Chemistry of Heterocyclic Compounds, Vol. 41, No. 1, 2005

SYNTHETIC ROUTES TOWARDS TETRAZOLIUM AND TRIAZOLIUM DINITROMETHYLIDES

A. R. Katritzky[1], G. L. Sommen[1], A. V. Gromova[1], R. M. Witek[1], P. J. Steel[2], and R. Damavarapu[3]

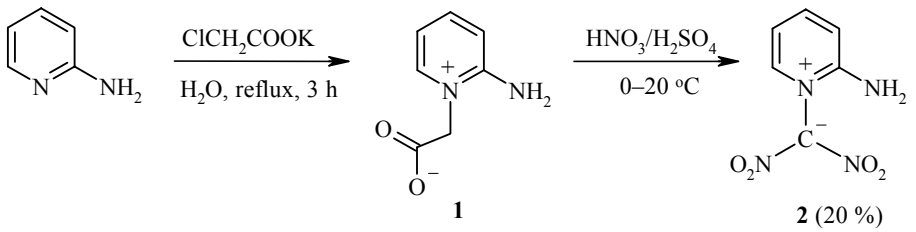
Tetrazolium-5-dinitromethylide sodium salt has been prepared (91%) by cyclization of 1-amino-1-hydrazino-2,2-dinitroethene with nitrous acid in water. 5-Imino-1-(hydroxyiminonitromethyl) derivatives were obtained by nitration of 2-(5-amino-1,3-dimethyl-1H-1,2,4-triazol-4-ium-4-yl)- and 2-(5-amino-4-methyl-1H-tetrazolium-1-yl)acetate complex salts. Treatment of 4-methyl-1-(2-oxopropyl)-1-tetrazolium methylsulfate with nitric and sulfuric acid gave methyl (3-nitro-1,2,4-oxadiazol-5-yl)amine (27%) probably via dinitromethylide followed by cyclization and loss of nitrogen.

Keywords: nitrolic acid, oxadiazole, tetrazolium-5-dinitromethylide sodium salt, X-Ray structure.

Polynitroaromatics are valuable to the pharmaceutical industry as nitrogen-containing synthetic intermediates and important as energetic compounds for use in propellants and explosives [1]. A focus of recent interest in new energetic compounds has been the synthesis of azaheterocycles polynitrated in a side chain possessing high performance and low sensitivity to friction and impact [2-4]. Known classes include 5-(dinitromethyl)tetrazoles [4, 5], 2-aminopyridinium dinitromethylides [6, 7], and 1,1-diamino-2,2-dinitroethane derivatives [3].

Pyridinium dinitromethylides including 2-amino derivative **2** have been obtained by nitration of N-ethanoic acid derivatives of aromatic N-heterocycles [6, 7] (Scheme 1).

Scheme 1

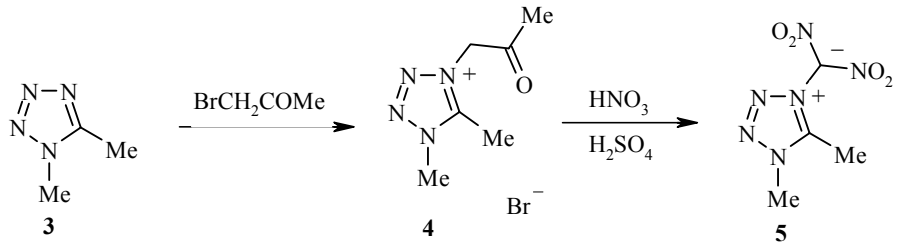


Although aminotriazolium dinitromethylides are apparently unknown, 1-methyltetrazolium dinitromethylide **5** has been prepared by nitration of 1,5-dimethyl-4-acetonyltetrazolium bromide (**4**) [6], itself made by N-acetonylation [8] of 1,5-dimethyltetrazole **3** (Scheme 2).

---

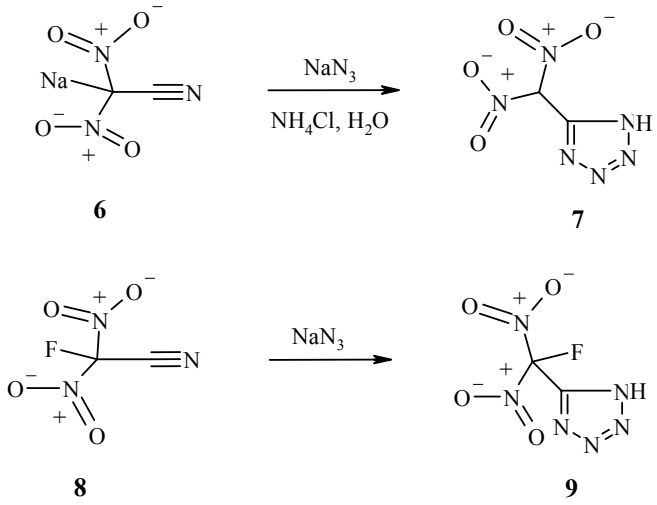
[1] Center for Heterocyclic Compounds, University of Florida, Department of Chemistry, Gainesville, Florida 32611-7200, USA; e-mail: Katritzky@chem.ufl.edu. [2] Department of Chemistry, University of Canterbury, Christchurch, New Zealand. [3] US Army ARDEC, Picatinny Arsenal, USA. Published in Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 127-134, January, 2005. Original article submitted October 4, 2004.

Scheme 2



5-(Dinitromethyl)-1H-tetrazoles have been prepared: i) from the sodium salt of dinitroacetonitrile (**6**) in two steps involving nucleophilic attack of the azide ion on the carbon atom of the nitrile group (8-12%) followed by ring closure to give 5-dinitromethyl-1H-tetrazole (**7**) with 8% yield (Scheme 3) [9]; and also by ii) 1,3-dipolar addition of fluorodinitroacetonitrile (**8**) with sodium azide providing 5-[fluoro(dinitro)methyl]-1H-tetrazole (**9**) with 85% yield [4].

Scheme 3



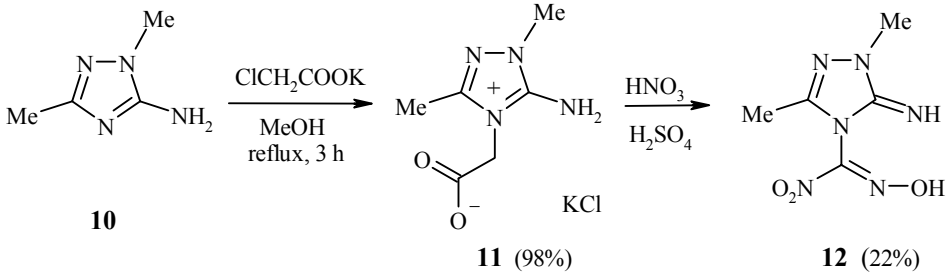
As part of our broader studies on the nitration of heterocycles [10-13], we have previously prepared polynitroimidazoles [14] and trinitroazetidine [15]. In the area of energetic materials, we now report the results of our investigation on new synthetic routes to tetrazolium and triazolium dinitromethylides.

RESULTS AND DISCUSSION

2-Aminopyridinium-1-dinitromethylide (**2)** [7] was prepared (20%) by a modification of the literature method [16] (Scheme 1): betaine **1** was nitrated at 0-20°C avoiding the extra step for preparation of 2-oxo-2,3-dihydro-1H-imidazo[1,2-*a*]pyridin-4-ium chloride. Spectral data and mp of **2** were in agreement with the literature data [7].

5-Amino-1,3-dimethyl-1H-triazole (**10)** with potassium chloroacetate gave salt **11** (98%) (Scheme 4); structure **11** was supported by CHN elemental analysis, by a singlet at 3.69 ppm for two protons (NC$\underline{H}_2$CO) in the ^{1}H NMR spectrum, and by the appearance of two new signals at 45.3 (N$\underline{C}$H$_2$CO) and 168.5 ppm ($\underline{C}$O) in the ^{13}C NMR spectrum. However, treatment of compound **11** with HNO_3–H_2SO_4 gave nitrolic acid **12**.

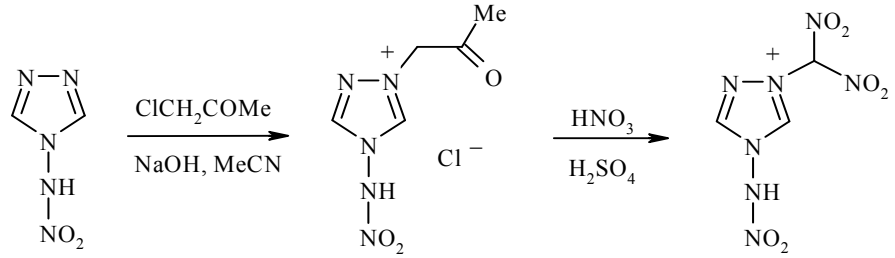
Scheme 4



10 **11** (98%) **12** (22%)

Prolonged heating (at 60°C in acetonitrile for 7 days) of 4-nitroamino-1,2,4-triazole (**13**) with chloroacetone and NaOH provided compound **14** (46%) (Scheme 5). Nitration of **14** with HNO_3–H_2SO_4 from 0-20°C gave dinitromethylide **15** with peaks at 8.77 (1H, s), 8.22 (1H, s), and 7.98 ppm (1H, s) in the ^{1}H NMR spectrum, and the signals in the ^{13}C NMR spectrum were seen at 153.9, 145.3, and 106.1 ppm. Although neither methyl protons nor carbonyl and methyl carbons of acetic acid were observed in the ^{1}H and ^{13}C NMR spectra, elemental analyses of compound **15** correspond to the acetic acid salt. Due to the instability of dinitromethylide **15**, HRMS failed to provide useful data concerning the proper structural assignment.

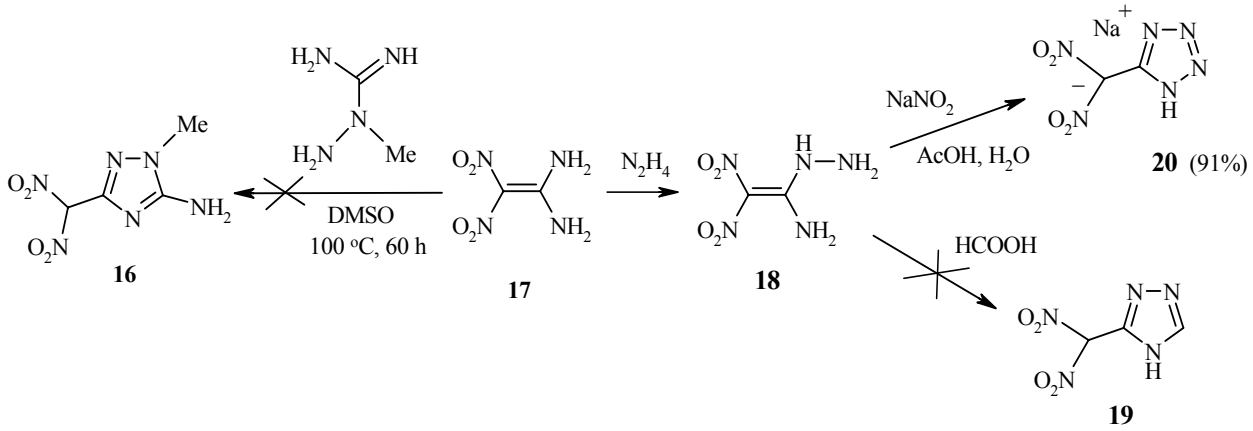
Scheme 5



13 **14** (46%) **15** (17%)

Transamination of 1,1-diamino-2,2-dinitroethene (**17**) with hydrazine hydrate gave aminohydrazine **18** [3]. Attempted reactions of this compound with formic acid to provide 3-(dinitromethyl)-4H-1,2,4-triazole (**19**) failed (Scheme 6). However, its reaction with sodium nitrite in acetic acid and water provided 1-tetrazolium-5-dinitromethylide sodium salt (**20**) in 91% yield.

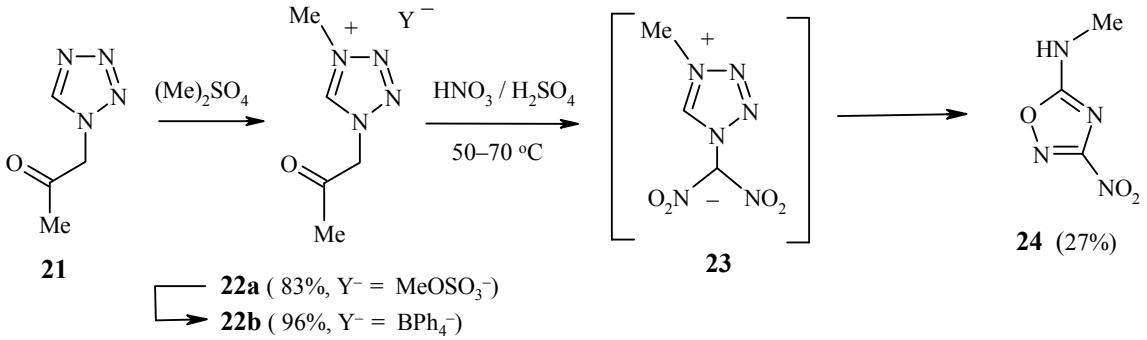
Scheme 6



16 **17** **18** **20** (91%) **19**

Attempted nitration of tetrazolium methylsulfate **22a** with HNO_3–H_2SO_4 at 0-20°C failed to give 4-methyl-1-tetrazolium-1-dinitromethylide (**23**) (Scheme 7). However, heating the reaction mixture at 50-70°C gave an unexpected product characterized by CHN and X-ray structure analysis as oxadiazole **24**, a product of cyclization and loss of nitrogen from dinitromethylide **23**.

Scheme 7



Compound **24** exists in two crystalline modifications (blocks and plates). X-Ray crystal structure determinations were carried out on both forms, which were found to have the same basic structure. This is shown in Fig. 1 and is a disubstituted 1,2,4-oxadiazole. Because of the unexpected structure of this reaction product, the identity (C, N or O) of all non-hydrogen atoms was carefully determined by separate refinement of all atom types for each of the individual atoms in the structure. The two polymorphs crystallize in the monoclinic space groups $P2_1/c$ (blocks) and $C2/c$ (plates). They differ only in that in the plate form the methyl group is disordered over two conformations and the molecular packings in the solid state are somewhat different.

Reaction of 5-amino-1-methyl-1H-tetrazole (**25**) with potassium chloroacetate at reflux for 3 h in water gave betaine **26** in 95% yield. Instead of 5-amino-4-methyl-1H-tetrazolium-1-dinitromethylide, nitration of betaine **26** with HNO_3/H_2SO_4 at 0-20°C gave nitrolic acid **27** as evidenced by CHN analysis (Scheme 8).

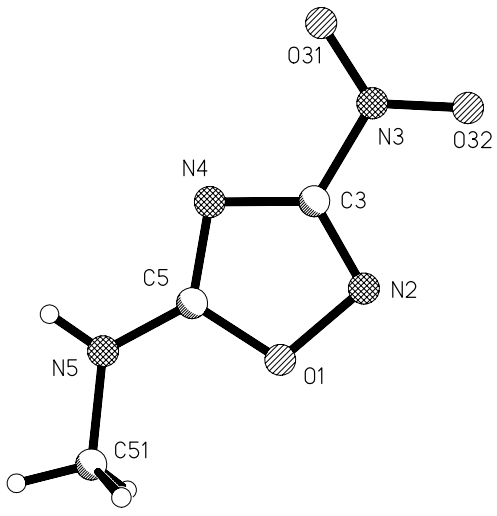
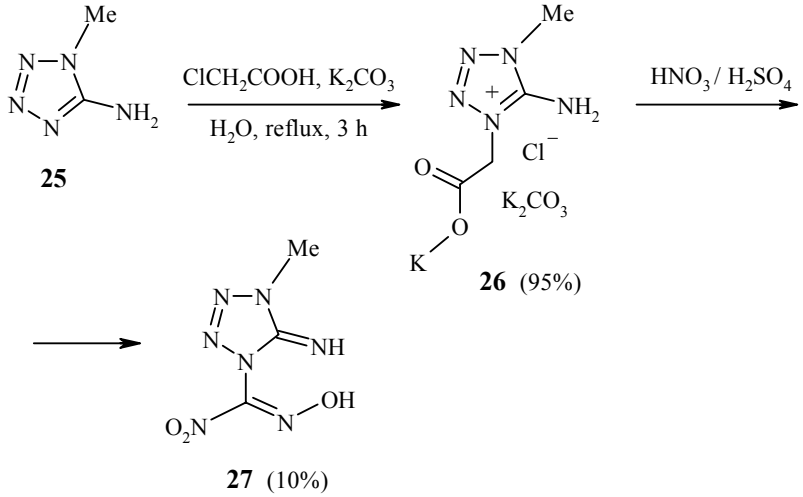


Fig. 1. X-Ray crystal structure of methyl (3-nitro-1,2,4-oxadiazol-5-yl)amine (**24**).

Scheme 8



Thus, new general reactions for the preparation of triazolium and tetrazolium dinitromethylides were developed that employ nitration by mixtures of nitric and sulfuric acid. Two new stable nitrolic acid derivatives have been synthesized and characterized.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded (with TMS for ^{1}H and DMSO-d_6 for ^{13}C as the internal reference) unless specified otherwise. 5-Amino-1,3-dimethyl-1H-triazole (**10**) was prepared (68%, mp 152-153°C; lit. yield 70%, mp 155-156°C) from S-methyl-2-thiopseudourea sulfate and methyl hydrazine according to a previously described method [17]. 5-Amino-1-methyl-1H-tetrazole (**25**) was prepared (68%, mp 214-216°C; lit. yield 23%, mp 220-223°C) from 5-aminotetrazole and methyl sulfate as described in [18]. 1-Amino-1-hydrazino-2,2-dinitroethene (**18**) was synthesized (81%, mp 131°C; lit. yield 67%, mp 127°C) according to a literature procedure [3]. 4-Nitroamino-1,2,4-triazole (**13**) (56%, mp 175-176°C; lit. yield 40%, mp 179°C) [19] and 1-(2-oxopropyl)-1,2,4-triazolium-4-nitroimide (**14**) (46%, mp 150-152°C; lit. yield 96%, mp 153-154°C) [20] were prepared by previously reported procedures.

Preparation of 2-(5-Amino-1,3-dimethyl-1H-1,2,4-triazol-4-ium-4-yl)acetate Potassium Chloride Double Salt (11). To a stirred solution of chloroacetic acid (1.0 g, 11.0 mmol) in 25 ml of methanol, potassium carbonate (0.90 g, 6.0 mmol) was added until the pH of the solution became alkaline. 5-Amino-1,3-dimethyl-1H-triazole (**10**) was then added (1.18 g, 11.0 mmol) and the reaction mixture was refluxed for 3 h and dried under reduced pressure to give a crude powder. Extraction with 3 × 20 ml of methanol gave the desired product as colorless cubes (98%); mp 129-130°C (methanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.98 (3H, s, CH_3); 3.41 (3H, s, NCH_3); 3.69 (2H, s, NCH_2); 6.01 (2H, br. s, NH_2). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 13.8, 32.8, 45.3, 155.5, 155.6, 168.5. Found, %: C 29.29; H 4.02. $C_6H_{10}ClKN_4O_2$. Calculated, %: C 29.45; H 4.12.

5-Imino-4-(hydroxyiminonitromethyl)-1,3-dimethyl-1,5-dihydro-1,2,4-triazole (12). To a stirred solution of compound **11** (1.02 g, 6.0 mmol) in 96% sulfuric acid (3.3 ml) at 0-2°C is added a mixture of 70% nitric acid (0.9 ml, 9.0 mmol) and sulfuric acid (0.9 ml, 9.0 mmol). The reaction mixture was gradually warmed to room temperature and stirred overnight before being poured into ice water and extracted with 3 × 30 ml of chloroform. The combined extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give white needles (22%); mp 173-174°C (methanol). UV (in $CHCl_3$), λ_{max}, nm (lg ε): 291 (4.71).

IR spectrum(thin layer), ν, cm^{-1}: 3324 (NH, OH), 1736, 1620, 1380, 1370. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.32 (3H, s, CH_3); 3.55 (3H, s, NCH_3), N–OH and C=NH are exchangeable. ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 11.2, 34.3, 146.8, 150.0, 163.4. Found, %: C 30.90; H 4.32. $C_5H_8N_6O_3$. Calculated, %: C 30.00; H 4.03.

4-Nitroamino-1,2,4-triazole (13). 4-Amino-1,2,4-triazole (10.6 g, 20 mmol) was dissolved in 90% sulfuric acid (50 ml). The resulting solution was cooled to 0°C in an iced bath, and 70% concentrated nitric acid (50 ml) was added dropwise over a period of 10 min maintaining the temperature at 0°C. The mixture was stirred for 30 min at 0°C and was gradually warmed up to room temperature. This mixture was kept for an additional 1 h and was poured into water (200 ml). The white precipitate was filtered off and washed with water to give colorless needles (86%); mp 175-176°C (methanol); mp 179°C [19]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 7.99 (1H, br. s, NH); 9.59 (2H, s, N–CH=N). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 144.1.

4-Nitroamino-1-(2-oxopropyl)-1,2,4-triazolium Chloride (14). Potassium hydroxide (0.44 g, 7.81 mmol) was added in one portion to a suspension of 4-nitroamino-1,2,4-triazole (**13**) (1 g, 7.81 mmol) in water (15 ml). This mixture was stirred at room temperature for 1 h before being evaporated to dryness to give a white powder, which was dissolved with acetonitrile (10 ml). 1-Chloropropan-2-one was added dropwise (0.63 ml, 7.81 mmol) and the reaction mixture was heated at 60°C for 7 days. After cooling to 5°C, the yellow precipitate was filtered off, washed with diethyl ether and crystallized from ethanol to give yellow needles (46%); mp 150-152°C, mp 153-154°C [20]. ^1H NMR spectrum (in $CDCl_3$), δ, ppm: 2.31 (3H, s, CH_3); 5.61 (2H, s, CH_2); 9.36 (1H, s, N–CH=N), 10.22 (1H, s, N–CH=N), NH exchangeable. ^{13}C NMR spectrum (in $CDCl_3$), δ, ppm: 27.0, 60.3, 142.6, 143.9, 199.2.

4-Nitroamino-1,2,4-triazolium-1-dinitromethylide (15). Compound **14** (400 mg, 1.80 mmol) in 96% concentrated sulfuric acid (3 ml) was treated at 2°C with a mixture of 90% concentrated nitric acid (0.8 ml) and 96% concentrated sulfuric acid (0.8 ml). This mixture was kept at room temperature with stirring overnight before being poured into ice. The solid precipitate was filtered, washed with water, methanol, and diethyl ether, and dried in vacuo to give dinitromethylide **15** as white needles (17%); mp 93-95°C (from methanol). ^1H NMR spectrum (in $CDCl_3$), δ, ppm: 7.98 (1H, s, NH); 8.22 (1H, s, N–CH=N); 8.77 (1H, s, N–CH=N), CH_3–CO_2^- not observed. ^{13}C NMR spectrum (in $CDCl_3$), δ, ppm: 106.1, 145.3, 153.9, acetate C=O not observed. Found, %: C 20.25; H 2.35; N 33.28. $C_3H_3N_7O_6 \cdot CH_3CO_2H$. Calculated, %: C 20.49; H 2.41; N 33.45.

1-Tetrazolium-5-dinitromethylide Sodium Salt (20). A mixture of sodium nitrite (35 mg, 0.5 mmol), 1-amino-1-hydrazino-2,2-dinitroethene (**18)** (81 mg, 0.5 mmol) in glacial acetic acid (0.5 mmol), and water (2 ml) was stirred at room temperature for 24 h. The mixture was then concentrated *in vacuo* and the residue was crystallized from methanol to give orange needles of compound **20** in 91% yield; explodes violently at 155°C [9]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.98 (1H, br. s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 149.5, 158.0. Found, %: C 12.40; H 0.83; N 42.50. $C_2HN_6NaO_4$. Calculated, %: C 12.25; H 0.51; N 42.86.

Preparation of 4-Methyl-1-(2-oxopropyl)-1-tetrazolium Methylsulfate (22a). To a stirred solution of 1-tetrazol-1-ylpropan-2-one (3.02 g, 24.0 mmol) in 10 ml of toluene, dimethylsulfate (2.5 ml, 26.4 mmol) was added. The reaction mixture was then stirred overnight before separating the heavy oil. This organic extract was dried *in vacuo* to give **22** as a yellow oil (83%). Further characterization was made with 4-methyl-1-(2-oxopropyl)-1-tetrazolium tetraphenylborate. ^1H NMR spectrum (DMSO-d_6), δ, ppm, (3:1 mixture of two regioisomers): (Major isomer) 2.26 (3H, s, CH_3–C=O); 3.39 (3H, s, $CH_3SO_3^-$); 4.42 (3H, s, CH_3); 5.97 (2H, s, CH_2), 10.37 (1H, s, CH=N); (Minor isomer) 2.28 (3H, s, CH_3–C=O); 3.17 (3H, s, $CH_3SO_3^-$); 4.46 (3H, s, CH_3); 6.38 (2H, s, CH_2), 10.37 (1H, s, CH=N). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: (Major isomer) 27.1, 29.9, 52.9, 59.0, 144.1, 198.0.

Preparation of 4-Methyl-1-(2-oxopropyl)-1-tetrazolium Tetraphenylborate (22b). To a saturated solution of sodium tetraphenylborate in 10 ml water, an aqueous solution of 2(1)-methyl-1(2)-(2-oxopropyl)-1H-1,2,3,4-tetrazol-2-ium methylsulfate (0.252 g, 0.001 mol) was added. The reaction mixture was stirred overnight. The obtained solid was filtered out and washed with water, ethanol, and hexane to give compound

22b as a white microcrystal (96%); mp 117-118°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz), (4:1 mixture of two regioisomers): (Major isomer) 2.33 (3H, d, *J* = 3.2, CH_3); 4.37 (3H, s, CH_3); 5.93 (2H, s, CH_2); 6.79 (4H, t, *J* = 7.0, Ph); 6.93 (8H, t, *J* = 7.3, Ph); 7.18 (8H, br. s, Ph), 10.92 (1H, s, N–CH=N). Most aromatic peaks of the minor isomer are unresolved and overlap with the major isomer, precluding proper assignment. (Minor isomer) 2.49 (3H, s, CH_3); 4.40 (3H, s, CH_3); 6.34 (2H, s, CH_2), 10.33 (1H, s, N–CH=N). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: (Major isomer) 174.7, 135.6, 133.1, 128.3, 126.6, 125.3, 124.7, 121.5, 102.9, 26.2, 10.0. Found, %: C 75.53; H 6.39; N 11.97. $C_{29}H_{29}BN_4O$. Calculated, %: C 75.66; H 6.35; N 12.17.

Methyl (3-Nitro-1,2,4-oxadiazol-5-yl)amine (24). Compound **22a** (2.0 g, 8.0 mmol) in 96% concentrated sulfuric acid (12 ml) was treated at 2°C with a mixture of 70% concentrated nitric acid (5 ml) and 96% concentrated sulfuric acid (5 ml). This mixture was then heated at 50-60°C for 1 h before being cooled to room temperature and poured into ice water. The aqueous phase was washed with 3 × 30 ml of chloroform and the combined organic phase was dried over magnesium sulfate, filtered, and evaporated under reduced pressure to give colorless blocks and plates (27%); mp 125-126°C (methanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.94 (3H, d, *J* = 3, CH_3); 9.26 (1H, br. s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 29.2, 169.5, 172.5. Found, %: C 25.76; H 2.70. $C_3H_4N_4O_3$. Calculated, %: C 25.01; H 2.80.

Preparation of the Triple Salt of 2-(5-Amino-4-methyl-1H-tetrazolium-1-yl)acetate Complexed with Potassium Chloride and Potassium Carbonate (26). To a stirred solution of chloroacetic acid (0.48 g, 5.05 mmol) in 30 ml of water, potassium carbonate (0.42 g, 3.03 mmol) was added until the pH of the solution became alkaline. 5-Amino-1-methyl-1H-tetrazole (**25**) was then added (0.50 g, 5.05 mmol) and the reaction mixture was refluxed for 3 h and dried under reduced pressure to give a crude powder. Extraction with 3 × 20 ml of methanol gave compound **26** as colorless needles (95%); mp 196-197°C (methanol).

^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 (3H, s, NCH_3); 3.87 (2H, s, CH_2); 6.72 (2H, br. s, NH_2). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 31.5, 44.6, 155.9, 168.7. Found, %: C 16.20; H 2.25; N 18.35. $C_4H_7N_5O_2{\cdot}KCl{\cdot}K_2CO_3$. Calculated, %: C 16.24; H 1.91; N 18.93.

5-Imino-1-(hydroxyiminonitromethyl)-4-methyl-1H-tetrazole (27). A solution of salt **26** (2.0 g) in 96% concentrated sulfuric acid (6 ml) was treated at 2°C with a mixture of 70% concentrated nitric acid (3 ml) and 96% concentrated sulfuric acid (3 ml). This mixture was kept at room temperature with stirring overnight before being poured into ice. The aqueous phase was washed with 3 × 30 ml of chloroform. The combined organic phase was dried over magnesium sulfate and evaporated under reduced pressure to give a yellow oil (10%). ^{1}H NMR spectrum (in $CDCl_3$), δ, ppm: 3.94 (3H, s, NCH_3), C=N–OH and C=NH are exchangeable. ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 33.5, 131.6, 150.4. Found, %: C 19.46; H 3.01; N 52.25. $C_3H_5N_7O_3$. Calculated, %: C 19. 6; H 2.69; N 52.40.

X-Ray Crystallography. Data were collected with a Siemens SMART CCD area detector, using graphite monochromatized Mo*K*α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS [21] and refined on F^2, using all data, by full-matrix least-squares procedures using SHELXTL [22]. The identities (C, N or O) of the non-hydrogen atoms were carefully verified by refinement. Methyl hydrogen atoms were included in calculated positions, with isotropic displacement parameters 1.5 times the isotropic equivalent of the carrier carbon; the NH hydrogen was found in a difference map and its position refined.

Crystal Data for Oxadiazole 24 (Plates): $C_3H_4N_4O_3$, MW 144.10, monoclinic, *C*2/*c*; *a* = 18.856(6), *b* = 3.946(1), *c* = 15.269(5) Å; β = 95.929(4)°; *V* = 1129.9(6) Å^3; *Z* = 8; T -100°C; *F*(000) = 592; μ(Mo*K*α) = 0.151 mm^{-1}; D_{calc} = 1.694 g·cm^{-3}; $2\theta_{max}$ = 50° (CCD area detector, 99% completeness); $wR(F^2)$ = 0.0871 (all 995 data); *R* = 0.0307 (872 data with $I > 2\sigma I$).

Crystal Data for Oxadiazole 24 (Blocks): $C_3H_4N_4O_3$, MW 144.10, monoclinic, $P2_1/c$; *a* = 8.806(4), *b* = 12.997(5), *c* = 5.037(2) Å; β = 95.673(5)°; *V* = 573.8(4) Å^3; *Z* = 4; T -100°C; *F*(000) = 296; μ(Mo*K*α) = 0.148 mm^{-1}; D_{calc} = 1.668 g·cm^{-3}; $2\theta_{max}$ = 50° (CCD area detector, 100% completeness); $wR(F^2)$ = 0.1028 (all 1002 data); *R* = 0.0370 (872 data with $I > 2\sigma I$).

REFERENCES

1. R. W. Millar, R. P. Claridge, J. P. B. Sandall, and C. Thompson, *ARKIVOC*, issue **iii**, 19 (2002).
2. A. Puchala, F. Belaj, J. Bergman, and C. O. Kappe, *J. Heterocycl. Chem*., **38**, 1345 (2001).
3. A. J. Bellamy, N. V. Latypov, and P. Goede, *J. Chem. Res*. (*S*), 257 (2002).
4. V. Grakauskas and A. H. Albert, *J. Heterocycl. Chem*., **18**, 1477 (1981).
5. A. N. Terpigorev, I. V. Tselinskii, A. V. Makarevich, G. M. Frolova, and A. A. Mel'nikov, *J. Org. Chem*. (*USSR*) (*Engl. Transl*.), **23**, 214 (1987).
6. V. V. Semenov, S. A. Shevelev, and L. G. Mel'nikova, *Mendeleev Commun*., 58 (1993).
7. C. G. Newton, W. D. Ollis, and D. E. Wright, *J. Chem. Soc*., *Perkin Trans. 1*, 69 (1984).
8. V. V. Semenov, V. S. Bogdanov, B. S. El'yanov, L. G. Mel'nikova, S. A. Shevelev, V. M. Zhulin, and A. A. Fainzil'berg, *Chem. Heterocycl. Compd*., 859 (1982).
9. F. Einberg, *J. Org. Chem*., **29**, 2021 (1964).
10. A. R. Katritzky and W. Q. Fan, *Heterocycles*, **34**, 2179 (1992).
11. A. R. Katritzky, J. Lewis, S. Q. Abbas Rizvi, G. Roch, and E. Lunt, *Anal. Quim.*, **70**, 994 (1974); *Chem. Abstr*., **84**, 17100 (1976).
12. J. Epsztajn, E. Lunt, and A. R. Katritzky, *Tetrahedron*, **26**, 1665 (1970).
13. J. Epsztajn and A. R. Katritzky, *Tetrahedron Lett*., 4739 (1969).
14. A. R. Katritzky, D. J. Cundy, and J. Chen, *J. Energetic Mat*., **11**, 345 (1993).
15. A. R. Katritzky, D. J. Cundy, and J. Chen, *J. Heterocycl. Chem*., **31**, 271 (1994).
16. M. E. Baumann, H. Bosshard, W. Breitenstein, and G. Rist, *Helv. Chim. Acta*, **69**, 396 (1986).
17. J.-L. Barascut, P. Viallefont, and J. Daunis, *Bull. Soc. Chim. Fr*., 1649 (1975).
18. R. A. Henry and W. G. Finnegan, *J. Am. Chem. Soc*., **76**, 923 (1954).
19. T. P. Kofman, G. Y. Kartseva, and M. B. Shcherbinin, *J. Org. Chem.* (*USSR*) (*Engl. Trans*.), **38**, 1343 (2002).
20. O. P. Shitov, V. L. Korolev, V. S. Bogdanov, and V. A. Tartakovsky, *Russ. Chem. Bull. Int. Ed*., 695 (2003).
21. G. M. Sheldrick, *Acta Crystallogr*., **A46**, 467 (1990).
22. G. M. Sheldrick, *SHELXTL*, Bruker Analytical X-ray Systems, (1997).