SYNTHESIS AND STRUCTURE OF 1-METHYL-2,3-DIHYDRO-1,2,4-TRIAZOLIUM SALTS AND THEIR FREE BASES

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1-Methyl-2,3-dihydro-1,2,4-triazolium iodides can be obtained by reacting methylhydrazones with S-methylthioamide hydriodides, by condensing 2-methylamidrazone hydriodides with aldehydes and ketones, or by reacting methyl iodide with 1-alkylidene(or arylidene)benzamidrazones. In solutions these salts are capable of undergoing tautomerism to 1-alkylidene(or arylidene)-2-methylamidrazone hydriodides. The influence of the structural factors on the position of the tautomeric equilibrium has been studied. The free bases obtained by neutralization of the respective salts by an alkali metal hydroxide are heretofore undescribed 1-alkylidene(or arylidene)-2-methylhydrazidoimines or 4-triazolines, depending on their structure. Under the action of oxygen, these compounds are readily oxidized to substituted 1-methyl-1,2,4-triazoles with heating.

Hydrazones having functional substituents in the hydrazine fragment are capable, in principle, of ring–chain transformations as a result of intramolecular nucleophilic attack at the C=N bond [1]. While in the case of acylhydrazones, the linear form is the only form, semicarbazones [2] and thiosemicarbazones [3] can undergo cyclization in an acid medium, and thioacylhydrazones have a tendency to exist in the form of a cyclic tautomer [4, 5]. According to the data in [6], salts of 1-alkylidene(arylidene)amidrazones, which may be considered nitrogenous analogs of acylhydrazones, are capable of ring–chain tautomerism in solutions. In this case, the values of the thermodynamic stability of the linear and cyclic forms are close only when there is a substitutent on the nitrogen atom in position 2 [7, 8].

In the present work we studied the influence of structural factors on the position of the tautomeric equilibrium between 1-alkylidene(or arylidene)-2-methylamidrazone hydriodide

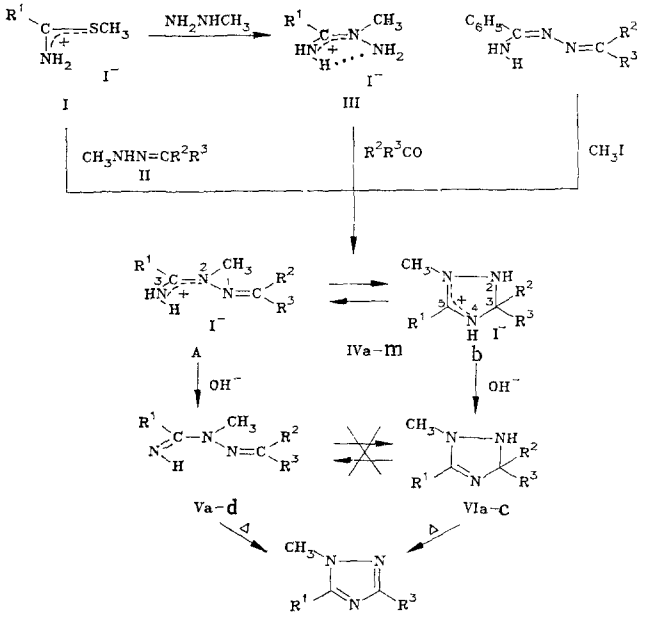

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TABLE 1. Physicochemical Constants of Compounds IVa-m

Compound	R^1	R^2	R^3	mp, *°C	Found, % N	Found, % I	Empirical formula	Calculated, % N	Calculated, % I	Yield, %
IVa	CH_3	H	CH_3	192—193	17,4	52,7	$C_5H_{11}N_3 \cdot HI$	17,4	52,7	70
IVb	CH_3	CH_3	CH_3	128—130	16,6	49,8	$C_6H_{13}N_3 \cdot HI$	16,5	49,8	90
IVc	CH_3	CH_3	$C(CH_3)_3$	210—213	14,2	42,7	$C_9H_{19}N_3 \cdot HI$	14,1	42,7	85
IVd	CH_3	H	C_6H_5	245—247	13,8	41,8	$C_{10}H_{13}N_3 \cdot HI$	13,9	41,9	95
IVe	CH_3	CH_3	C_6H_5	161—162	13,3	40,1	$C_{11}H_{15}N_3 \cdot HI$	13,2	40,0	88
IVf	CH_3	CH_3	p-$NH_2C_6H_4$	148—149	17,0	38,1	$C_{11}H_{16}N_4 \cdot HI$	16,9	38,2	35
IVg	CH_3	CH_3	p-$CH_3OC_6H_4$	143—144	12,3	36,6	$C_{12}H_{17}N_3O \cdot HI$	12,1	36,6	85
IVh	CH_3	CH_3	p-ClC_6H_4	194—195	11,9	36,2	$C_{11}H_{14}ClN_3 \cdot HI$	12,0	36,1	89
IVi	CH_3	CH_3	m-ClC_6H_4	148—149	12,1	36,1	$C_{11}H_{14}ClN_3 \cdot HI$	12,0	36,1	82
IVj	C_6H_5	H	CH_3	202—203	14,0	41,8	$C_{10}H_{13}N_3 \cdot HI$	13,9	41,9	65
IVk	C_6H_5	CH_3	CH_3	198—201	13,3	40,1	$C_{11}H_{15}N_3 \cdot HI$	13,2	40,0	92
IVl	C_6H_5	CH_3	$C(CH_3)_3$	187—189	11,6	35,3	$C_{14}H_{21}N_3 \cdot HI$	11,7	35,4	87
IVm	C_6H_5	H	C_6H_5	211—213	11,7	34,7	$C_{15}H_{15}N_3 \cdot HI$	11,5	34,8	90

*The salts were crystallized from the following solvents: IVa, d, e, and k from methanol; IVb from acetone; IVc and IVc and l from 3:1 methyl acetate—acetonitrile; IVf and m from acetonitrile; IVg and h from 3:1 ethyl acetate—methanol; IVi from 1:1 ethyl acetate—acetonitrile, IVj from 5:1 ethyl acetate—methanol.

and 1, 3, 5-trisubstituted 2,3-dihydro-1,2,4-triazolium iodide (IV, A ⇄ IV, B, see the scheme), as well as the structures of the free bases obtained by the alkaline treatment of salts IV.

Compounds IVa-m can be obtained by reacting S-methylthioamide hydriodides (I) with methylhydrazones (II, method A)* or by condensing 2-methylamidrazonium iodides (III [6]) with carbonyl compounds (method B). The low stability of acetaldehyde methylhdrazone makes method B preferable for the synthesis of compounds IVa and j, both methods are approximately equivalent for compounds IVd and m, and in the remaining cases, method A has clear preference. Compounds IVj-m were also synthesized by the iodomethylation of alkylidene derivatives of benzamidrazone [9] (method C). The unique alkylation at the nitrogen atom in the latter is attributed to the presence in them of an intramolecular hydrogen bond. Table 1 presents the characteristics and yields of compounds IVa-m obtained according to method A.

In the crystalline state compounds IVa-m exist in a simple form (A or B), as is indicated by the data from the ^1H and ^{13}C NMR spectra for freshly prepared solutions, in which there was only one set of resonance signals (Tables 2 and 3). The criteria for the assignment of the signals were previously considered in [7, 8] and will not be discussed here.

As is seen from the data in Table 2, the position of the A ⇄ B tautomeric equilibrium established in the solution after approximately 3 days varies over a broad range. In the case of benzamidrazone derivatives IVj-l as opposed to the corresponding acetamidrazone derivatives IVa-c, there is a shift toward the cyclic form. This also occurs when the volume of the substituents in the alkylidene fragment is increased, apparently due to the greater sensitivity of the linear tautomer to the increase in the total steric stresses in the molecule. The aromatic substituent R^3 stabilizes the linear form owing to its conjugation with the C=N bond. This is indicated by the satisfactory correlation of the logarithms of the tautomeric equilibrium constants ($K_T = [A]/[B]$) for compound IVe-i with the σ constants of the substituents: $\log K_T = (-0.8 \pm 0.02) + (1.13 \pm 0.006)\sigma$ ($n = 5$, $r = 0.98$).†

The tendencies noted in the variation of the position of the ring-chain equilibrium are similar to those for the closely related 2-methylthiosemicarbazone S,S,S-trioxides [10].

When salts IV are treated under alkaline conditions, the free bases, which are also capable, in principle, of ring—chain tautomerism, form quantitatively. It was found, however, that neutralization of the salts having a linearly structure of type A in the crys-

*The reaction of S-methylthioacetamide hydriodide with p-nitroacetophenone methylhydrazone produced compound IVf owing to the reduction of the nitro group by the methanethiol released during the reaction.

†In the derivation of the equation, the content of form B for compound IVi was assumed to be equal to 3%.

TABLE 2. PMR Spectra and Tautomeric Composition of Compounds IVa-m, ppm (spin–spin coupling constants, Hz)

Compound	Form in crystalline state	Form A					Form B					% of form A
		R^1	R^2	R^3	CH_3N	NH_2	R^1	R^2	R^3	CH_3N	NH	
IVa	A	2,44 (E), 2,41 (Z)	7,80 q (5,0, E); 7,77 q (5,5, Z)	2,09 d (5,0, E); 2,03 d (5,5, Z)	3,37*	9,09, 9,53 (E); 9,06, 9,65 (Z)	2,30	5,19 q (6,0)	1,27 d (6,0)	3,23	6,02; 10,13	59 (E : Z = =9 : 1)
IVb	B	2,59	2,13	2,06	3,43	8,10; 8,98	2,42	1,48		3,35	6,87; 10,46	31
IVc	B	2,39	1,95	1,19	3,27	†	2,31	1,42	0,89	3,22	6,70; 10,03	11
IVd	A	2,53	8,49	7,5—8,2 m	3,55	9,37; 9,75	—	—	—	—	—	>97
IVe	A	2,48	2,41	7,3—8,1 m	3,43	8,98	2,37	1,77	7,3–8,1 m	3,29	†	80
IVf	A	2,15	2,04	7,5—7,7 m, 6,9 n. s	2,95	9,11	—	—	—	—	—	>97
IVg	A	2,63	2,46	7,0—8,0 m; 3,89	3,55	8,37; 9,15	2,27	1,84	7,0—8,0 m; 3,79 (*n*-OCH_3)	3,43	†	94
IVh	A	2,52	2,33	7,5—8,0 m	3,45	7,80	2,28	1,80	7,5—8,0 m	3,31	†	78
IVi	A	2,69	22,56	7,5—8,1 m	3,62	7,70	2,51	1,91	7,5–8,1	3,45	†	70
IVj	B	7,6—7,9 m	7,94 q (5,2)	2,17 d (5,2)	3,25	9,65; 9,90	7,6—7,9 m	5,42 q (5,7)	1,42 d (5,7)	3,31	6,63; 10,70	30
IVk	B	7,4—7,9 m	2,21	2,11	3,15	8,55; 9,31	7,4—7,9 m	1,56		3,31	7,05; 10,85	18
IVl	B	7,7—7,8 m	2,11	1,26	3,12	†	7,7—7,8 m	1,58	1,02	3,29	7,03; 10,55	4
IVm	A	7,4—8,3 m	8,61	7,4—8,3 m	3,41	8,46; 8,51	—	—	—	—	—	>97

*The signals of the Z and E isomers overlap.
†Not localized.

TABLE 3. Carbon-13 NMR Spectra of Compounds IVa, j, and m (DMSO-d_6) and Compounds Va, Vd, and VIc ($CDCl_3$)

Compound	Form A			Form B			Other signals	% of form A
	$C{=}N_{(1)}$	$C{=}N_{(2)}$	$CH_3N_{(2)}$	C-5	C-3	$CH_3N_{(1)}$		
IVa	152,6 (E), 151,3 (Z)	163,3 (E), 165,4 (Z)	34,0 (E), 33,0 (Z)	160,6	69,1	34,7	18,5 (A_E, CH_3); 17,8 (A_Z, CH_3); 18,8 (A_E, $CH_3C{=}N_{(1)}$); 11,5 (A_Z, $CH_3C{=}N_{(1)}$); 20,7 ($CH_3C_{(5)}$); 11,0 ($CH_3C_{(3)}$)	59
IVj	154,4	163,3	35,9	159,9	69,7	36,3	19,0 (A, $\mathbf{CH_3}C{=}N_{(1)}$); 20,1 (E, $CH_3C_{(3)}$); 120,9; 128,0; 128,7; 129,4; 131,6; 132,6; 133,9 (Carom)	30
IVm	151,4	163,8	36,5	—	—	—	132,7; 132,0; 131,7; 131,6; 129,1; 128,8; 128,2; 128,1 (Carom)	100
Va	133,6 (E), 137,9 (Z); $^1J_{CH}$ 158,4; $^2J_{CCH}$ 6,9	165,6 (E)*	28,1 (E), 26,6 (Z)	—	—	—	18,3 (A_E, CH_3); 22,7 (A_E, $CH_3C{=}N_{(1)}$); 20,9 (A_Z, $CH_3C{=}N_{(1)}$)	
Vd	126,5; $^1J_{CH}$ 160,0	167,2	29,3; $^1J_{CH}$ 138,7	—	—	—	137,0; 134,8; 134,4; 128,0; 127,6; 127,4; 127,2; 126,8 (Carom)	
VIc	—	—	—	164,5	84,6	40,7	27,9	

*The low intensity of the signal of the Z isomer requires a large number of scans.

talline state (for example, IVa, d, e, and m), results in the formation of the corresponding alkylidene derivatives of acetic acid 2-methylhydrazidoimines (Va-d), whereas salts IVb, j, and k, which exist in the form of substituted 2,3-dihydro-1,2,4-triazolium iodides (B), give 4-triazolines (VIa-c, Tables 3 and 4).

Compounds Va-d exist in a configuration with a syn arrangement of the $N_{(1)}$ and $N_{(3)}$ nitrogen atoms, which is stabilized by an intramolecular hydrogen bond. This is evinced by the weak temperature and concentration dependences of the chemical shift of the signal for NH in the PMR spectra, as well as the presence of a broad band at 3250 cm^{-1} in the IR spectra.

At room temperature a V $\rightleftarrows$ VI tautomeric equilibrium is not realized in solution, and we consequently have a method for the synthesis of the previously unknown classes of compounds V and VI.

Compounds V and VI are oxidized slowly in air and quantitatively with heating for several hours to substituted 1-methyl-1,2,4-triazoles (see Experimental). The aromatization of the alkylidene hydrazidoimine derivatives of type V involves the intermediate formation of cyclic form VI, whose signals were detected in the PMR spectra. The aldo derivatives (Va, Vb, and VIb) are oxidized with the elimination of a water molecule, and the acetone and acetophenone derivatives (Vc, VIa, and VIc) are oxidized with the elimination of methanol. It is interesting to note that it is not possible to obtain the free base from the pinacoline derivative (IVc), apparently due to the steric stresses in the cyclic molecule, which cause rapid aromatization with the elimination of tert-butanol and the formation of 1,3,5-trimethyl-1,2,4-triazole. The accessibility of the original compounds, as well as the smooth course of the aforementioned processes, makes them promising for the synthesis of 1-alkyl-1,2,4-trizoles (see, for example, [11]).

We also considered the iodomethylation of free bases V and VI, which was of additional interest in connection with the possibility of the synthesis of salts of type VI with a great degree of substitution and the consequent possible expansion of the group of tautomeric compounds investigated. Derivatives Vd and VIa were selected as the objects of investigation.

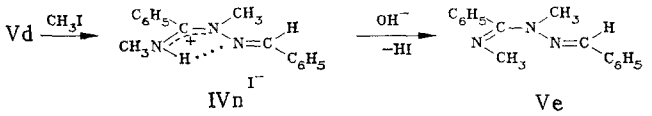
Following the alkylation of benzoic acid 1-benzylidene-2-methylhydrazidoimine (Vd) by methyl iodide in benzene, the precipitate contained not only the expected 1-benzylidene-2,3-dimethylbenzamidrazone hydriodide (IVn), but also iodide IVm. The original compound Vd,

TABLE 4. Physicochemical Constants of Compounds Va-d and VIa-c

Compound*	R¹	R²	R³	PMR spectrum (CCl_4), ppm (spin–spin coupling constant, Hz)					Found, %			Empirical formula	Calculated, %		
				R¹	R²	R³	NCH_3	NH	C	H	N		C	H	N
Va	CH_3	H	CH_3	2,21 (E); 2,24 (Z); E : Z = 9 : 1	6,71 q (5,0, E); 6,91 q (5,0, Z)	1,93 d (5,0, E); 2,0 d (5,0, Z)	3,31 (E); 3,24 (Z)	6,36 (E) (Z) not localized	53,2	9,8	37,2	$C_5H_{11}N_3$	53,1	9,8	37,1
Vb	CH_3	H	C_6H_5	2,39	7,38	7,2–7,6 m	3,43	6,85	68,5	7,4	24,0	$C_{10}H_{13}N_3$	68,5	7,5	24,0
Vc	CH_3	CH_3	C_6H_5	2,21	2,03	7,1–7,8 m	3,06	6,27	69,9	7,9	22,3	$C_{11}H_{15}N_3$	69,8	8,0	22,2
Vd	C_6H_5	H	C_6H_5	7,0–7,3 m	7,35	7,0–7,3 m	3,39	6,80	75,8	6,5	17,9	$C_{15}H_{15}N_3$	75,9	6,4	17,7
VIa	CH_3	CH_3	CH_3	1,82	1,19		2,80	3,77	56,6	10,2	33,1	$C_6H_{13}N_3$	56,7	10,3	33,0
VIb	C_6H_5	H	CH_3	7,3–7,8 m	5,07 q (6,0)	1,25 d (6,0)	2,79	4,20	68,4	7,4	24,1	$C_{10}H_{13}N_3$	68,5	7,5	24,0
VIc	C_6H_5	CH_3	CH_3	7,2–7,7 m	1,33		2,81	4,40	69,6	8,0	22,1	$C_{11}H_{15}N_3$	69,8	8,0	22,2

*The bp for Va is 58°C (5.3 hPa), and the bp for VIa is 48°C (9.0 hPa).

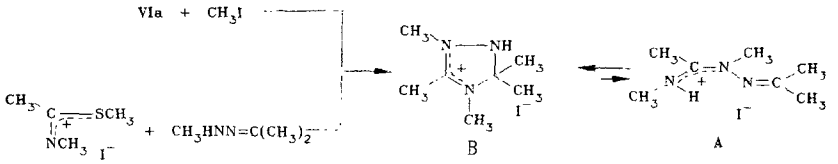
being a strong base, clearly converts some of the IVn into benzoic acid 1-benzylidene-2,3-dimethylhydrazidoimine (Ve), which is soluble in benzene (see Experimental).



IVn Ve

Compound Ve has a fixed hydrazidoimine form and is not capable of undergoing a transition to a ring, unlike IVn. However, IVn, which was characterized in the form of the picrate, also exists exclusive in the form of the linear tautomer. Thus, the introduction of an additional methyl group into the molecule in comparison to IVm is insufficient for the appearance of the cyclic tautomer in equilibrium.

The alkylation of 1,3,3,5-tetramethyl-2,3-dihydro-1,2,4-triazole (VIa) occurs exclusively at the nitrogen atom in position 4. The formation of iodide IVm was proved by a back synthesis, i.e., by reaction S,N-dimethylthioacetamide hydriodide (I) with acetone methylhydrazone (see Experimental).



B A

IVo

Compound IVo exists in solution entirely as a cyclic tautomer. The shift of the equilibrium in the direction of form B in comparison to compound IVb confirms the widely known conclusion [1] regarding the steric cooperation of cyclic form.

Thus, according to their ability to undergo ring-chain tautomerism, the salts of the 1-alkylidene (or arylidene) derivatives of amidrazones occupy an intermediate position between acyl and thiocylhydrazones, and variation of the electronic and steric properties of the substituents alters the tautomeric equilibrium constant over a broad range. In addition, on the basis of the readily accessible salts of type IV there is a possibility for the synthesis of such previously unknown compounds as derivatives of hydrazidoimines and 4-triazolines, which, in turn, can be used to obtain substituted 1-alkyl-1,2,4-triazoles.

EXPERIMENTAL

The IR spectra were recorded on a Specord 751R instrument in the 4000-500-cm^{-1} region in KBr tablets and for 1% solutions in $CHCl_3$. The PMR spectra were obtained on a Tesla BS-497 spectrometer (100 MHz) for 10% solutions with HMDS as an internal reference. The quantitative determination of the tautomeric composition was carried out by PMR for equilibrium (holding at room temperature for 3 days) solutions in DMSO-d_6 on the basis of two measurements by electronic integration of suitable indicator signals. The error in a determination was ±3%. The ^{13}C NMR spectra of the individual compounds were recorded on a CFT-20 spectrometer (20 MHz) for saturated solutions in DMSO-d_6 and $CDCl_3$ under conditions of complete suppression of the ^{13}C-H spin-spin interaction and under monresonance conditions.

S-Methylthioacet-, S,N-dimethylthioacet-, and S-methylthiobenzamide hydriodide (I) were synthesized according to [12, 13], the methylhydrazones of monocarbonyl compounds (II) were obtained according to [14], and 2-methylacet- and 2-methylbenzamidrazone hydriodide (III) were obtained according to [9].

Compounds IVa-ℓ were synthesized according to [7, 8] (method A) and [9] (method B). The iodomethylation of the benzamidrazone derivatives [7] (method C) was carried out by adding equimolar quantities of methyl iodide to a benzene solution of the corresponding free base. After 24 h the crystals were filtered out and recrystallized (Table 1).

Free Bases V and VI. A 50-mmole portion of salt IV in 15 ml of methanol was given an addition of 50 mmole of sodium methoxide in 30 ml of methanol in the cold, the solvent was removed in a vacuum, and the residue was extracted by benzene. The benzene extract was dried by $MgSO_4$, the benzene was removed in a vacuum, and the residue was distilled or re-

crystallized from hexane (Table 4). Analytically pure preparations were obtained in the form of viscous oils.

The heating of compounds V and VI at 100°C for 4 h gives 1-methyl-1,2,4-triazoles (according to the PMR data). Compounds Va and VIa give, 1,3,5-trimethyl-1,2,4-triazole [15], Vb and c give 1,5-dimethyl-3-phenyl-1,2,4-triazole [16, 17], VIb and c give 1,3-dimethyl-5-phenyl-1,2,4-triazole [16, 17], and Vd gives 1-methyl-3,5-diphenyl-1,2,4-triazole [17].

Alkylation of Benzoic Acid 1-Benzylidene-2-methylhydrazidoimine (Vd). A 1.2-g portion (5 mmole) of Vd in 50 ml of benzene was given an addition of 0.8 g (.55 mmole) of methyl iodide. After 24 h the precipitate was filtered out, the filtrate was evaporated in a vacuum, and the remaining oil was purified in a column with Al_2O_3 (the eluent was a 1:3 methanol—chloroform mixture), R_f 0.75. The yield of benzoic acid 1-benylidene-2,3-methylhydrazidoimine (Ve) was 15%. Found: N, 16.8%. Calculated for $Z_{16}H_{17}N_3$: N, 16.7%. IR spectrum (CCl_4): 1620 cm^{-1} (C=N). PMR spectrum ($CDCl_3$): 2.96 (s, 3H, $CH_3N_{(3)}$), 3.49 (s, 3H, $CH_3N_{(2)}$), 7.49 (s, 1H, $HC=N_{(1)}$), 7.1-7.4 ppm (m, 10 H, H_{arom}). It was not possible to separate hydroiodides IVm and IVn by recrystallization; therefore, IVn was isolated in the form of the picrate. The pricrate was obtained by applying an excess of a saturated methanol solution of picric acid to the free base. The yield was quantitative, and the mp 61°C (from methanol). Found: N, 17.7%. Calculated for $C_{22}H_{20}N_6O_7$: N, 17.5%. PMR spectrum (DMSO-d_6): 2.85 (d, 5.0 Hz, 1H, $CH_3N_{(3)}$, 3.30 (s, 3H, $CH_3N_{(2)}$), 8.57 (s, 1H, $HC=N_{(1)}$), 7.5-8.2 (m, 10 H, H_{arom}), 10.16 ppm (q, 5.0 Hz, 1H, $N_{(3)}H$).

1,3,3,4,5-Pentamethyl-2,3-dihydro-1,2,4-triazolium Iodide (IVo) was synthesized with a practically quantitative yield by applying a small excess of methyl iodide to a benzene solution of free base VIa. The salt was separated in the form of an oil and was converted into the picrate to obtain an analytically pure preparation. The mp was 129-131°C (from methanol). Found: 22.7%. Calculated for $C_{13}H_{18}N_6O_7$: N, 22.7%. PMR spectrum (DMSO-d_6): 1.46 [s, 6H, $(CH_3)_2C_{(3)}$], 3.08 (s, 3H, CH_3N), 6.61 (br. s, 1H, NH), 8.62 ppm (s, 2H, H_{arom}). An identical compound was obtained by reacting S,N-dimethylthioacetamide hydriodide with acetone methylhydrazone.

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