Chemistry of Heterocyclic Compounds, Vol. 35, No. 9, 1999

REGIOSELECTIVE SYNTHESIS OF NEW FUNCTIONALLY SUBSTITUTED TETRAZOLIUM SALTS

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The 1,4-, 1,3-di- and 1,3,5-trisubstituted tetrazolium salts were obtained regioselectively and with high yields by the quaternization of 1- and 2-monosubstituted and 1,5-disubstituted tetrazoles with diacetone alcohol in perchloric acid. An X-ray crystallographic analysis of 1-(2-methylpentan-4-on-2-yl)-4-methyltetrazolium perchlorate was undertaken.

The quaternization of tetrazoles is one of the most widely used methods for the synthesis of 1,3(1,4)-disubstituted and 1,3,5(1,4,5)-trisubstituted tetrazolium salts, which exhibit broad synthetic possibilities as generators of carbenes, precursors of reactive tetrazolines, various bipolar ionic systems, etc. [1]. However, the application of this method is restricted by the narrow range of salts, and this is due to the insufficient selectivity of the processes involved in their synthesis and to the small number of investigated quaternizing agents and in particular functionally substituted quaternizing agents [2, 3].

The results from the quaternization of the N-substituted tetrazoles in acidic media (HBF_4, H_2SO_4, $HClO_4$) with 2-methyl-2-propanol [4, 5] and 1-adamantanol [6] and also of α-ferrocenylalkylcarbinols in two-phase systems consisting of methylene chloride and an aqueous solution of acid [7] demonstrated the prospects of the proposed approaches to the regioselective synthesis of tetrazolium salts.

While continuing investigations of quaternization in acidic media and also with a view to bringing functionally substituted alcohols into these reactions in the present work we studied the behavior of diacetone alcohol (I) toward various N-substituted tetrazoles in perchloric acid. Here the 1,4-disubstituted tetrazolium salts III were unexpectedly obtained exclusively with good yields from the 1-monosubstituted tetrazoles II (Table 1). These results differ substantially from data on *tert*-butylation of the tetrazoles, where the preferential (in 48% hydrofluoroboric acid) [4] or regioselective (in 72% perchloric acid) [8] formation of tetrazolium salts followed by slow (four days) isomerization to the 1,4-salts [8] was observed. Such a difference is clearly due to the nature of the quaternizing agents. As known, an equilibrium between the alcohol I and mesityl oxide is established when the individual alcohol I is dissolved in acids [9]; the mesityl oxide is protonated with the formation of the mesomeric cation IV [10]. The 1R-tetrazole II is protonated at the most nucleophilic nitrogen atom $N_{(4)}$ [1, 11], being transformed into the 1R-4H-tetrazolium cation V, which can attack the carbcation IV at both the $C_{(2)}$ and the $C_{(4)}$ atom. The unstable intermediate VI and the 3-(2-methylpentan-4-on-2-yl)-1R-tetrazolium cation (VII) formed here isomerize to the thermodynamically more stable 1-(2-methylpentan-4-on-2-yl)-4R-tetrazolium cation (III).

Data on the quaternization of 1-methyltetrazole (IIa) by the alcohol I in the sample tube of the PMR spectrometer partly confirm the proposed mechanism. Thus, the perchlorate VIIa was detected spectrally in the reaction mixture; the singlet of the 5-H proton of the salt VIIa is observed in its PMR spectrum at 9.91 ppm, whereas the signals of the analogous protons of the individual salt IIIa and the protonated form of 1-methyltetrazole Va under the same conditions are very close and appear in the region of 10.59-10.62 ppm. The

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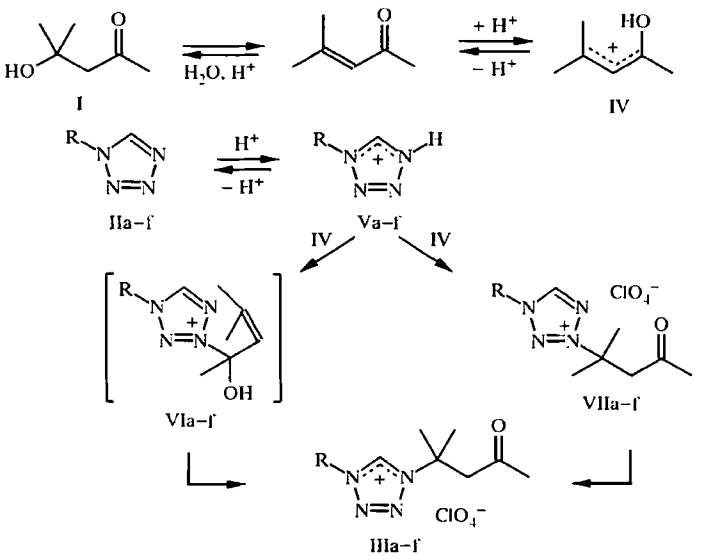
 0009-3122/99/3509-1078$22.00

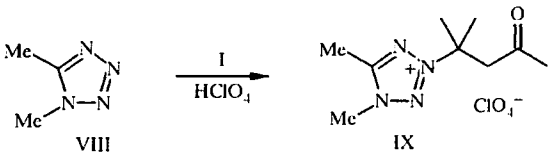
change in the content of the perchlorate VIIa in the mixture during the synthesis indicates that it isomerizes to the salt IIIa. Thus, the mole portion of the salt VIIa in relation to the total amount of the salts IIIa, Va, and VIIa (determined from the intensities of the singlets in the PMR spectra indicated above) first increases to 0.14 (1.5 h after the beginning of the reaction), then decreases (0.12 after 3.5 h, 0.7 after 6.5 h), and reaches 0.01 after 12 h.



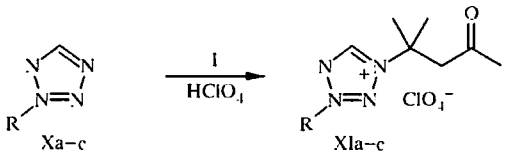
II, III, V–VII a R = Me, b R = *cyclo*-C_6H_{11}, c R = CH_2Ph, d R = Ph, e R = *p*-MeOPh, f R = *m*-$NO_2C_6H_4$

The ease with which the cation IV reacts with 1-substituted tetrazoles prompted us to investigate these reactions in less acidic media. It was shown for the case of the tetrazole IIa that its quaternization in commercial (~60%) and in more dilute (up to 40%) perchloric acid also results in the formation of the 1,4-salt IIIa. In the present case the generation of the carbcation and the heterolysis of the exocyclic N–$C(CH_3)_2CH_2COCH_3$ bond in compounds VII, essential for the occurrence of quaternization and isomerization, probably require a significantly lower concentration of the acid than in the case of the N-*tert*-butylation of tetrazoles [8, 12].

During the alkylation of 1,5-dimethyltetrazole VIII isomerization according to the indicated scheme is probably hindered on account of steric hindrances, and the quaternization process, as also in the case of *tert*-butylation [4], results in the formation of the 1,3,5-trisubstituted salt IX.



The 2-substituted tetrazoles X, which have only one nucleophilic center (the $N_{(4)}$ atom) capable of being quaternized [1, 13], form the 1,3-disubstituted salts XI, as also in reaction with other alkylating agents [1, 4].



X–XI a R = Me, b R = Et, c R = *i*-Pr

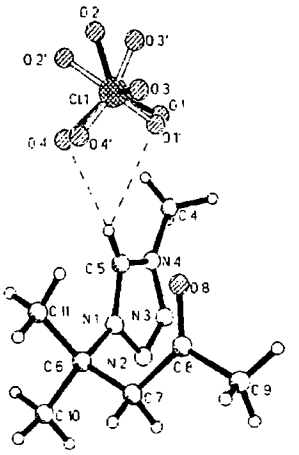


Fig. 1. A fragment of the crystal structure of IIIa.
The dashed lines indicate possible hydrogen bonds.

It is clear that if the substituent R is capable of generating a sufficiently stable carbcation in acidic media the quaternization process will be accompanied by isomerization with migration of the group R to the $N_{(4)}$ atom, and the 1,4-disubstituted tetrazolium salts will be formed together with the 1,3-disubstituted salts. We observed such an effect during the prolonged treatment (seven days) of the 2-*tert*-butyltetrazole and the alcohol I mixture in perchloric acid; a mixture of the isomeric 1-(2-methylpentan-4-on-2-yl)-N-*tert*-butyltetrazoliums but with a preference for the 1,3 isomer was obtained with a 72% yield. [The molar ratio of the isomers (1:0.6) was estimated by comparison of the intensities of the singlets for the 5-H protons, which appear in the PMR spectrum of the mixture at 11.25 and 10.57 ppm.] The analogous process in the case of 1-adamantanol takes place considerably more quickly, and this probably explains the formation of the 1,4-diadamantyltetrazolium salt during the quaternization of 2-adamantyltetrazole with 1-adamantanol in 95% sulfuric acid after only 2 h [6].

Compounds III and XI were assigned as the 1,4- and 1,3-salts respectively on the basis of their spectral (PMR) characteristics (Table 1), compared with the analogous data of known tetrazolium salts [4]. Thus, the chemical shifts δ of the 5-H protons in the PMR spectra of the 1,4- and 1,3-salts differ substantially. They amount to 11.30-11.52 ppm for the 1,4-salts III and 10.52-10.57 ppm for the salts XI under similar conditions. The salt IX was assigned to the 1,3,5-salts on the basis of the similarity of their spectral characteristics (^1H, ^{13}C NMR) to the characteristics of the previously described 1R-3R'-5-methyltetrazolium salts [4, 13].

An X-ray crystallographic analysis carried out for the salt IIIa confirmed its structure proposed on the basis of the PMR spectra. We note that there are no published data on the structure of 1,4-tetrazolium salts. As in the other investigated tetrazole derivatives, the tetrazole ring in the cation is planar. (The average deviation of the ring atoms from the mean-square plane is 0.001 Å.) Attention is drawn to the fact that the lengths of the endocyclic $C_{(5)}$–$N_{(1)}$ and $C_{(5)}$–$N_{(4)}$ bonds in the above-mentioned tetrazolium cation are practically identical (Table 2) and have an intermediate value between the lengths of a double and a single bond, while the shortest is the $N_{(2)}$–$N_{(3)}$ bond, which is close to a double bond in length (1.24 Å). These data make it possible to assign for the 1-(2-methylpentan-4-on-2-yl)-4-methyltetrazolium cation the structural formula of IIIa with the delocalized positive charge in the $N_{(4)}$–$C_{(5)}$–$N_{(1)}$ fragment. The $N_{(1)}$ and $N_{(4)}$ atoms have a planar-trigonal bond configuration; the sums of the bond angles at these atoms are equal to 360.0°. The bond angles in the ring are equal (the angles at the $N_{(2)}$ and $N_{(3)}$ atoms) or close (the angles at the $N_{(1)}$ and $N_{(4)}$ atoms) to the angles of a regular pentagon (108.0°). The smallest angle in the ring (at the $C_{(5)}$ atom) is 106.6(2)°, and the largest (at the $N_{(4)}$ atom) is 109.1(3)°, whereas the bond angles in the ring of the 1,3,5-salts lie in the ranges of 103.0-115.5° [1] and 104.0-114.8° [5]. The obtained data indicate that, in spite of the presence of the bulky substituent at $N_{(1)}$, the structure of the 1,4-disubstituted thiazole ring is close to symmetrical. The lengths of the exocyclic N–C_{alkyl} bonds in the cation IIIa are close to the lengths of the corresponding bonds in the 1,3,5-trisubstituted tetrazolium salts [1, 5]. According to

TABLE 1. The Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				PMR spectrum, δ, ppm	mp, °C	Yield, %
		C	H	N	Cl			
IIa	$C_8H_{15}ClN_2O_5$	34.12 / 33.99	5.23 / 5.35	19.96 / 19.82	12.34 / 12.54	11.34 (1H, s, HC_{ring}); 4.32 (3H, s, N–CH_3); 3.40 (2H, s, CH_2CO); 2.08 (3H, s, CH_3CO) 1.75 (6H, s, $2CH_3$)	120-122	72
IIb	$C_{13}H_{23}ClN_4O_5$	44.34 / 44.51	6.35 / 6.61	16.16 / 15.97	9.89 / 10.11	11.30 (1H, s, HC_{ring}); 4.84 (1H, m, N–CH); 3.39 (2H, s, CH_2CO); 2.09 (3H, s, CH_3CO) 1.76 (6H, s, $2CH_3$); 1.00-2.40 (10H, m, $(CH_2)_5$)	146-148	63
IIc	$C_{14}H_{19}ClN_4O_5$	46.99 / 46.87	5.40 / 5.34	15.49 / 15.62	9.76 / 9.88	11.52 (1H, s, HC_{ring}); 7.20-7.60 (5H, m, H_{arom}); 5.92 (2H, s, $CH_2C_6H_5$) 3.38 (2H, s, CH_2CO); 2.09 (3H, s, CH_3CO); 1.77 (6H, s, $2CH_3$)	113-115	77
IId	$C_{13}H_{17}ClN_4O_5$	45.40 / 45.29	5.07 / 4.97	16.28 / 16.25	10.45 / 10.28	10.73* (1H, s, HC_{ring}); 7.70-7.99 (5H, m, H_{arom}); 3.39 (2H, s, CH_2CO) 2.09 (3H, s, CH_3CO); 1.80 (6H, s, $2CH_3$)	132-134	88
IIe	$C_{14}H_{19}ClN_4O_6$	44.99 / 44.87	5.19 / 5.11	15.19 / 14.95	9.30 / 9.46	10.65* (1H, s, HC_{ring}); 7.83 (2H, m, H_{arom}); 7.20 (2H, m, H_{arom}); 3.89 (3H, s, OCH_3) 3.37 (2H, s, CH_2CO); 2.09 (3H, s, CH_3CO); 1.88 (6H, s, $2CH_3$)	122-124	94
IIf	$C_{13}H_{18}ClN_5O_7$	40.10 / 40.07	4.01 / 4.14	18.09 / 17.97	9.11 / 9.10	10.92* (1H, s, HC_{ring}); 8.77 (1H, m, H_{arom}); 8.59 (1H, m, H_{arom}); 8.38 (1H, m, H_{arom}) 7.99 (1H, m, H_{arom}); 3.41 (2H, s, CH_2CO); 2.11 (3H, s, CH_3CO); 1.90 (6H, s, $2CH_3$)	>112 decomp.	88
IIg	$C_9H_{17}ClN_2O_5$	37.01 / 36.44	5.56 / 5.78	19.17 / 18.88	11.68 / 11.95	4.27 (3H, s, N–CH_3); 3.49 (2H, s, CH_2CO); 2.75 (3H, s, C_{ring}–CH_3); 2.11 (3H, s, CH_3CO) 1.76 (6H, s, $2CH_3$). ^{13}C NMR: 208.54 (C=O), 162.79 (C_{ring}); 73.99 (N–$\underline{C}(CH_3)_2$); 54.43 (CH_2) 40.59 (N–CH_3); 34.49 ($CO\underline{C}H_3$); 30.11 (N–C($\underline{C}H_3)_2$); 13.01 (C_{ring}–$\underline{C}H_3$)	115-117	75
IIe	$C_8H_{15}ClN_2O_5$	33.54 / 33.99	5.06 / 5.35	20.08 / 19.82	12.36 / 12.54	10.52 (1H, s, HC_{ring}); 4.65 (3H, s, N–CH_3); 3.40 (2H, s, CH_2CO); 2.07 (3H, s, CH_3CO) 1.76 (6H, s, $2CH_3$)	133-135	94
IIf	$C_9H_{17}ClN_2O_5$	36.08 / 36.44	5.90 / 5.78	18.78 / 18.88	11.69 / 11.95	10.55 (1H, s, HC_{ring}); 4.98 (3H, q, N–CH_2); 3.39 (2H, s, CH_2CO); 2.03 (3H, s, CH_3CO) 1.77 (6H, s, $2CH_3$); 1.62 (3H, t, $CH_2\underline{C}H_3$)	79-81	63
IIg	$C_{10}H_{19}ClN_4O_5$	38.13 / 38.66	5.79 / 6.16	18.15 / 18.03	11.08 / 11.41	10.57 (1H, s, HC_{ring}); 5.39 (3H, m, N–CH); 3.40 (2H, s, CH_2CO); 2.09 (3H, s, CH_3CO) 1.79 (6H, s, $2CH_3$); 1.66 (6H, t, $(C\underline{H}_3)_2CH$)	69-71	70

* Solvent CD_3CN. When dissolved in DMSO the salts decompose with the release of free nitrogen, similar to the decomposition of 1,4-disubstituted tetrazolium salts by the action of bases [14].

TABLE 2. The Bond Lengths and Bond Angles in the Structure of IIIa

Bond	d, Å	Angle	ω, deg
$N_{(1)}$–$C_{(5)}$	1.317(4)	$C_{(5)}$–$N_{(1)}$–$N_{(2)}$	108.4(2)
$N_{(1)}$–$N_{(2)}$	1.361(3)	$C_{(5)}$–$N_{(1)}$–$C_{(6)}$	131.5(2)
$N_{(1)}$–$C_{(6)}$	1.504(4)	$N_{(2)}$–$N_{(1)}$–$C_{(6)}$	120.1(2)
$N_{(2)}$–$N_{(3)}$	1.276(4)	$N_{(3)}$–$N_{(2)}$–$N_{(1)}$	108.0(2)
$N_{(3)}$–$N_{(4)}$	1.349(3)	$N_{(2)}$–$N_{(3)}$–$N_{(4)}$	107.9(2)
$N_{(4)}$–$C_{(5)}$	1.315(4)	$C_{(5)}$–$N_{(4)}$–$N_{(3)}$	109.1(3)
$N_{(4)}$–$C_{(4)}$	1.468(4)	$C_{(5)}$–$N_{(4)}$–$C_{(4)}$	129.4(3)
$C_{(6)}$–$C_{(11)}$	1.520(4)	$N_{(3)}$–$N_{(4)}$–$C_{(4)}$	121.4(3)
$C_{(6)}$–$C_{(7)}$	1.529(4)	$N_{(4)}$–$C_{(5)}$–$N_{(1)}$	106.6(2)
$C_{(6)}$–$C_{(7)}$	1.534(4)	$N_{(1)}$–$C_{(6)}$–$C_{(10)}$	107.2(3)
$C_{(7)}$–$C_{(8)}$	1.509(4)	$N_{(1)}$–$C_{(6)}$–$C_{(11)}$	108.0(2)
$C_{(8)}$–$O_{(8)}$	1.207(4)	$C_{(10)}$–$C_{(6)}$–$C_{(11)}$	110.4(3)
$C_{(8)}$–$C_{(9)}$	1.499(4)	$N_{(1)}$–$C_{(6)}$–$C_{(7)}$	107.4(2)
$O_{(1)}$–$Cl_{(1)}$	1.43(1)	$C_{(11)}$–$C_{(6)}$–$C_{(7)}$	110.6(3)
$O_{(2)}$–$Cl_{(1)}$	1.339(6)	$C_{(11)}$–$C_{(6)}$–$C_{(7)}$	113.0(3)
$O_{(3)}$–$Cl_{(1)}$	1.441(5)	$C_{(8)}$–$C_{(7)}$–$C_{(6)}$	117.3(2)
$O_{(4)}$–$Cl_{(1)}$	1.401(5)	$O_{(8)}$–$C_{(8)}$–$C_{(9)}$	121.9(3)
$O_{(1')}$–$Cl_{(1)}$	1.39(2)	$O_{(8)}$–$C_{(8)}$–$C_{(7)}$	122.4(3)
$O_{(2')}$–$Cl_{(1)}$	1.51(1)	$C_{(9)}$–$C_{(8)}$–$C_{(7)}$	115.7(3)
$O_{(3')}$–$Cl_{(1)}$	1.32(1)	$O_{(1)}$–$Cl_{(1)}$ –$O_{(2)}$	109.0(6)
$O_{(4')}$–$Cl_{(1)}$	1.27(2)	$O_{(1)}$–$Cl_{(1)}$–$O_{(3)}$	108.1(5)
		$O_{(1)}$–$Cl_{(1)}$–O(4)	108.5(5)
		$O_{(2)}$–$Cl_{(1)}$–$O_{(3)}$	110.5(6)
		$O_{(2)}$–$Cl_{(1)}$–$O_{(4)}$	114.1(6)
		$O_{(3)}$–$Cl_{(1)}$–$O_{(4)}$	106.3(5)
		$O_{(1)}$–$Cl_{(1)}$–$O_{(2')}$	112(2)
		$O_{(1')}$–$Cl_{(1)}$–$O_{(3')}$	116(2)
		$O_{(1')}$–$Cl_{(1)}$–$O_{(4')}$	110(2)
		$O_{(2')}$–$Cl_{(1)}$–$O_{(3')}$	101(1)
		$O_{(2')}$–$Cl_{(1)}$–$O_{(4')}$	101(2)
		$O_{(3')}$–$Cl_{(1)}$–$O_{(4')}$	116(2)

the PMR data the hydrogen atom at the $C_{(5)}$ atom of the salt IIIa is fairly mobile and consequently tends to participate in the formation of a hydrogen bond. However, analysis of the structure indicates the absence of obviously shortened intramolecular and interionic contacts. It is also known that the perchlorate anion is a weakly coordinating anion, as a result of which considerable librational movements are detected in most of the structures. Similar movements probably also occur in our investigated structure; the perchlorate anion is disordered with respect to two positions (Fig. 1). However, it is probably not possible to conclude about the absence of specific interactions between the oxygen atoms of the perchlorate anion and the hydrogen atom at $C_{(5)}$. The shortest distance between the hydrogen atom at $C_{(5)}$ and the oxygen atom $O_{(4)}$ of the perchlorate anion at the position with a population of 0.715(16) is 2.73(3) Å [$d(C_{(5)}\cdots O_{(4)})$ = 3.252(9) Å, $\omega(C_{(5)}–H\cdots O_{(4)})$ = 175(3)°], and with the oxygen atom $O_{(1')}$ of the anion at the position with a population of 0.286(16) it amounts to 2.47(3) Å [$d(C_{(5)}\cdots O_{(1')})$ = 3.13(2) Å, $\omega(C_{(5)}–H\cdots O_{(1')})$ = 132(3)°]. Such a situation probably indicates some fixation of the librational movements of the perchlorate anion as a result of weak C–H···O interactions [15], but it will only be possible to reach a final conclusion after a low-temperature experiment.

EXPERIMENTAL

The NMR spectra of the salts in $(CD_3)_2SO$ solutions were recorded on a Tesla BS-567A spectrometer at 100 MHz (^1H) and 25.142 MHz (^{13}C). The initial 1-substituted thiazoles were obtained by the heterocyclization of the corresponding amines [16]. The 2-methyl-, 2-ethyl-, and 1,5-dimethyltetrazoles were obtained by the alkylation

TABLE 3. The Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Parameters (Å$\times 10^3$) of the Atoms in the Structure of IIIa

Atom	x/a	y/b	z/c	$U_{(eq)}$
$N_{(1)}$	2673(2)	6327(3)	7586(2)	43(1)
$N_{(2)}$	3364(2)	6681(4)	6846(2)	59(1)
$N_{(3)}$	2611(2)	6916(4)	6156(2)	58(1)
$N_{(4)}$	1436(2)	6724(3)	6441(2)	46(1)
$C_{(4)}$	347(3)	6901(5)	5803(3)	58(1)
$C_{(5)}$	1482(3)	6361(3)	7322(2)	45(1)
$C_{(6)}$	3311(3)	6025(3)	8510(2)	46(1)
$C_{(7)}$	3841(3)	7647(4)	8859(2)	50(1)
$C_{(8)}$	2937(3)	9039(3)	8926(2)	49(1)
$C_{(9)}$	3505(4)	10629(4)	9208(3)	69(1)
$C_{(10)}$	4360(3)	4824(4)	8366(3)	63(1)
$C_{(11)}$	2347(3)	5306(4)	9142(2)	54(1)
$O_{(8)}$	1829(2)	8889(3)	8763(2)	60(1)
$O_{(1)}$*	1390(10)	2712(12)	7433(7)	92(3)
$O_{(2)}$*	2920(6)	1385(17)	6723(7)	149(4)
$O_{(3)}$*	1670(12)	3112(8)	5872(4)	116(3)
$O_{(4)}$*	866(7)	738(7)	6373(6)	110(3)
$O_{(1')}$*[2]	1214(19)	2640(40)	7360(19)	102(9)
$O_{(2')}$*[2]	2470(20)	420(20)	6851(14)	117(7)
$O_{(3')}$*[2]	2620(30)	2800(30)	6210(20)	154(11)
$O_{(4')}$*[2]	900(20)	1360(50)	6070(20)	229(19)
$Cl_{(1)}$	1749(1)	1937(1)	6604(1)	56(1)

* Population of position 0.715(16).

*[2] Population of position 0.285(16).

of tetrazole and 5-methyltetrazole with alkyl halides by a method similar to that described in [17]. The 2-isopropyl- and 2-*tert*-butyltetrazoles were obtained by the method in [11].

A crystal of the salt IIIa (0.5 × 0.25 × 0.15 mm) was used for the X-ray crystallographic experiment. A three-dimensional set of intensities was collected on an automatic Nicolet R3m diffractometer: MoKα radiation, graphite monochromator, θ/2θ scan, $2\theta_{max}$ = 55°. The total number of measured reflections was 3096, and the number of unique reflections was 2970 (R_{int} = 0.0406). The crystals of IIIa ($C_8H_{15}N_4OClO_4$) were monoclinic; space group $P2_1/c$. The unit cell parameters were: a = 10.705(4), b = 8.269(3), c = 14.543(6) Å, β = 92.33(3)°, V = 1286.3(9) Å^3, Z = 4, $d_{X\text{-ray}}$ = 1.460 g/cm^3, μ = 3.17 cm^{-1}. The structure was solved by the direct method. The hydrogen atoms were localized from a Fourier difference synthesis (except for the hydrogen atoms of the $C_{(9)}H_3$ methyl group, the positions of which were calculated by geometry.) The refinement was made by full-matrix least-squares treatment with allowance for the anisotropy of the thermal vibrations of the nonhydrogen atoms. The hydrogen atoms were refined isotropically (the methyl group $C_{(9)}H_3$ in terms of a "riding" model). The final values of the uncertainty factor were: R_1 = 0.0601, wR_2 = 0.1542 [$I = 4\sigma(I)$]; R_1 = 0.0865, wR_2 = 0.1927 (all data); goodness of fit GooF = 1.062. All the calculations were performed with the SHELX-97 software [18-20]. The coordinates and equivalent isotropic temperature factors of the atoms in structure IIIa are given in Table 3.

General Method for the Synthesis of the Salts III, IX, and XI. To a solution of the tetrazole II, VIII, or X (0.06 mol) in perchloric acid (25 ml, 72%) diacetone alcohol (7.14 g, 0.07 mole) was added. The mixture was kept at room temperature for 12 h [48 h for the tetrazoles X]. The product was precipitated by the addition of 50 ml of water. In the case of the tetrazoles Ia,b the product was isolated by the addition of 30 ml of 2-propanol and cooling the solution to 0°C. The product was recrystallized from ethanol. The salt IIIf was recrystallized from a 1:1 mixture of 2-propanol and acetonitrile.

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