively to the N(2)=N(3) double bond. It is also seen that in a crystal of compound **5a** the S-2 sulfur atom is turned toward the N-3 nitrogen atom and the chlorine atom is situated near the N-5 nitrogen atom.

Table 2

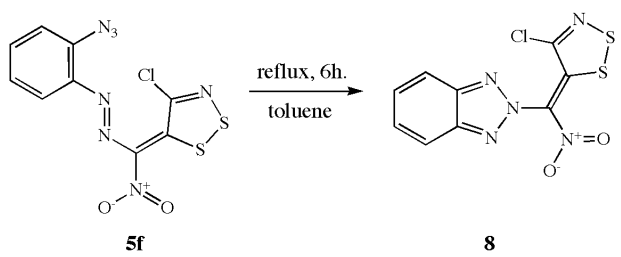
Reaction Conditions, Melting points, and Yields of Compounds **5**, **6**, and **7**

Entry	Reaction conditions	R^1	R	mp (°C) from Dichloro-methane	Yields (%)
5a	Methylene chloride,	NO_2	2-CNC_6H_4-	193-194	60
5b	2 eq. pyridine	NO_2	2-FC_6H_4-	170-171	30
5c		NO_2	2-$NO_2C_6H_4$-	153-154	31
5d		NO_2	2-$CH_3OC_6H_4$-	157-158	25
5e		NO_2	2-$CH_3SC_6H_4$-	175-176	25
5f		NO_2	2-$N_3C_6H_4$-	173-175	34
6a	Methylene chloride, 2 eq.	4-$NO_2C_6H_4$-	2-$NO_2C_6H_4$-	157-158	37
6b	2,4,6-collidine	4-$NO_2C_6H_4$	3-$NO_2C_6H_4$-	210-212	24
6c		4-$NO_2C_6H_4$	5-nitrofuran-2-	203-205	23
6d		4-$NO_2C_6H_4$	5-(4-ClC_6H_4)-1,3-thiazole-2-	200-202	19
6e		4-$NO_2C_6H_4$	5-(4-BrC_6H_4)-1,3-thiazole-2-	205-207	21
6f		4-$NO_2C_6H_4$	5-(2,4-$Cl_2C_6H_3$)-1,3-thiazole-2-	178-180	23
7a	Methylene chloride, 2 eq.	2,4-$(NO_2)_2C_6H_3$-	4-$FC_6H_4C(O)$-	172-174	16
7b	2,4,6-collidine	2,4-$(NO_2)C_6H_3$-	3-$CH_3C_6H_4C(O)$-	164-165	19

Scheme 2



Scheme 3



The formation of azomethylene derivatives likely includes the generation of the corresponding anion **A** or **B** under the action of a base. Then this anion adds to the Appel salt molecule, and the azo derivative of 1,2,3- dithiazole is formed after another proton and chlorine atom are eliminated from the heterocycle (Scheme 2).

Thus, the reaction of N-monosubstituted aldehyde hydrazones with the Appel salt is accompanied by the elimination of two protons from different N and C atoms. This is the basic difference of the process from the reactions involving the Appel salt described in the literature, where two protons are eliminated from the same N or C atom. The reaction in which protons are eliminated from two different C or N atoms extends synthetic potentialities of the reactions involving the Appel salt and can be useful for the synthesis of various new products.

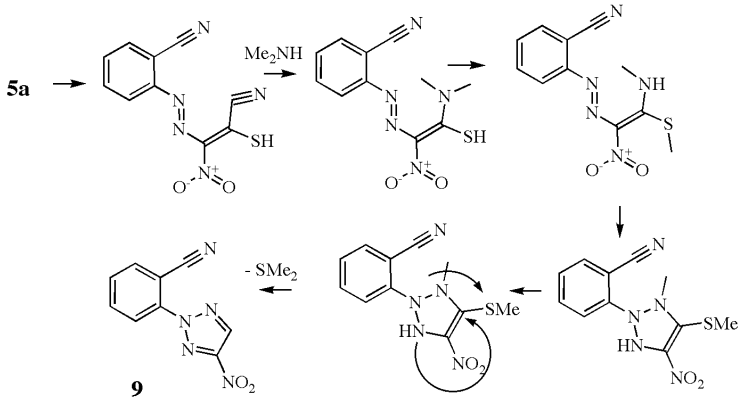
As mentioned above, 1,2,3-dithiazole derivatives find use in the synthesis of heterocyclic compounds. We have shown that the diazo group and dithiazole cycle in azomethylene derivatives of dithiazole can be used in the syntheses of heterocyclic structures.

It is known that triazole derivatives are used as photostabilizers of light filters and herbicides [19-24]. We found that the thermolysis of compound **5f** containing the azide group in the *ortho*-position relative to the diazo group produced the previously unknown benzotriazole **8** containing the 1,2,3-dithiazole fragment in high yield (~90%) (Scheme 3).

The 1,2,3-dithiazole cycle is known to undergo various transformations under the action of amines or on heating [25-27].

Short boiling of 1,2,3-dithiazole azo derivative **5a** in DMF produces triazole **9**. A possible mechanism of this unusual reaction includes the interaction of compound **5a** with dimethylamine formed from DMF on its heating (Scheme 4). The structure of compound **9** was proven by X-ray diffraction (Figure 4).

Scheme 4



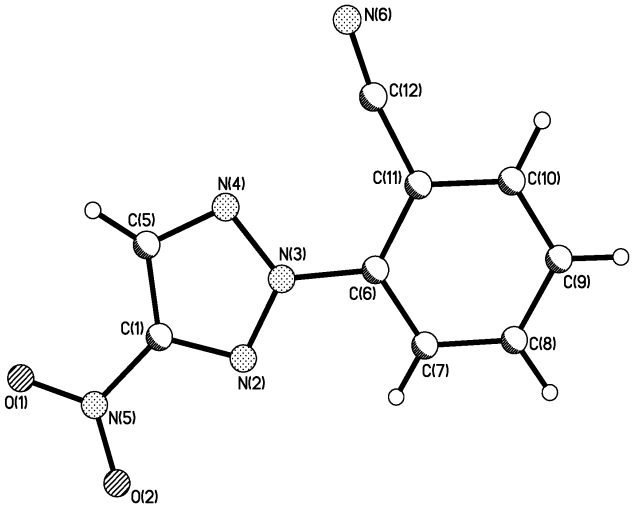


Figure 4. X-ray structure of compound **9**, selected bond lengths (Å) and angles (deg): N(3)-N(4) 1.3396(16), N(2)-N(3) 1.3214(15), C(1)-N(2) 1.3133(18), C(1)-C(5) 1.370(2), N(4)-C(5) 1.319(2), C(7)-C(6)-N(3) 118.49(12), N(2)-N(3)-N(4) 114.88(12), C(5)-N(4)-N(3) 103.75(13), C(1)-N(2)-N(3) 102.62(11), N(6)-C(12)-C(11) 171.50(15).

The reactions of amines with 1,2,3-dithiazole resulting in ring opening and the formation of the cyanoformamidine fragment have been previously described [25,26]. It can be assumed that the use of diamines should results in the formation of the heterocyclic structure. Indeed, the reactions of azo derivatives **5a,d** with ethylenediamine afford previously unknown dihydroimidazoles **10a,b** (Scheme 5).

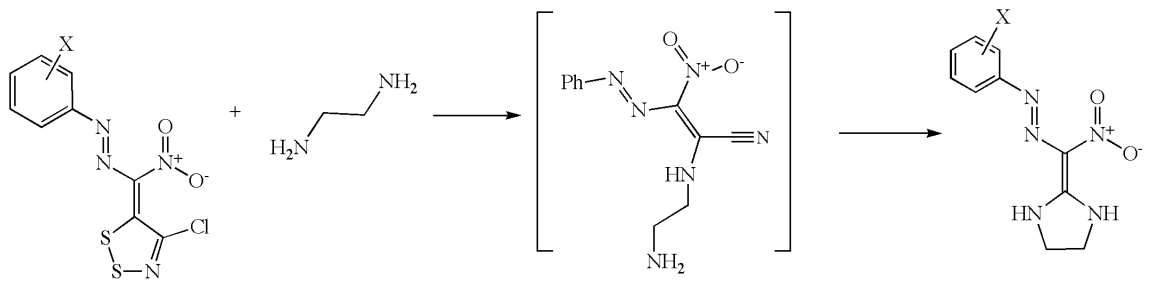
EXPERIMENTAL

^{1}H NMR spectra were recorded on Bruker WM-200 (200 MHz) and Bruker WM-250 (250 MHz) instruments in DMSO-d_6 relatively to HMDS. Mass spectra were obtained on a Varian MAT CH-6 instrument with the direct injection of a sample into the ion source, ionization energy of 70 eV, and an accelerating voltage of 1.75 kV. Melting points were measured on a Boetius heating stage. All reactions mixtures were analyzed and purity of isolated products was monitored by TLC on Silufol UV-254 plates in the dichlormethane:hexane (1:1, vol/vol) system.

General Procedure for the Preparation of Compounds **5a-f**.

Pyridine (0.01 mol, 15 ml) was added dropwise over 3-5 min at a temperature of at most 20 °C to a suspension of nitroformaldehyde phenylhydrazone **2a-f** (0.005 mol) and Appel salt **1** (0.005 mol) in dichloromethane (15 ml). After pyridine was added, the reaction mixture was stirred for another 30 min. The product was

Scheme 5



5a,d **10a,** X= *o*-CN **10b,** X= *p*-F **10a,b**

isolated from the reaction mixture using flash chromatography (silica gel, dichloromethane :petroleum ether (1:2) as an eluent) and crystallized from dichloromethane.

2-{[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-nitro-methyl]-azo}-benzonitrile (**5a**).

This compound has mp 193-194 °C; ^{1}H nmr (DMSO-d_6): δ 7.55 (t, 1H, *J*=7.52 Hz), 7.70 (t, 1H, *J*=7.52 Hz), 7.85 (d, 1H, *J* = 7.28 Hz), 8.15 (d, 1H, *J* = 7.70 Hz); ms: m/z 326 (M^+).

Anal. Calcd. for $C_{10}H_4ClN_5O_2S_2$: C, 36.87; H, 1.24; Cl, 10.88; N, 21.50; S, 19.69. Found: C, 36.91; H, 1.27; Cl, 10.91; N, 21.57; S, 19.75.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-nitro-methyl]-(2-fluoro-phenyl)-diazene (**5b**).

This compound has mp 170-171 °C ; ^{1}H nmr (DMSO-d_6): δ 7.45 (t, 1H, *J*=7.49 Hz), 7.55 (m, 2H), 7.90 (d, 1H, *J*=7.31 Hz); ms: m/z 319(M^+).

Anal. Calcd. for $C_9H_4ClFN_4O_2S_2$: C, 33.91; H, 1.26; Cl, 11.12; N, 17.58; S, 20.12. Found: C, 33.87; H, 1.25; Cl, 11.10; N, 17.57; S, 20.19.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-nitro-methyl]-(2-nitro-phenyl)-diazene (**5c**).

This compound has mp 153-154 °C; ^{1}H nmr (DMSO-d_6): δ 7.65 (t, 1H, *J*=7.54 Hz), 7.80 (m, 2H), 8.05 (d, 1H, *J*=7.61 Hz); ms: m/z 346 (M^+).

Anal. Calcd. for $C_9H_4ClN_5O_4S_2$: C, 31.26; H, 1.17; Cl, 10.25; N, 20.26; S, 18.55. Found: C, 31.29; H, 1.17; Cl, 10.23; N, 20.23; S, 18.59.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-nitro-methyl]-(2-methoxyphenyl)-diazene (**5d**).

This compound has mp 157-158 °C; ^{1}H nmr (DMSO-d_6): δ 4.15 (s, 3H); 7.10 (t, 1H, *J*=7.43 Hz), 7.35 (t, 1H, *J*=7.52 Hz,), 7.55 (d, 1H, *J*=7.28 Hz), 7.90 (d, 1H, *J*=7.32 Hz); ms: m/z 331 (M^+).

Anal. Calcd. for $C_{10}H_7ClN_4O_3S_2$: C, 36.31; H, 2.13; Cl, 10.72; N, 16.94; S, 19.39. Found: C, 36.34; H, 2.14; Cl, 10.69; N, 16.95; S, 19.41.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-nitro-methyl]-(2-methyl-sulfanyl-phenyl)-diazene (**5e**).

This compound has mp 175-176 °C; ^{1}H nmr (DMSO-d_6): δ 3.30 (c, 3H), 7.30 (t, 1H, *J*=7.32 Hz), 7,55 (m, 2H), 7.90 (d, 1H, *J*=7.37 Hz); ms: m/z 347 (M^+).

Anal. Calcd. for $C_{10}H_7ClN_4O_2S_3$: C, 34.63; H, 2.03; Cl, 10.22; N, 16.15; S, 27.74. Found: C, 34.66; H, 2.02; Cl, 10.24; N, 16.11; S, 27.76.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-nitro-methyl]-(2-azi-dophenyl)-diazene (**5f**).

This compound has mp 173-175 °C; ^{1}H nmr (DMSO-d_6): δ 7.31 (m, 1H), 7.57 (m, 2H), 7,90 (m, 1H); ms: m/z 342 (M^+).

Anal. Calcd. for $C_9H_4ClN_7O_2S_2$: C, 31.63; H, 1.18; Cl, 10.37; N, 28.69; S, 18.77. Found: C, 31.65; H, 1.17; Cl, 10.35; N, 28.70; S, 18.76.

Synthesis of Compounds **6** and **7**.

The Appel salt **1** (0.002 mol) was added over 2—3 min in small portions at a temperature of at most 20 °C to a suspension of the starting hydrazone **3a-f** or **4a,b** (0.002 mol) and 2,4,6-collidine (0.004 mol) in dichloromethane (15 ml). The reaction mixture was stirred for another 30 min. The reaction product was isolated from the reaction mixture using flash chromatography (silica gel, dichloromethane:petroleum ether (1:1) as an eluent) and crystallized from dichloromethane.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-(2-nitro-phenyl)-methyl]-(4-nitro-phenyl)-diazene (**6a**).

This compound has mp 157-158 °C; ^{1}H nmr (DMSO-d_6)**:** δ 7.55 (br.m, 1H), 7.80 (br.m, 2H), 8.05 (d, 2H, *J*=7.57 Hz), 8.20 (m, 2H), 8,25 (s, 1H); ms: m/z 422 (M+).

Anal. Calcd. for $C_{15}H_8ClN_5O_4S_2$: C, 42.71; H, 1.91; Cl, 8.40; N, 16.60; S, 15.20. Found: C, 42.74; H, 1.92; Cl, 8.39; N, 16.58; S, 15.24.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-(3-nitro-phenyl)-methyl]-(4-nitro-phenyl)-diazene (**6b**).

This compound has mp 210-212 °C; ^{1}H nmr (DMSO-d_6): δ 7.70 (t, 1H, *J*=7.21 Hz), 7.90 (d, 1H, *J*=7.55 Hz), 8.10 (d, 2H, *J*=7.58 Hz), 8.35 (d, 2H, *J*=7.52 Hz), 8.45 (d, 2H, *J*=7.56 Hz); ms: m/z 422 (M^+).

Anal. Calcd. for $C_{15}H_8ClN_5O_4S_2$: C, 42.71; H, 1.91; Cl, 8.40; N, 16.60; S, 15.20. Found: C, 42.73; H, 1.92; Cl, 8.41; N, 16.61; S, 15.22.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-(5-nitro-furan-2-yl)-methyl]-(4-nitro-phenyl)-diazene (**6c**).

This compound has mp 203-205 °C; ^{1}H nmr (DMSO-d_6): δ 7.35 (d, 1H, *J*=7.57 Hz), 7.95 (d, 1H, *J*=7.76 Hz), 8.15 (d, 2H, *J*=7.13 Hz), 8.20 (d, 2H, *J*=7.47 Hz); ms: m/z 412 (M^+).

Anal. Calcd. for $C_{13}H_6ClN_5O_5S_2$: C, 37.92; H, 1.47; Cl, 8.61; N, 17.01; S, 15.57. Found: C, 37.98; H, 1.50; Cl, 8.55; N, 17.11; S, 15.46.

4-Chloro-5-[4-(4-chlorophenyl)-1,3-thiazol-2-yl]-diazenyl-(4-nitrophenyl)-methyl]-5*H*-1,2,3-dithiazole (**6d**).

This compound has mp 200-202 °C; ^{1}H nmr (DMSO-d_6): δ 7,48 (m, 3H), 7.74 (d, 2H, *J*=8.66 Hz), 7.94 (d, 2H, *J*=8.41 Hz), 8.39 (d, 2H, *J*=8.49 Hz); ms: m/z 496 (M^+).

Anal. Calcd. for $C_{18}H_9Cl_2N_5O_2S_3$: C, 43.73; H, 1.83; N, 14.17; S, 19.46. Found: C, 43.74; H 1.83; N, 14.16; S, 19.48.

4-Chloro-5-[4-(4-bromophenyl)-1,3-thiazol-2-yl]-diazenyl-(4-nitrophenyl)-5*H*-1,2,3-dithiazole (**6e**).

This compound has mp 205-207 °C; ^{1}H nmr (DMSO-d_6): δ 7,61 (d, 3H, *J*=8.06 Hz), 7.74 (m, 2H), 7.85 (m, 1H), 8.01 (d, 1H, *J*=8.66 Hz), 8.32 (d, 1H, *J*=8.36 Hz), 8.39 (d, 1H, *J*=8.21 Hz); ms: m/z 583 (M^+).

*Anal***.** Calcd. for $C_{18}H_9BrClN_5O_2S_3$: C, 40.12; H, 1.68; N, 13.00; S, 17.85. Found: C, 40.13; H, 1.68; N, 13.01; S, 17.86.

4-Chloro-5-[4-(2,4-dichlorophenyl)-1,3-thiazol-2-yl]-diazenyl-(4-nitrophenyl)-methyl]-5*H*-1,2,3-dithiazole (**6f**).

This compound has mp 178-180 °C; ^{1}H nmr (DMSO-d_6): δ 7,38 (t, 1H, *J*=8.13 Hz), 7.55 (d, 1H, *J*=7.07 Hz), 7.74 (d, 1H, *J*=8.57 Hz), 7.86 (s, 1H), 8.01 (s, 1H), 8.35 (m, 3H). ; ms: m/z 530 (M^+).

Anal. Calcd. for $C_{18}H_8Cl_3N_5O_2S$: C, 40.88; H, 1.52; N, 13.24; S, 18.19. Found: C, 40.90; H, 1.52; N, 13.22; S, 18.20.

2-(4-Chloro-[1,2,3]dithiazol-5-ylidene)-2-(2,4-dinitro-phenylazo)-1-(4-fluoro-phenyl)-ethanone (**7a**).

This compound has mp 172-174 °C; ^{1}H nmr (DMSO-d_6): δ 7.40 (m, 2H); 7.65 (m, 1H), 7.85 (d, 1H, *J*=7.47 Hz), 8.10 (br.m, 2H), 8.50 (br.m, 1H); ms: m/z 468 (M^+).

Anal. Calcd. for $C_{16}H_7ClFN_5O_5S_2$: C, 41.08; H, 1.51; Cl, 7.58; N, 14.97; S, 13.71. Found: C, 41.11; H, 1.51; Cl, 7.55; N, 14.96; S, 13.74.

2-(4-Chloro-[1,2,3]dithiazol-5-ylidene)-2-(2,4-dinitro-phenylazo)-1-m-tolyl-ethanone (**7b**).

This compound has mp 164-165 °C; ^{1}H nmr (DMSO-d_6): δ 7.45 (m, 2H), 7.75 (d, 1H, *J*=8.01 Hz), 7.85 (s, 1H), 8.00 (d, 1H, *J*=7.78 Hz), 8.35 (d, 1H, *J*=7.59 Hz), 8.65 (s, 1H); ms: m/z 464 (M^+).

Anal. Calcd. for $C_{17}H_{10}ClN_5O_5S_2$: C, 44.02; H, 2.17; Cl, 7.64; N, 15.10; S, 13.83. Found: C, 44.03; H, 2.17; Cl, 7.65; N, 15.11; S, 13.84.

Crystallographic Data for **5a**.

At 120 K crystals are triclinic, space group *P*-1, a=7.140(4)Å, b=8.003(4)Å, c=11.318(6)Å, α=102.00(1)°, β=97.29(1)°, γ=96.28(1)°, V=621.3(6)Å^3, Z=2, *M*=325.75, D_c= 1.741 gcm^{-3}, μ(Mo-K_α)=0.651 mm^{-1}, F(000)= 328. Intensities of 4806 reflections were measured on a Bruker SMART 1000 CCD diffractometer [λ(Mo-K_α)=0.71072Å, ω scan mode, 2θ<58°], and 3266 independent reflections (Rint=0.0245) were used in the further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2= 0.1575 and GOOF=0.992 for all independent reflections [R_1=0.0577 was calculated against *F* for 2381 observed reflections with *I*>2σ(*I*)]. All calculations were performed using the SHELXTL software [28]. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers 227535.

[(4-Chloro-[1,2,3]dithiazol-5-ylidene)-nitromethyl]-2*H*-1,2,3-benzotriazole (**8**).

The starting azomethylene derivative compound **5f** (50 mg) was dissolved in toluene (1 ml), and the solution was refluxed for 6 h. The reaction mixture was cooled to room temperature, toluene was removed *in vacuo*, and a solid precipitate was recrystallized from a chloroform - hexane mixture; yield 91%, m.p. 88-90 °C; ^{1}H nmr (DMSO-d_6): δ 7.51 (m, 2H), 8.18 (m, 2H); ms: m/z 314.

Anal. Calcd. for $C_9H_4ClN_5O_2S_2$: C, 34.45; H, 1.29; Cl, 11.30; N, 22.32; S, 20.44. Found: C, 34.48; H, 1.29; Cl, 11.29; N, 22.31; S, 20.46.

2-(4-Nitro-2*H*-1,2,3-triazol-2-yl)benzonitrile (**9**).

Compound **5a** (500 mg) was dissolved in DMF (15 ml), and the solution was refluxed for 30 min until the color disappeared. After cooling, the reaction mixture was poured into water and extracted with ethyl acetate. The extract was dried over magnesium sulfate. After distillation, an oily substance was purified on a chromatographic column packed with silica gel using an ethyl acetate:hexane (2 :1) mixture as an eluent and crystallized from methanol; yield 48%, m.p. 97-98 °C; ^{1}H nmr (DMSO-d_6): δ 7.79 (m, 1H), 7.98 (m, 1H), 8.17 (m, 2H), 9.12 (s, 1H); ms: m/z 215.

Anal. Calcd. for $C_9H_5N_5O_2$: C, 50.24; H, 2.34; N, 32.55. Found: C, 50.26; H, 2.34; N, 32.53.

Crystallograhic Data for **9**.

At 293 K crystals are monoclinic, space group *P*-2, a=11.323(4)Å, b=10.911(4)Å, c=7.7527(6)Å, α=90.00(1)°, β=90.49(1)°, γ=90.00(1)°, V=957.8(3)Å^3, Z=4, *M*=215.18, D_c= 1.492 gcm^{-3}, μ(Mo-K_α)=0.113 mm^{-1}. Intensities of 4806 reflections were measured with a Bruker SMART 1000 CCD diffractometre [λ(Mo-K_α)=0.71072Å, ω-scan, 2θ<58°], and 3266 independent reflections (Rint=0.0245) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2= 0.1575 and GOF=0.992 for all independent reflections [R_1=0.0577 was calculated against *F* for 2381 observed reflections with *I*>2σ(*I*)]. All calculations were performed using SHELXTL software [28]. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers 227536.

General Procedure for Synthesis of Dihydroimidazoles **10a,b**.

A mixture of the initial azomethylene derivative **5** (1.4 mmol) and ethylenediamine (5 ml) was stirred for 30 min, poured into water (150 ml), and extracted with ethyl acetate. The extract was dried over magnesium sulfate, ethyl acetate was removed *in vacuo*, and the oily residue was purified on a chlromatographic column packed with silica gel using ethyl acetate:hexane (1:1) as an eluent, crystallized from methanol.

2-{[Imidazolidin-2-ylidene(nitro)methyl]diazenyl}benzonitrile (**10a**).

This compound was obtained in 53% yield, m.p. 226 – 228 °C (decomp.); ^{1}H nmr (DMSO-d_6): δ 3.85 (s, 4H), 7.39 (m, 1H), 7.73 (m, 2H), 7.88 (m, 1H), 9.81 (s, 2H); ^{13}C nmr (50 MHz, DMSO-d_6) δ 43.10, 108.04, 115.00, 115.88, 117.99, 127.35, 132.84, 134.14, 153.45, 154.55; ms: m/z 258.

Anal. Calcd. for $C_{11}H_{10}N_6O_2$: C, 51.16; H, 3.90; N, 32.54. Found: C, 51.19; H, 3.90; N, 32.53.

2-[[(4-Fluorophenyl)diazenyl](nitro)methylene]imidazolidine (**10b**).

This compound was obtained in 55% yield, m.p. 132 – 134 °C; ^{1}H nmr (DMSO-d_6): δ 3.79 (s, 4H), 7.27 (m, 2H), 7.76 (m, 2H), 9.62 (s, 2H); ms: m/z 251 (M^+).

Anal. Calcd. for $C_{10}H_{10}FN_5O_2$: C, 47.81; H, 4.01; N, 27.88. Found: C, 47.83; H, 4.02; N, 27.87.

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