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SYNTHESIS AND PROPERTIES OF ALKYL- AND PHENYLTETRAZOLIUM PICRATES

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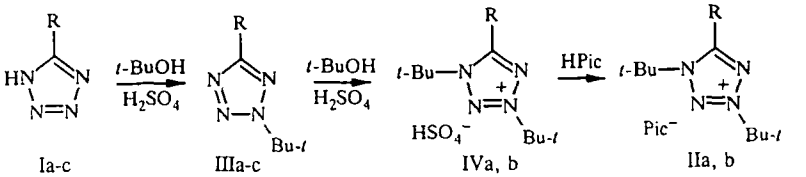
A series of tetrazolium picrates has been synthesized by quaternization of C- and N-mono substituted tetrazoles using dimethylsulfate and the system t-BuOH/H_2SO_4 and subsequent precipitation of the cations formed with picric acid. Their thermal stability has been studied using differential scanning calorimetry and thermogravimetric analysis. An x-ray structural investigation has been carried out on 1,3-di-tert-butyl-5-methyltetrazolium picrate.

Tetrazolium salts find practical application in different technological areas, e.g., in agriculture, medicine, and chemical analysis, as promising phase transfer catalysts [1], and as intermediates in organic synthesis [2-10]. The most studied of these are the tetrazolium salts with inorganic acid anions (halides, perchlorates, tetrafluoroborates, fluorosulfonates, etc.) [4-16]. Among the salts with organic acid anions there are principally known benzene- and toluenesulfonates and tetraphenylborates [17, 18]. At the same time, investigation of the synthetic route and properties of tetrazolium salts with organic anions can give much valuable scientific and practical information.

In this work we have chosen tetrazolium picrates as the targets of our investigation since they are of interest as components of energetic condensed systems of varying function [19]. From the series of compounds indicated there is reported in reasonable detail only 2,3,5-triphenyltetrazolium picrate [20] and there is information about the fission of 1,4-dimethyltetrazolium picrate by amines [21], but no kind of quantitative data were reported for the properties of the substrate or the products of the decomposition.

In this study, quaternization of the C- and N- mono substituted tetrazoles was achieved by reaction with dimethylsulfate or in the system *t*-BuOH/H_2SO_4. This system has been used successfully for the first time with this series and, as shown below, has several advantages over *t*-BuOH/HBF_4 [16]. In addition, the quaternization of N-unsubstituted tetrazoles [22, 23] has been little studied to this time but it is of interest both to show their synthetic potential and for a deeper understanding of the effect of the substrate structure on the selectivity of the alkylation process. A key problem in the quaternization of tetrazoles is the regioselectivity of the process due to the ambident nature of the tetrazole ring. Only in the case of alkylation of 2-mono- and 2,5-disubstituted tetrazoles and for the *tert*-butylation of 1,5-disubstituted tetrazoles are single tetrazolium salts obtained [1, 16]. Use of the *t*-BuOH/H_2SO_4 system permits the selective preparation of several tetrazolium salts. Hence, starting from tetrazole Ia and 5-methyltetrazole Ib we obtained single picrates of 1,3-di-*tert*-butyltetrazole IIa and 1,3-di-*tert*-butyl-5-methyltetrazole IIb. The mechanism of this reaction apparently includes a regioselective N_2-alkylation of the starting tetrazoles I by *tert*-butanol [24] and subsequent quaternization of the 2-*tert*-butyltetrazoles IIIa,b, producing the bisulfates IV.



I–IV a R = H, b R = Me; c R = Ph, Pic = 2,4,6-$(NO_2)_3C_6H_2O$

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TABLE 1. Physicochemical Parameters for Compounds Synthesized

Compound	Empirical formula	mp, °C	PMR spectrum, ppm			Basic thermal parameters				
			solvent	cation	anion	effect	$\lvert\Delta H\rvert$, J / g	T_i†	T_m‡	loss in mass, %
IIa	$C_{15}H_{21}N_7O_7$	112...114	CD_3CN	1,78 (9H, s, 3-CH_3) 1,82 (9H, s, 3-CH_3) 9,59 (1H, s, HC_{ring})	8,61 (2H, s, H_{arom})	endo endo exo	232 47 607	 132 195	 135 273	 47 53
IIb	$C_{16}H_{23}N_7O_7$	decomp. > 101	CD_3CN	1,76 (9H, s, 3-CH_3) 1,78 (9H, s, 3-CH_3) 2,83 (3H, s, H_3C-C_{ring})	8,61 (2H, s, H_{arom})	endo exo	427 86	101 253	105 260	49 51
VIIb	$C_{14}H_{11}N_7O_7$	decomp. > 100	$(CD_3)_2CO$	4,85 (3H, s, CH_3) 7,90...8,40 (5H, s, H_{arom}) 12,25 (1H, s, HC_{ring})	8,90 (2H, s, H_{arom})	exo exo	483 857	100 190	109 258	12 88
VIII	$C_{10}H_{11}N_7O_7$	164...166	CD_3CN	2,75 (3H, s, CH_3) 4,16 (6H, s, 2-CH_3)	8,60 (2H, s, H_{arom})	endo exo	80 2026	 215	 274	 67
IX	$C_{25}H_{17}N_7O_7$	187...188*	$(CD_3)_2CO$	7,70...7,91 (2H, m, H_{arom}) 7,91...8,08 (4H, m, H_{arom}) 8,25...8,35 (9H, m, H_{arom})	8,56 (2H, s, H_{arom})	exo exo	1107 4050	225 520	290 554	45 55

*Mp 186-188°C [20].

†T_n is the initial decomposition temperature, °C.

‡T_m is the temperature of maximum heat evolution or absorption, °C.

TABLE 2. Coordinates (in cell units, $\times 10^4$) and Equivalent Isotropic Thermal Parameters for the Atoms in the Structure of Compound IIb

Atom	x/a	y/b	z/c	$U_{(eq)}$ (Å^2 × 10^3)
N(1)	2907(2)	5677(2)	2531(1)	49(1)
N(2)	3679(2)	6458(2)	1831(2)	52(1)
N(3)	4350(2)	7052(2)	2473(2)	52(1)
N(4)	4084(2)	6700(2)	3559(2)	59(1)
C(5)	3164(2)	5818(2)	3591(2)	53(1)
C(6)	1975(3)	4793(3)	2062(2)	70(1)
C(7)	492(3)	4948(4)	2758(4)	112(1)
C(8)	1829(6)	5327(4)	855(3)	128(2)
C(9)	2778(4)	3263(3)	2143(3)	94(1)
C(10)	5360(3)	8064(3)	2028(3)	72(1)
C(11)	4718(4)	9464(3)	2494(4)	120(2)
C(12)	5403(4)	8176(5)	762(3)	120(1)
C(13)	6861(3)	7430(4)	2387(4)	108(1)
C(14)	2575(3)	5121(3)	4645(2)	79(1)
C(15)	-4(3)	10553(3)	7118(3)	78(1)
C(16)	148(3)	9502(3)	8045(2)	66(1)
C(17)	1220(3)	8324(2)	8072(2)	63(1)
C(18)	2280(3)	8118(2)	7172(2)	62(1)
C(19)	2272(3)	9083(3)	6257(2)	67(1)
C(20)	1184(3)	10258(3)	6236(2)	71(1)
N(5)	-926(3)	9647(4)	9040(3)	92(1)
N(6)	3413(3)	6887(3)	7205(3)	89(1)
N(7)	1256(4)	11253(3)	5258(3)	103(1)
O(1)	-1025(3)	11573(3)	7074(3)	135(1)
O(2)	-1512(3)	10830(4)	9279(3)	148(1)
O(3)	-1143(3)	8579(4)	9601(3)	137(1)
O(4)	3408(4)	6033(3)	8018(3)	138(1)
O(5)	4371(3)	6745(3)	6419(2)	121(1)
O(6)	2284(8)	11125(5)	4626(4)	285(4)
O(7)	378(6)	12215(5)	5101(4)	215(2)

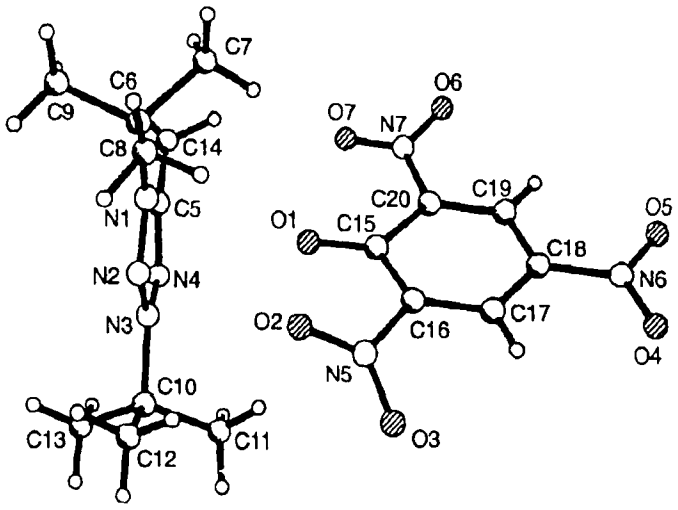


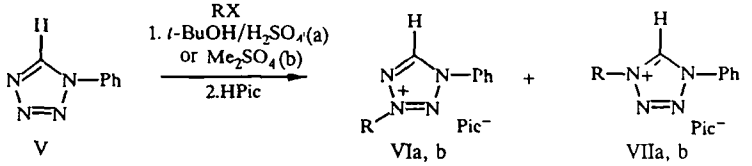
Fig. 1. Mutual orientation and conformation of ions in compound II.

Attempts to prepare 1,3-di-*tert*-butyl-5-phenyltetrazolium picrate IIc from tetrazole Ic in a similar way proved unsuccessful and this is evidently explained by steric hindrance to quaternization in the intermediate 2-*tert*-butyl-5-phenyltetrazole (IIIc) which was separated from the reaction mixture in 85% yield and identified according to [24]. A similar factor accounts for the lowering of the salt yield on crossing from tetrazole Ia to Ib.

TABLE 3. Bond Lengths and Valence Angles in the Cation of Compound IIb

Bond	d, Å	Valence angle	ω, deg
$N_{(1)}—N_{(2)}$	1,320(2)	$N_{(2)}—N_{(1)}—C_{(5)}$	109,2(2)
$N_{(1)}—C_{(5)}$	1,353(3)	$N_{(2)}—N_{(1)}—C_{(6)}$	118.9(2)
$N_{(1)}—C_{(6)}$	1,514(3)	$C_{(5)}—N_{(1)}—C_{(6)}$	131,9(2)
$N_{(2)}—N_{(3)}$	1,287(3)	$N_{(3)}—N_{(2)}—N_{(1)}$	104,0(2)
$N_{(3)}—N_{(4)}$	1,328(3)	$N_{(2)}—N_{(3)}—N_{(4)}$	114,8(2)
$N_{(3)}—C_{(10)}$	1,504(3)	$N_{(2)}—N_{(3)}—C_{(10)}$	122,6(2)
$N_{(4)}—C_{(5)}$	1,314(3)	$N_{(4)}—N_{(3)}—C_{(10)}$	122,6(2)
$C_{(5)}—C_{(14)}$	1,478(3)	$C_{(5)}—N_{(4)}—N_{(3)}$	103,6(2)
$C_{(6)}—C_{(8)}$	1,512(4)	$N_{(4)}—C_{(5)}—N_{(1)}$	108,5(2)
$C_{(6)}—C_{(7)}$	1,522(5)	$N_{(4)}—C_{(5)}—C_{(14)}$	123,0(2)
$C_{(6)}—C_{(9)}$	1,523(4)	$N_{(1)}—C_{(5)}—C_{(14)}$	128,5(2)
$C_{(10)}—C_{(11)}$	1,500(4)	$C_{(8)}—C_{(6)}—N_{(1)}$	107,5(2)
$C_{(10)}—C_{(12)}$	1,516(5)	$C_{(8)}—C_{(6)}—C_{(7)}$	111,7(3)
$C_{(10)}—C_{(13)}$	1,516(4)	$N_{(1)}—C_{(6)}—C_{(7)}$	108,7(2)
		$C_{(8)}—C_{(6)}—C_{(9)}$	110,8(3)
		$N_{(1)}—C_{(6)}—C_{(9)}$	107,2(2)
		$C_{(7)}—C_{(6)}—C_{(9)}$	110,8(3)
		$C_{(11)}—C_{(10)}—N_{(3)}$	107,1(2)
		$C_{(11)}—C_{(10)}—C_{(12)}$	110,9(3)
		$N_{(3)}—C_{(10)}—C_{(12)}$	107,2(2)
		$C_{(11)}—C_{(10)}—C_{(13)}$	113,5(3)
		$N_{(3)}—C_{(10)}—C_{(13)}$	107,2(2)
		$C_{(12)}—C_{(10)}—C_{(13)}$	110,6(3)

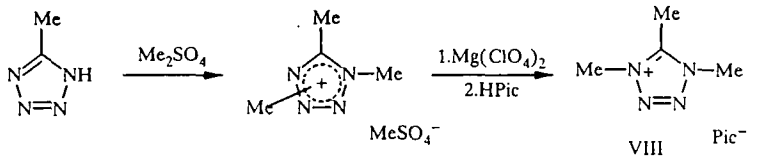
Phenyltetrazolium picrates were prepared by quaternization of 1-phenyltetrazole (V) according to the scheme:



VI, VII a R = *t*-Bu, X = OH; b R = Me, X = OSO_2OMe

In this case, using the system *t*-BuOH/H_2SO_4, the isomer ratio in the mixture calculated from the intensity of the protons signals for the cyclic carbon atom in the PMR spectrum and also their yield are very close to those previously obtained by *tert*-butylation in the system *t*-BuOH/HBF_4 [16].

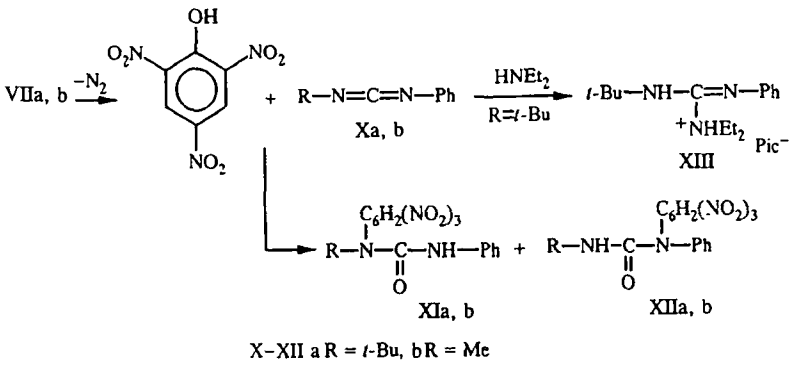
The results of fractional precipitation of the picrates from the reaction mixture point to the high solubility of the 1,3-isomers VI when compared with the 1,4-isomers VII, and this is a general feature of other tetrazolium salts [16]. However, a single salt could only be produced in the case of 1-phenyl-4-methyltetrazolium picrate (VIIb). At the same time, using the difference in solubility for the picrate and perchlorate isomers led to preparation of the single 1,4,5-trimethyltetrazolium picrate (VIII) according to the scheme:



The synthesized picrates are yellow crystalline materials (spectral and thermoanalytical parameters given in Table 1), not sensitive to impact or shock, and safe in our work. All of this also relates to the virtually unstudied 2,3,5-triphenyltetrazolium picrate (IX) [20], prepared by us previously for a comparative study in 90% yield by the reaction of 2,3,5-triphenyltetrazolium chloride and picric acid in water.

The PMR spectra of the prepared 5-unsubstituted tetrazolium picrates VIIa,b show a significant shift of the signal for the proton on the ring carbon atom to low field of the starting tetrazoles and similar to analogous tetrazolium salts with other anions. Thus, the chemical shift for this proton in the salt VIIb is 12.25 ppm (acetone-D_6 solvent, concentration 1 mol. %), whereas that for tetrazole V is 9.67 ppm (for 1-phenyl-4-ethyltetrazolium tetrafluoroborate, it is 11.30 ppm in similar conditions [25]). The high mobility of the hydrogen atom in the tetrazole ring of picrate VIIb leads to its complete decomposition, even on contact with water over 24 h. The picrate anion and water evidently are similar bases [13, 26], losing a proton from atom C_5, which leads to fragmentation of the tetrazole ring to a molecule of nitrogen and methylphenylcarbodiimide (Xb). Further addition of picric acid to the carbodiimide can theoretically lead to two isomeric trisubstituted ureas XIb and XIIb. However, only one product was practically separated. Reactions, similar to the latter, have been reasonably well studied in the case of symmetrical carbodiimides [27, 28], and available data do not allow an unambiguous identification of the product structure. With steric hindrance in mind, we propose that the compound obtained most likely corresponds to structure XIb.

For salt VIIa, only 10% of its starting amount decomposes by the indicated route. This is shown by the presence in the PMR spectrum (CD_3CN) of the products of reaction with water of *tert*-butyl group singlets (1.25 and 1.38 ppm) and phenyl group multiplets (7.00 to 7.30 ppm), very likely assignable to compounds XIa and XIIa. The higher stability of salt VIIa can apparently be attributed to steric hindrance towards loss of the proton at atom C_5 thanks to the presence of such bulky groups as tert-butyl and phenyl in neighboring positions. However, the strong base (diethylamine) decomposes salt VIIa, leading to the picrate of the substituted guanidine XIII, formation of which can be rationalized from data regarding the fragmentation of the tetrazole ring [13, 26] and information about the ability of carbodiimides to add amines [27, 28].



X-XII a R = *t*-Bu, b R = Me

We have used differential scanning calorimetry and complex thermal analysis to study the thermostability of the synthesized salts. The basic thermoanalytical parameters for the processes of their decomposition are given in Table 1. The results of the investigation show that the thermal stability of the studied tetrazolium salts depends significantly on the nature of the substituents and their position in the heterocycle. It was found that the most stable of the series are the picrates of the trisubstituted tetrazoles VIII and IX, vigorous decomposition of which begins at 215-225°C. The nature of the decomposition of salt IX does not differ significantly from the thermal behavior of the analogous halides [29]. The presence of a proton at position C_5 decreases considerably the thermal stability of salt VIIb and is evidently linked to the ready fission of this proton from the indicated position due to the nucleophilic properties of the picrate anion.

To establish the structural features of the tetrazolium picrates, we carried out an x-ray analysis of a monocrystal of salt IIb. Figure 1 shows the mutual orientation and conformation of the ions in the structure. The tetrazole ring is planar with a maximum deviation of the atoms not exceeding 0.004 Å from the root mean square plane of this ring. The substituent also lies in the ring plane with a maximum deviation not more than 0.03 Å. It should be noted that x-ray analysis exists for only two 1,3,5-trisubstituted tetrazolium salts which are 1,3-diphenyl-5-(1,5-diphenyl-3-formazanyl)tetrazolium chloride (XIV) [30] and 1-phenyl-3-methyl-5-(p-chlorophenyl)tetrazolium perchlorate (XV) [8]. Despite the significant differences in the nature of the substitution in these compounds, the tetrazole ring bond lengths $C_{(5)}-N_{(1)}$, $C_{(5)}-N_{(4)}$, $N_{(1)}-N_{(2)}$ and $N_{(3)}-N_{(4)}$ and valence angles for IIb (Tables 2 and 3) and XV [8] are virtually the same and only differ a little from the bond lengths for $C_{(5)}-N_{(1)}$ (1.362 Å), $C_{(5)}-N_{(4)}$ (1.325 Å), and $N_{(1)}-N_{(2)}$ (1.332 Å) in compound XIV [30]. The shortest ring bond in the cations of salts IIb, XIV, and XV is $N_{(2)}-N_{(3)}$, which supports conclusions made earlier [16, 18] (for several 1,3,5-tetrazolium salts) regarding the variation in centers of quaternization and localization of positive charge in the ring and also the presence of significant conjugation in its $N_{(1)}-N_{(2)}=N_{(3)}$ fragment. This is also in good agreement with the calculations using the AM-1

method for the experimental geometry of the π-order value of bonds $N_{(1)}-N_{(2)}$ and $N_{(2)}=N_{(3)}$, equal to 0.28 and 0.55 respectively.

The bond lengths and valence angles in the picrate ion salt IIb are typical (see [31]). The angle between the planes of the benzene and tetrazole rings is 89.49(7)°, which precludes, according to [31], additional π-bonding of these aromatic systems. The distances between the oxygen atom $O_{(1)}$ of the picrate anion C−O group and the atoms of the tetrazole ring are in the range 2.934-3.161 Å, which is considerably shorter than the corresponding distances between the chloride anion and the atoms of the heterocycle in the cationic salt XIV (3.413-3.702 Å). The shortest distance $N_{(1)}-O_{(1)}$ (2.93 Å) is close to the N−O distance in aromatic amine picrates (2.67-2.88 Å) [31]. Second in length is the $C_{(5)}-O_{(1)}$ distance (3.009 Å), which indirectly points to the presence of a positive charge on the tetrazole carbon atom. The C−O bond in the picrate anion of IIb (1.234 Å) is shorter than in picric acid (1.335 Å) and corresponds in length to bonds in aromatic amine picrates (1.229-1.259 Å) [31]. Evidently, such an ion paired structure for the tetrazolium picrates with a localized anion near atom C_5 leads to the high mobility of the hydrogen on the ring carbon atom observed in the PMR spectra and the hydrolytic and thermal instability of 5-unsubstituted tetrazolium picrates mentioned above.

EXPERIMENTAL

The starting tetrazole [32], 5-methyl- and 5-phenyltetrazole [33], and 1-phenyltetrazole [34] were prepared by known methods. PMR spectra were recorded on a Tesla BS-567 (100 MHz) spectrometer. Compound purity was demonstrated by TLC on Silufol UV-254 plates. IR spectra (in Vaseline oil) were taken on a Specord IR-75 instrument. Thermolysis of the synthesized salts was investigated using differential scanning calorimetry (DSC) on a Mettler TA-3000 instrument with a DSC-20 cell and complex thermal analysis on an OD-102 derivatograph (Paulik−Paulik−Erdey system) with a heating velocity of 5°/min in a nitrogen atmosphere. For the DSC experiments the crucible holders were encapsulated.

X-ray Structural Investigation of Compound IIb. Monocrystals of salt II were obtained by crystallization from acetone at 303 K. For the x-ray analysis, a crystal of size 0.7 × 0.6 × 0.4 mm was mapped. The compound crystallized in a triclinic system of space group P1. The unit cell parameters are: a = 9.342 (2); b = 9.640(2); c = 12.063(3) Å; α = 84.66(2); β = 83.19(2); γ = 79.02(2)°; Z = 2; V = 1056.2(4) Å^3. A three-dimensional set of x-ray diffraction data was gathered on a Nicolet R3m automatic, four circle diffractometer with MoK_α irradiation, graphite monochromator, and $\theta/2\theta$ scanning with $2\theta_{max}$ = 55°. The structure of IIb was solved by a direct method. The position of the hydrogen atoms was calculated geometrically. Refinement was carried out by full matrix least squares analysis with calculation based on the anisotropy of the thermal vibrations of nonhydrogen atoms. Hydrogen atoms were refined via the "riding" method. A total of 3896 independent reflections were used in the calculations. These were performed using the SHELXS-86 [35] and SHELXL-93 [36] programs (PC version) on an IBM 486. The coordinates and isotropic thermal parameters for the atoms are given in Table 2.

1,3-Di-*tert*-butyl-5R-tetrazolium Picrates (IIa, b). Tert-butanol (18 ml, 0.20 mole) was added to a solution of tetrazole or 5-methyltetrazole (0.05 mole) in sulfuric acid (70%, 20 ml). The mixture was held for 72 h, diluted with water to 200 ml, and a saturated aqueous solution of picric acid (11.45 g, 0.05 mole) was added. The solution was left for 7 days and the precipitated crystals were separated, washed with cold water, and dried at 40°C. Product yield of IIa, 62%. Found, %: C 43.91; H 5.08; N 23.93. $C_{15}H_{21}N_7O_7$. Calculated, %: C 43.80; H 5.15; N 23.83. Yield of IIb, 10%. Found, %: C 45.25; H 5.59; N 23.09. $C_{16}H_{23}N_7O_7$. Calculated, %: C 45.18; H 5.45; N 23.05.

Mixture of 1-Phenyl-3-tert-butyl- and 1-Phenyl-4-tert-butyltetrazolium Picrates (VIa, VIIa) and Their Reaction with Triethylamine. A mixture of 1-phenyltetrazole (1.46 g, 0.01 mole), tert-butanol (1.48 g, 0.02 mole), and sulfuric acid (70%, 15 ml) was left for 3 days. The mixture was diluted with water to 70 ml, and a saturated aqueous solution of picric acid (2.29 g, 0.01 mole) was added. The precipitate was separated, washed with cold water, and dried at 40°C. Product yield as a mixture of VIa and VIIa in the ratio 35:65 from PMR data was 2.9 g (70%). PMR spectrum (CD_3CN): VIa 1.85 (9H, s, 3-CH_3), 7.82-8.00 (5H, m, H_{arom}), 8.66 (2H, s, H_{arom}), 10.07 (1H, s, HC_{ring}), VIIa 1.85 (9H, s, 3-CH_3), 7.66-7.82 (5H, m, H_{arom}), 8.66 (2H, s, H_{arom}), 10.98 ppm (1H, s, HC_{ring}). Found, %: C 47.31; H 4.08; N 22.89. $C_{17}H_{17}N_7O_7$. Calculated, %: C 47.34; H 3.97; N 22.73.

Diethylamine (1 ml, 0.0097 mole) was added to a solution of mixed VIa and VIIa (2.1 g, 0.005 mole) in benzene (50 ml) and the mixture was left for 3 h at ~20°C before the benzene was removed under vacuum and the product recrystallized twice from ethanol. The yield of N-tert-butyl-N′,N′-diethyl-N″-phenylguanidine picrate (XIII) was 0.8 g (50%) obtained as

yellow crystals with mp 153-155°C. IR spectrum: 3215-3410 (NH), 1625 (C=N), 1608 (C=C_{arom}), 1555 (NO_2), 1495 (CH_3), 1410, 1340 (NO_2), 1310, 1290, 1260 (C–N), 1190, 1150, 1075, 1060, 985, 940, 910 (HC_{arom}), 840, 810 (NO_2), 780, 710, 620, 545, 520, 498, 460 cm^{-1}. PMR spectrum (acetone-D_6): 1.18 (6H, t, CH_3), 1.50 (9H, s, C_4H_9), 2.85 (2H, br.s, 2-NH), 3.42 (4H, q, 2-CH_2), 7.16-7.65 (5H, m, H_{arom}), 8.63 ppm (2H, s, H_{arom}). Found, %: C 53.09; H 5.89; N 17.82. $C_{21}H_{28}N_6O_7$. Calculated, %: C 52,94; H 5.92, N 17.64. The mother liquor obtained from the recrystallization contained a mixture of VIa and XIII picrates according to PMR data.

1-Phenyl-4-methyltetrazolium Picrate (VIIb) and Its Fission Using Water. A solution of 1-phenyltetrazole (9.3 g, 0.064 mole) in dimethylsulfate (24.1 g, 0.19 mole) was held at ~20°C for 72 h. The obtained white crystalline mass was dissolved in water (100 ml) and, after removal of the organic layer, an aqueous solution of picric acid (9.4 g, 0.041 mole) was added to the solution. The precipitate was separated, washed with cold water, and dried at 40°C to give a mixture of picrates VIb and VIIb (8.25 g, 53%) in the isomer ratio 4:96. PMR spectra (acetone-D_6): VIb 5.15 (3H, s, CH_3), 7.88-8.35 (5H, m, arom), 8.90 (2H, s, H_{arom}), 11.09 (1H, s, HC_{ring}), VIIb (see Table 1). By portionwise addition of picric acid at the earlier stage, the picrate VIIb (3.70 g, 15%) could be separated from the solution as a single compound. Found, %: C 43.31; H 2.78; N 25.08. $C_{14}H_{11}N_7O_7$. Calculated, %: C 43.20; H 2.85; N 25.19.

A mixture of salt VIIb (2 g, 0.0051 mole) in water (20 ml) was stirred for 24 h at room temperature, filtered, and the precipitate separated and recrystallized from ethanol to give N′-methyl-N-(2,4,6-trinitrophenyl)-N′-phenylurea (XIb, 0.73 g, 40%) as yellow crystals decomposing at 170°C. IR spectrum: 3430 (NH), 1690 (C=O), 1650, 1601 (C=C_{arom}), 1540, 1501 (NO_2), 1490 (CH_3), 1410 (C=C_{arom}), 1345 (NO_2), 1300, 1245 (C–N), 1160, 1100, 1080, 940, 925, 900 (HC_{arom}), 830, 800 (NO_2), 760, 700, 665, 650, 605, 540, 515, 490, 460 cm^{-1}. PMR spectrum (acetone-D_6): 2.75 (3H, s, CH_3), 2.94 (1H, br s, NH), 7.26-7.40 (5H, m, H_{arom}), 8.93 ppm (2H, s, H_{arom}). Found, %: C 46.66; H 3.01; N 19.50. $C_{14}H_{11}N_5O_7$. Calculated, %: C 46.55; H 3.07; N 19.38.

1,4,5-Trimethyltetrazolium Picrate (VIII). A solution of 5-methyltetrazole (8.4 g, 0.1 mole) in dimethylsulfate (37.8 g, 0.03 mole) was held for 2 h on a boiling water bath, cooled, the excess dimethylsulfate extracted with ether (3 × 15 ml), and the residue dried *in vacuo*. The obtained oil was dissolved in water (30 ml), magnesium perchlorate (7.2 g, 0.032 mole) added, cooled to 5°C, filtered, and the precipitated crystals washed with iced water (10 ml). The 1,4,5-trimethyltetrazolium perchlorate obtained (8.4 g, 0.04 mole) was dissolved in water (50 ml), and a solution of saturated aqueous picric acid (9.2 g, 0.04 mole) added. The solution was evaporated to 80 ml and cooled to 5°C. The precipitate was separated, washed with cold water, and dried at 50°C to give 12 g of product (35%). Found, %: C 35.31; H 3.18; N 28.63. $C_{10}H_{11}N_7O_7$. Calculated, %: C 35.20; H 3.25; N 28.73.

2,3,5-Triphenyltetrazolium Picrate (IX). A solution of picric acid (2.29 g, 0.01 mole) in a minimum amount of hot water (at ~60°C) was added to a solution of 2,3,5-triphenyltetrazolium chloride (3.35 g, 0.01 mole) in water (20 ml). The solution was cooled to room temperature and the precipitate was separated, washed with cold water, dried at 50°C, and recrystallized from acetone to give 4.74 g (90%). Found, %: C 56.99; H 3.12; N 18.53. $C_{25}H_{17}N_7O_7$. Calculated, %: C 56.93; H 3.25; N 18.59.

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