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Reactions Between Azolium Salts and Nucleophilic Reagents

VI. Preparation of 1,2-Disubstituted 1,2,3-Triazolium Salts and Their Reactions with Sodium Hydroxide and Methoxide

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2-Substituted 1,2,3-triazoles, *e.g.* (I), react with methyl fluorosulfonate to give 1,2-disubstituted 1,2,3-triazolium fluorosulfonates, *e.g.* (II). The latter are brominated in alkaline solution with *N*-bromoacetamide. The 5-bromo compounds (VI) thus formed, react with hydroxide or methoxide ions to form 1,2-disubstituted 1,2,3-triazol-5-ones. The reaction routes may be predicted from the deuterium exchange rates of the heteroaromatic protons of (II). The bromination power of some 1,2-disubstituted-bromo-1,2,3-triazolium salts has been studied.

1-Substituted 1,2,3-triazoles react readily with methyl tosylate, producing 1,3-disubstituted 1,2,3-triazolium tosylates in high yields.[1,2] In contrast, 2-substituted 1,2,3-triazoles (I), when treated with methyl tosylate, methyl iodide, or dimethyl sulfate, do not react or give quaternary salts in low yield only. This difference in reactivity agrees with the fact that 1-substituted 1,2,3-triazoles are much more basic than the isomeric 2-substituted compounds.[3] Consequently, the quaternization of the latter requires a stronger alkylation agent. Methyl fluorosulfonate has been shown to be an effective methylating agent,[4] and it was therefore decided to try whether 2-substituted 1,2,3-triazoles could be quaternized using this compound.

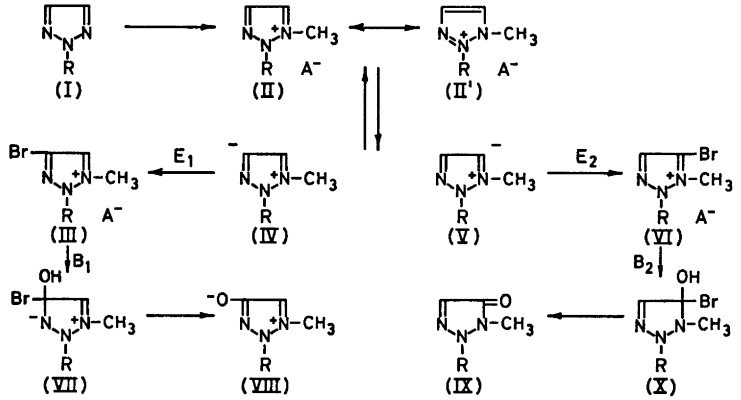
It was found that treatment of 2-methyl-1,2,3-triazole (Ia) with methyl-fluorosulfonate afforded 1,2-dimethyl-1,2,3-triazolium fluorosulfonate (IIa) in 79 % yield. Similarly, 2-phenyl-1,2,3-triazole (Ib) gave 1-methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (IIb) (99 %), and 2-methyl-4,5-dibromo-1,2,3-triazole (XIa) afforded 1,2-dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (XIIa) (99 %). The 1,2-dimethyl-compounds (IIa) and (XIIa) showed two different methyl group signals in the NMR-spectra (Table 1), indicating that the two methyl groups are situated on different nitrogen atoms. The high field methyl group signal of (IIa) is assigned to the 1-methyl group, since it is broadened due to coupling with the 5-proton. The broadening almost

Table 1. NMR spectra of 1,2-disubstituted 1,2,3-triazolium salts in deuterium oxide with DSS as an internal standard.

Compound	H-4 ppm	H-5 ppm	N_1-CH_3 ppm	N_2-CH_3 ppm	J_{H4H5} Hz
1,2-Dimethyl-triazolium fluorosulfonate (IIa)	8.32	8.77	4.47	4.55	0.7
1,2-Dimethyl-4,5-dibromo-triazolium fluorosulfonate (XIIa)			4.45	4.62	
1-Methyl-2-phenyl-triazolium fluorosulfonate (IIb)	8.62	9.10	4.40		1.2
The 1,2-dimethyl-4-bromo-triazolium salt (IIIa)		9.01	4.51	4.59	
The 1,2-dimethyl-5-bromo-triazolium salt (VIa)	8.37		4.50	4.55	

disappeared when the proton was exchanged with deuterium (see later). The low field position of the 2-methyl group seems reasonable due to the deshielding by the two adjacent nitrogen atoms. Similarly, the high field methyl group signal of the dibromo-compound (XIIa) (Table 1) is attributed to the 1-methyl group.

The methyl-phenyl-compound (IIb) showed two different heteroaromatic proton signals (Table 1), indicating that the methyl- and the phenyl-groups are situated on different nitrogen atoms. The low field heteroaromatic signal was a broad doublet, whereas the high field signal was a sharp doublet. This indicates that the high field signal is due to the 4-proton which couples to the



Scheme 1.

5-proton, exclusively. The 5-proton couples to both the 4-proton and to the methyl group. It seems reasonable that the 5-proton is the most deshielded, since the positive charge of the ring is mesomerically delocalized on N-1 and N-2 (*cf.* (II) and (II')). Similar assignments were made for the ring protons of (IIa) (Table 1).

Like the heteroaromatic protons of 1,3-disubstituted 1,2,3-triazolium salts.[1,2] the heteroaromatic protons of 1,2-disubstituted salts (II) have acidic properties, and can be exchanged with deuterium in aqueous base. The lone-pair orbitals of the carbanions (IV) and (V) are coplanar with the triazole-ring, and overlap with the $2p$-orbitals is therefore impossible. Consequently, (IV) and (V) are expected to be stabilized by inductive factors only.[2] The positive charge of the ring is mesomerically delocalized over N-1 and N-2, and consequently, the transition state leading to the anion (V) is expected to be more stable than that leading to the anion (IV). Therefore, the 5-proton should be more acidic than the 4-proton. In fact, the exchange rate of the 5-proton in (IIa) or (IIb) is about 2×10^5 times faster than the exchange rate of the 4-proton (Table 2).

Table 2. Deuterium exchange rates of 1,2-disubstituted 1,2,3-triazolium salts.

Compound	Proton	pD	$T_{½}$[a] min	Relative[b] rate
1,2-Dimethyl-triazolium chloride (IIa)	H_4	12.58[c]	233[e]	1.08×10^{-4}
	H_5	7.96[d]	73	14
1-Methyl-2-phenyl-triazolium fluorosulfonate (IIb)	H_4	12.58[c]	54[e]	4.7×10^{-3}
	H_5	7.96[d]	9.5	111

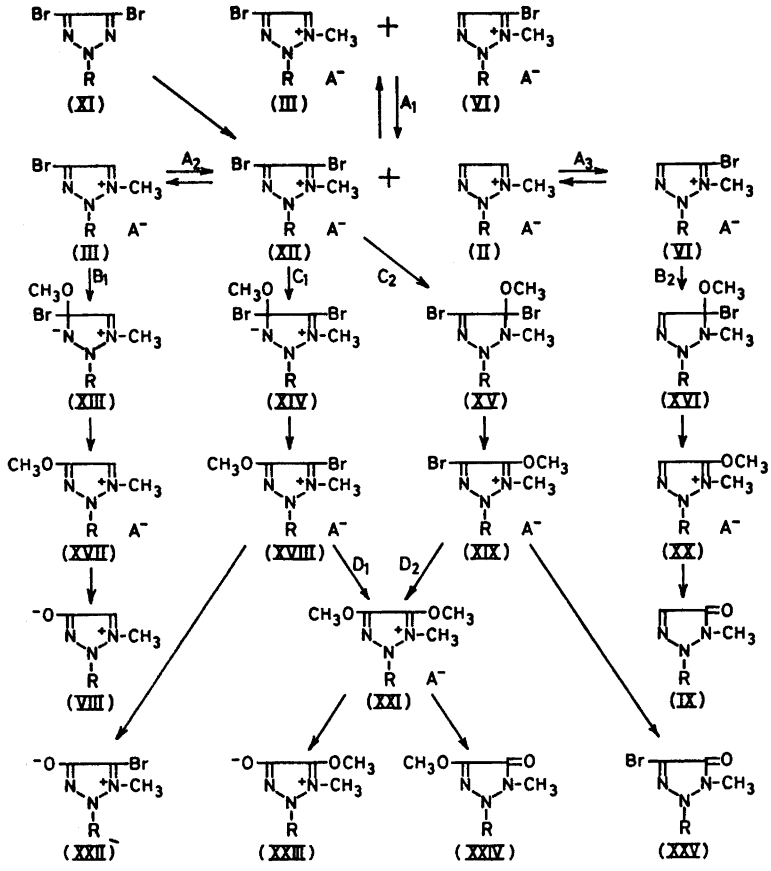
[a] Rates measured by NMR at 36°.
[b] In comparison to 1,3-dimethyl-1,2,3-triazolium tosylate.[1]
[c] Glycine buffer.
[d] Phosphate buffer.
[e] Approximate value, since decomposition takes place to a minor extent during the exchange reaction.

The nature of the substituent in the 2-position seems to influence the exchange rates of the 4- and 5-protons. Thus a 2-phenyl group increases the acidity of the 5-proton 7.7 times that of a 2-methyl group (Table 2).

The heteroaromatic ring of 1,3-disubstituted 1,2,3-triazolium salts is brominated by *N*-bromoacetamide in alkaline solution.[1,2,5] The triazolium salt looses a proton giving an anion, which then, apparently, is attacked by a bromonium ion. The faster the exchange rate of the heteroaromatic proton, the faster the bromination. According to the exchange rates (Table 2), the 1,2-disubstituted 1,2,3-triazolium salts should be brominated *ca.* 2×10^5 times faster at the 5-position than at the 4-position, *i.e.*, k_{E2} should be equal to *ca.* 2×10^5 k_{E1}.

The initially formed 4-(5)-bromo-1,3-disubstituted 1,2,3-triazolium salts react readily with aqueous sodium hydroxide with substitution, possibly by

an AE-mechanism.[1,2,5] The substitution is slower than the initial bromination. Substitution of (III) and (VI) would be expected to give the intermediates (VII) and (X), respectively. The transition state leading to the polar intermediate (VII) is less stable than the transition state leading to (X), and therefore substitution of (VI) is expected to proceed at a higher rate than the substitution of (VII), *i.e.*, k_{B2} is expected to be larger than k_{B1}. Actually, the difference in reactivity between bromine in the 4- and 5-positions of 1,2-disubstituted 1,2,3-triazolium salts should be comparable to the difference in reactivity between the isosteric 4- and 3-bromo-1,2-disubstituted pyrazolium salts. The 4-bromo-pyrazolium salts react with sodium hydroxide under forced conditions only, whereas the 3-bromo-pyrazolium salts react readily at room temperature.[6] To conclude, the reaction of 1,2-disubstituted 1,2,3-triazolium salts (II) with *N*-bromoacetamide and sodium hydroxide is expected



Scheme 2.

Table 3. NMR-spectra in deuteriochloroform with TMS as an internal standard, and infrared absorptions of the carbonyl groups of 1,2-disubstituted 1,2,3-triazol-5-ones.

Compound	IR cm^{-1}	NMR H−5 ppm	NMR O-CH_3[b] ppm	NMR $J_{^{13}C-H}$ Hz	NMR N_1-CH_3 ppm	NMR $J_{^{13}C-H}$ Hz	NMR N_2-CH_3 ppm	NMR $J_{^{13}C-H}$ Hz
1,2-Dimethyl-triazol-5-one[a] (IXa)	1650	7.06			3.53	142	3.62	142
1,2-Dimethyl-4-bromo-triazol-5-one (XXVa)	1665				3.54	143	3.57	143
1,2-Dimethyl-4-methoxy-triazol-5-one	1675		4.06	150	3.12	142	3.44	143
1-Methyl-2-phenyl-triazol-5-one (IXb)	1655	7.25			3.48	143		
1-Methyl-2-phenyl-4-methoxy-triazol-5-one (XXIVb)	1700		3.76	149	3.27	141		

[a] Data have been reported previously,[7] but are repeated here for comparison.
[b] In cases where both N-CH_3 and O-CH_3 groups are present, the absorptions have been identified through the $^{13}C-H$ coupling constants.[8]

to give 1,2-disubstituted 1,2,3-triazol-5-ones (IX) *via* the 5-bromo-compounds (VI). In fact, 1,2-dimethyl-1,2,3-triazolium fluorosulfonate (IIa), when treated with *N*-bromoacetamide and sodium hydroxide at room temperature, afforded the 1,2-dimethyl-5-bromo-1,2,3-triazolium salt (VIa). (VIa) was identified through its NMR-spectrum, which shows a single proton signal in the region where 4-protons of other 1,2-disubstituted 1,2,3-triazolium salts absorb (Table 1). In addition, a minor amount of 1,2-dimethyl-4-bromo-1,2,3-triazole-5-one (XXVa) was isolated. The identification of (XXVa) is described below. (XXVa) probably arises by substitution of the dibromo-compound (XIIa), formed by bromination of the monobromo-compound (VIa) with *N*-bromoacetamide.*

The bromo-compound (VIa) undergoes substitution when treated with sodium hydroxide, yielding the previously described [7] 1,2-dimethyl-1,2,3-triazol-5-one (IXa). The formation of (IXa) as the sole product indicates that the mono-bromo-compound (VIa) undergoes substitution much faster than it halogenates itself (see later).

Similarly, 1-methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (IIb), *N*-bromo-acetamide, and sodium hydroxide afforded 1-methyl-2-phenyl-1,2,3-triazole-5-one (IXb), identified through its spectra (Table 3). The NMR-spectrum shows a methyl group signal in the region where the methyl groups of 1,2-dimethyl-1,2,3-triazol-5-one (IXa) absorb. The signal of the 4-proton is in the region of the 4-protons of other 1,2-disubstituted-1,2,3-triazol-5-ones.[7-9] The IR-spectrum of (IXa) showed a carbonyl group absorption at 1655 cm^{-1}, characteristic of other 1,2-disubstituted-1,2,3-triazol-5-ones.[7-9] The strong polar carbonyl group of the isomeric 1,2-disubstituted-1,2,3-triazolio-4-oxides (VIII) are expected to absorb at a lower frequency. Thus the polar carbonyl groups of 1,3-disubstituted-1,2,3-triazolio-4-oxides absorb at *ca.* 1635 cm^{-1}.[8,9] In contrast to (IXa), (IXb) was formed readily at room temperature, suggesting that the 2-phenyl group stabilizes the transition state involved to give the intermediate (X), thereby facilitating substitution.

1,2-Dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (XIIa) (Scheme 2), when treated with sodium hydroxide at room temperature, afforded 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa). Apparently, the bromine in the 4-position stabilizes the transition state leading to the intermediate (X) (Scheme 1), thereby facilitating substitution of the bromine at C-5. (XXVa) was identified through its IR- and NMR-spectra (Table 3), which showed absorptions in the regions characteristic of 1,2,3-triazol-5-ones.

When 1,2-disubstituted 1,2,3-triazolium salts (II) are treated with *N*-bromoacetamide in sodium methoxide, the initially formed bromo-compounds (III) or (VI) are expected to give the methoxy-compounds (XVII) or (XX) (Scheme 2) by nucleophilic substitution. As before, k_{B2} is expected to be larger than k_{B1}. Consequently, the 1,2-disubstituted 5-methoxy-1,2,3-triazolium salt (XX) should be formed more rapidly than the isomeric 4-methoxy-compound (XVII). (XX), like the 1,3-disubstituted 4-methoxy-1,2,3-triazolium

* The formation of the bromo-triazolone (XXVa) by bromination of the triazolone (IXa) may be excluded, since a separate experiment indicated that (IXa) does not react with *N*-bromoacetamide under the conditions of the reaction.

salts,[5] is expected to dequaternize under the conditions of the reaction by loosing either the *O*-methyl or one of the *N*-alkyl groups. However, 1,2-disubstituted-3-methoxy-pyrazolium salts, which are isosteric with (XX), dequaternize, loosing the *O*-methyl group forming pyrazol-3-ones as the sole products.[6] Consequently, (XX) is expected to give 1,2-disubstituted-1,2,3-triazol-5-ones (IX), exclusively. In fact, 1,2-dimethyl-1,2,3-triazolium fluorosulfonate (IIa), *N*-bromoacetamide (molar ratio 1 : 1), and sodium methoxide afforded 1,2-dimethyl-1,2,3-triazol-5-one (IXa) in quantitative yield. When the molar ratio between (IIa) and *N*-bromoacetamide was 1 : 2.5, 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa) was formed as a byproduct. The latter is probably produced *via* bromination of the intermediate bromo-compound (VIa) or of the methoxy-compound (XX). A bromine atom or a methoxy-group increases the exchange rate of adjacent ring protons in 1,3-disubstituted-1,2,3-triazolium salts by a factor of *ca.* 450 and 2, respectively.[2] Bromine atoms in pyrazolium salts have the same effect.[6] It is therefore most likely that it is the bromo-compound (VIa), and not the methoxy-compound (XX), which is brominated. This gives the dibromo-compound (XIIa), which subsequently undergoes substitution of the more reactive 5-bromine atom, giving the bromo-methoxy-compound (XIXa). The latter finally dequaternizes, producing the bromo-triazolone (XXVa).

The pure dibromo-compound (XIIa), when treated with sodium methoxide, afforded the bromo-triazolone (XXVa) as the major product. Besides, a byproduct, which is assumed to be 1,2-dimethyl-4-methoxy-1,2,3-triazol-5-one (XXIVa), was isolated. (XXIVa) was identified through its spectra (Table 3). The NMR-spectrum showed three methyl-group signals. The magnitude of the $J_{^{13}C-H}$ coupling constants indicated the presence of two *N*-methyl groups and one methoxy-group.[8] The IR-spectrum showed a carbonyl absorption in the region characteristic of 1,2-disubstituted 1,2,3-triazol-5-ones.[7,9] In addition to dequaternization, the initially formed bromo-methoxy-compound (XIXa) probably reacts to a minor extent with further substitution, producing the dimethoxy-compound (XXIa), which subsequently looses an *O*-methyl group. Hence, the product must be either the triazolone (XXIVa) or the 1,2-disubstituted-1,2,3-triazolio-4-oxide (XXIIIa). The carbonyl group absorption in infrared indicates that the product is the triazolone (XXIV), and not a triazolio-oxide, which would be expected to absorb at a low frequency.

The ratio between (XXIVa) and (XXVa) indicates that dequaternization of (XIXa) is faster than substitution of this compound. Similar results were found in the 1,3-disubstituted-1,2,3-triazolium salt series.[8,10] The fact that no bromo-triazolone (XXVa) is formed when the molar ratio between 1,2-dimethyl-1,2,3-triazolium fluorosulfonate and *N*-bromoacetamide is 1 : 1 (see above) indicates that the substitution of the bromo-compound (VIa) is much faster than the bromination of this compound. Similar results were found in the 1,3-disubstituted 1,2,3-triazolium salts series.[8,10] 1-Methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (IIb), when treated with *N*-bromoacetamide (molar ratio 1 : 1) and sodium methoxide, gave 1-methyl-2-phenyl-1,2,3-triazol-5-one (IXb) as the major product. In addition, a byproduct, assumed to be 1-methyl-2-phenyl-4-methoxy-1,2,3-triazol-5-one (XXIVb), was isolated. This was identified by IR- and NMR-spectra (Table 3). As above,

(XXIVb) is probably formed *via* (VIb), (XIIb), (XIXb), and (XXIb). The formation of (XXIVb) and the lack of bromo-triazolone (XXVb) indicates that the bromo-methoxy-compound (XIXb) is substituted much faster than it dequaternizes. This suggests that the 2-phenyl-group stabilizes the transition state, and thus facilitates substitution.

4-Bromo-1,3-disubstituted 1,2,3-triazolium salts have brominating properties in alkaline solution.[1,2,5,10] The bromine is probably cleaved off as a bromonium ion, leaving a carbanion. Factors that stabilize this carbanion will increase the rate of formation of the bromonium ion. Hence, the relative ability to brominate may be proportional to the rate of the proton abstraction of the corresponding salt, in which halogen is replaced by hydrogen. Thus, according to the exchange rates of (IIa) (Table 2), the 5-bromine of the dibromo-compound (XIIa) should be more easily cleaved off as a bromonium ion than the 4-bromine. This was confirmed by the fact that (XIIa), when treated with sodium borohydride in aqueous solution, afforded the 1,2-dimethyl-4-bromo-1,2,3-triazolium salt (IIIa) in quantitative yield. The product was identified by its NMR-spectrum (Table 1), which showed a heteroaromatic proton signal in the region characteristic of H-5 of 1,2-disubstituted 1,2,3-triazolium salts. In order to investigate further the bromination properties of the dibromo-compound (XIIa), it was treated with the unsubstituted compound (IIa) in sodium hydroxide or methoxide. In analogy with the results obtained with the 1,3-disubstituted triazolium salts, this would be expected to lead to interbromination, followed by subsequent substitution.[1,10] However, no interbromination took place in the present case, but (XIIa) reacted by direct substitution, giving (XXVa). This indicates that the rate of substitution of (XIIa) is very high compared to the rate of interbromination. It might similarly be expected that reaction of the monobromo-compounds (IIIa) and (VIa) with sodium hydroxide or methoxide would proceed *via* an interhalogenation reaction.[1,10] However, as mentioned above, (VIa) gave only the substitution product (IXa) in these reactions. Under similar conditions, (IIIa) gave only destruction products.

As seen from the exchange rates, the 5-bromo-compound (VIa) is expected to be a better bromonium ion donor than the isomeric 1,3-dimethyl-4-bromo-1,2,3-triazolium salt, and the 4-bromo-compound (IIIa) should be a better bromonium ion acceptor than the isomeric 1,3-dimethyl-4-bromo-1,2,3-triazolium salt. In fact, a 1 : 1 mixture of the two monobromo-compounds (VIa) and (IIIa), when treated with sodium hydroxide or methoxide, gave a mixture of 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa) and the 1,2-dimethyl-1,2,3-triazolium salt (IIa), indicating that (VIa) has brominated (IIIa), forming a 1 : 1 mixture of the unsubstituted triazolium salt (II) and the dibromo-compound (XIIa). The latter subsequently produces the bromo-triazolone (XXVa) by substitution. The experiments indicate that the rate of the halogenation of the 4-bromo-compound (IIIa) with the 5-bromo-compound (VIa) is at least of the same order of magnitude as the rate of the substitution of the 5-bromo-compound (VIa).

EXPERIMENTAL

Thin layer and column chromatography were carried out as described previously.[11] NMR-spectra were obtained on a Varian A-60 instrument. Position of signals are given in ppm (δ-values), relative to TMS, when not otherwise stated. Deuteriochloroform was used as a solvent, unless otherwise stated. Melting points are uncorrected.

Preparation of 1,2-disubstituted 1,2,3-triazolium salts

1,2-Dimethyl-1,2,3-triazolium fluorosulfonate (*IIa*) *and chloride* (*IIa*, $A^- = Cl^-$). 2-Methyl-1,2,3-triazole (Ia)[3] (2.37 g) and methyl fluorosulfonate [4] (3.20 ml) were mixed with cooling to 0°. The mixture was kept at 0° for 2 h, and was then kept at room temperature overnight. The product was washed with ether (3 × 25 ml), dissolved in water (30 ml), and washed with methylene chloride (3 × 10 ml). The aqueous solution was filtered through activated carbon. The water was then removed *in vacuo*, yielding 4.42 g (79 %) of 1,2-dimethyl-1,2,3-triazolium fluorosulfonate (IIa) as a colourless oil. Reprecipitation from methanol-ether and drying gave colourless crystals, m.p. 53 – 58°. A minute amount of an acidic impurity could only be removed by conversion to the corresponding chloride (IIa, $A^- = Cl^-$): (IIa) (2.38 g) was dissolved in water and passed through Amberlite IRA 400 (150 ml) on the chloride form. The water was removed *in vacuo*, and the residue was recrystallized from methanol-ether. This gave 1.48 g (92 %) of 1,2-dimethyl-1,2,3-triazolium chloride (IIa, $A^- = Cl^-$) as colourless crystals, m.p. 211° (dec.). (Found: C 36.15; H 5.98; N 31.21; Cl 26.51. Calc. for $C_4H_8N_3Cl$: C 35.96; H 6.04; N 31.46; Cl 26.54.)

1-Methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (*IIb*). 2-Phenyl-1,2,3-triazole (Ib)[12] (1.90 g) and methyl fluorosulfonate (1.45 ml) were kept at room temperature for 24 h. The crystals were then washed with ether affording 3.37 g (99 %) of 1-methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (IIb) as colourless crystals, m.p. 153 – 169°. Recrystallization from methanol-ether raised the melting point to 170 – 173°. (Found: C 41.82; H 3.98; N 16.40; S 12.29; F 7.42. Calc. for $C_9H_{10}N_3O_3SF$: C 41.73; H 3.89; N 16.21; S 12.37; F 7.32.)

1,2-Dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (*XIIa*). 2-Methyl-4,5-dibromo-1,2,3-triazole (XIa)[1] (1.52 g) and methyl fluorosulfonate (0.70 ml) were heated to 60° for 1 h, then to 100° for 2 h, and were kept at room temperature for 24 h. Washing with ether then gave 2.21 g (99 %) of 1,2-dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (XIIa) as colourless crystals, m.p. 189 – 190°. Recrystallization from methanol-ether raised the melting point to 196 – 199°. (Found: C 13.69; H 1.86; N 11.70; S 8.89; Br 45.15; F 5.22. Calc. for $C_4H_6N_3O_3SBr_2F$: C 13.53; H 1.70; N 11.84; S 9.03; Br 45.02; F 5.35.)

The 1,2-dimethyl-4-bromo-1,2,3-triazolium salt (*IIIa*). (XIIa) (440 mg) in water (4.40 ml) was heated to 40°, and sodium borohydride (89 mg) was added with stirring during 5 min. The stirring was continued for 30 min at room temperature Hydrochloric acid was then added to pH *ca.* 3, and the water was removed *in vacuo*. The residue contained the 1,2-dimethyl-4-bromo-1,2,3-triazolium salt (IIIa), identified by its NMR-spectrum (see p. 2094). (IIIa) could not be separated from the inorganic salts.

Reactions with sodium hydroxide

1,2-Dimethyl-1,2,3-triazolium fluorosulfonate (*IIa*) (861 mg), *N*-bromoacetamide (1.50 g), and 1 N sodium hydroxide (14.0 ml) were kept at room temperature for 14 days. The solvent was then removed *in vacuo* at room temperature, and the residue was extracted with boiling ethyl acetate (5 × 10 ml). The ethyl acetate was removed, leaving 558 mg of colourless crystals which were chromatographed on silica gel (10 g), using ethyl acetate as eluent. The first fraction contained 434 mg of *N*-methyl-*N'*-acetyl urea as colourless crystals, m.p. 175 – 176° (reported [13] m.p. 179 – 180°). The compound was identified by its IR- and NMR-spectra. The next fraction contained 41 mg (5 %) of 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa), identical with the material described below.

The residue from the ethyl acetate extraction contained the 1,2-dimethyl-5-bromo-1,2,3-triazolium salt (VIa), identified by its NMR-spectrum (see p. 2092). (VIa) could not be separated from the inorganic salts.

1-Methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (*IIb*) (306 mg), *N*-bromoacetamide (205 mg), and 1 N sodium hydroxide (3.90 ml) were kept at room temperature for 14 days. The solvent was then removed *in vacuo*, and the residue was extracted with boiling ethyl acetate (5 × 10 ml). Removal of the ethyl acetate gave 120 mg of a red oil which was chromatographed on a column of silica gel (20 g), using ethyl acetate as eluent. Two minor fractions were collected, and the column was then eluted with ethyl acetate-methanol (1 : 1). This gave 61 mg of colourless oil which was crystallized from ether, affording 46 mg (22 %) of 1-methyl-2-phenyl-1,2,3-triazol-5-one (IXb), m.p. 74 – 75°. (Found: C 61.86; H 5.21; N 23.93. Calc. for $C_9H_9N_3O$: C 61.70; H 5.18; N 23.98.)

The 1,2-dimethyl-5-bromo-1,2,3-triazolium salt (*VIa*). Crude (VIa), prepared from 1,2-dimethyl-1,2,3-triazolium fluorosulfonate (IIa) (861 mg), was heated to reflux with 1 N sodium hydroxide (14.0 ml) for 3 h. Removal of the solvent, extraction with ethyl acetate, filtering through activated carbon, and removal of the ethyl acetate gave 183 mg (37 %) of 1,2-dimethyl-1,2,3-triazol-5-one (IXa) as a colourless oil. Reprecipitation from ether gave colourless, hygroscopic crystals, m.p. 59 – 67°. IR- and NMR-spectra were identical with those of the material described previously.[7]

The 1,2-dimethyl-4-bromo-1,2,3-triazolium salt (*IIIa*). Crude (IIIa), prepared from 1,2-dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (XIIa) (440 mg), and 1 N sodium hydroxide (4.40 ml) were heated to reflux for 3 h. The mixture was worked up as described in the preceding experiment. The ethyl acetate extract contained 6 mg of a yellow oil, which was not identified further.

The 1,2-dimethyl-4-bromo-1,2,3-triazolium salt (*IIIa*) *and the 1,2-dimethyl-5-bromo-1,2,3-triazolium salt* (*VIa*). Crude (IIIa), prepared from (XIIa) (344 mg), and crude (VIa), prepared from (IIa) (191 mg), were kept at room temperature for 14 days with 1 N sodium hydroxide (3.30 ml). Working up as before gave an ethyl acetate extract which was purified by column chromatography on silica gel (10 g), using ethyl acetate as eluent. This gave 22 mg (12 %) of 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa), identified as above. The column was then eluted with ethyl acetate-methanol (1 : 1), giving 4 mg (3 %) of 1,2-dimethyl-1,2,3-triazol-5-one (IXa), identified through its IR- and NMR-spectra. The residue from the ethyl acetate extraction contained the 1,2-dimethyl-1,2,3-triazolium salt (IIa) and the 5-bromo-derivative (VIa) (1 : 1.4). In addition, sodium formate was present. (IIa) and (VIa) were identified by NMR by adding, one by the other, the pure compounds to the solution. The presence of (VIa) and (IXa) is probably due to partially basecatalysed decomposition of the 4-bromo-compound (IIIa), leaving a corresponding amount of (VIa). The latter, in its turn, gives (IXa) by substitution.

1,2-Dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (*XIIa*) (389 mg) and 1 N sodium hydroxide (3.50 ml) were kept at room temperature for 14 days (or, alternatively, heated to 100° for 5 min). Removal of the water and extraction with ethyl acetate as before, followed by filtration through activated carbon, and recrystallization from ethyl acetate-hexane gave 184 mg (88 %) of 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa) as colourless crystals, m.p. 89 – 90°. Further recrystallization from ether raised the melting point to 96 – 97°. (Found: C 25.17; H 3.31; N 21.69; Br 41.59. Calc. for $C_4H_6N_3OBr$: C 25.02; H 3.15; N 21.89; Br 41.62.)

1,2-Dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (*XIIa*) *and 1,2-dimethyl-1,2,3-triazolium fluorosulfonate* (*IIa*). A mixture of (XIIa) (491 mg), (IIa) (272 mg), and 1 N sodium hydroxide (4.40 ml) was kept at room temperature for 14 days. The mixture was worked up as before. The ethyl acetate extract was filtered through activated carbon, and the solvent was removed. The residue, which contained 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa) as the sole product, as shown by NMR, was recrystallized from ether, yielding 240 mg (91 %) of (XXVa), m.p. 89 – 90°. IR- and NMR-spectra proved the identity with the material described above. The residue from the ethyl acetate extraction contained unchanged (IIa) as shown by NMR.

In another experiment, an NMR-spectrum was obtained *ca.* 1 min after the addition of the sodium hydroxide. The spectrum indicated that all of the dibromo-compound (XIIa) had disappeared, whereas the unsubstituted salt (IIa) was unchanged.

Reactions with sodium methoxide

1,2-Dimethyl-1,2,3-triazolium fluorosulfonate (IIa). *A.* (IIa) (863 mg), *N*-bromoacetamide (638 mg) (molar ratio 1 : 1). and 1 N sodium methoxide (14.0 ml) were kept at room temperature for 14 days. The solvent was then removed, and the residue was extracted with boiling ethyl acetate (5 × 10 ml). The solution was filtered through activated carbon. Removal of the solvent and reprecipitation from ether afforded 497 mg (100 %) of 1,2-dimethyl-1,2,3-triazol-5-one (IXa) as a colourless, hygroscopic oil. IR- and NMR-spectra were identical with those of the material described previously.[7]

B. Similarly, (IIa) (193 mg), *N*-bromoacetamide (339 mg), and 1 N sodium methoxide (3.15 ml) gave a crude product which was chromatographed on silica gel (10 g) with ethyl acetate as an eluent. The first fraction contained 130 mg of *N*-methyl-*N'*-acetyl urea, identified through its melting point, and IR- and NMR-spectra. The next fraction contained 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa). The material was dissolved in ethyl acetate, filtered through activated carbon, and recrystallized from ether. This yielded 77 mg (41 %) of the pure material, identified as described above. The column was then eluted with ethyl acetate-methanol (1 : 1). This gave 1,2-dimethyl-1,2,3-triazol-5-one (IXa), which was dissolved in ethyl acetate, filtered through activated carbon, and reprecipitated from ether; yield 54 mg (49 %).

1-Methyl-2-phenyl-1,2,3-triazolium fluorosulfonate (IIb) (467 mg), *N*-bromoacetamide (260 mg) (molar ratio 1 : 1), and 1 N sodium methoxide (5.80 ml) were kept at room temperature for 14 days. The mixture was worked up as described above. The ethyl acetate extract was filtered through activated carbon, the solvent was removed, and the residue was recrystallized twice from ethyl acetate-hexane. This afforded 254 mg (82 %) of 1-methyl-2-phenyl-1,2,3-triazol-5-one (IXb), m.p. 70 – 73°. The combined mother liquors were evaporated to dryness, and the residue was chromatographed on silica gel (10 g), using ethyl acetate as eluent. The first fraction contained 16 mg (4 %) of 1-methyl 2-phenyl-4-methoxy-1,2,3-triazol-5-one (XXIVb) as a yellow oil, which could not be induced to crystallize. The material was reprecipitated twice from hexane. The compound was very hygroscopic, and a correct analysis could therefore not be obtained. (Found: C 58.66; H 6.40; N 16.53. Calc. for $C_{10}H_{11}N_3O_2$: C 58.53; H 5.40; N 20.48.) The next fraction contained a minor amount of unidentified material. The column was then eluted with ethyl acetate-methanol (1 : 1), affording 29 mg (9 %) of 1-methyl-2-phenyl-1,2,3-triazol-5-one (IXb), m.p. 69 – 70°, bringing the total yield of this compound up to 91 %. Further recrystallization of (IXb) raised the melting point to 74 – 75°.

The 1,2-dimethyl-4-bromo-1,2,3-triazolium salt (IIIa). Crude (IIIa), prepared from 230 mg of 1,2-dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (XIIa), and 1 N sodium methoxide (2.20 ml) were kept at room temperature for 14 days. The mixture was worked up as described above. The ethyl acetate extract contained 40 mg of a brown oil. An NMR-spectrum indicated the presence of several compounds, none of which were identical with the triazolio-oxide (VIIIa) of the triazolone (IXa). Boiling of the mixture of (IIIa) and 1 N sodium methoxide (the same amounts as above) for 3 h, and working up as above, gave 32 mg of a brown oil. An NMR-spectrum indicated the presence of several compounds, none of which were the triazolio-oxide (VIIIa) or the triazolone (IXa).

The 1,2-dimethyl-4-bromo-1,2,3-triazolium salt (IIIa) and the 1,2-dimethyl-5-bromo-1,2,3-triazolium salt (VIa). Crude (IIIa), prepared from (XIIa) (476 mg), and crude (VIa), prepared from (IIa) (191 mg), were kept at room temperature for 14 days with 1 N sodium methoxide (4.5 ml). Working up, as in the experiment with sodium hydroxide, afforded 31 mg (12 %) of 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa) and 66 mg (43 %) of 1,2-dimethyl-1,2,3-triazol-5-one (IXa), identified as above. The residue from the ethyl acetate extraction contained the 1,2-dimethyl-triazolium salt (IIa) and sodium formate. (IIa) was identified by NMR by adding of the pure substance to the solution. Most likely, (IXa) is formed by substitution of the starting material (VIa), remaining after partial decomposition of the 4-bromo-compound (IIIa).

1,2-Dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (XIIa) (665 mg) and 1 N sodium methoxide (6.00 ml) were kept at room temperature for 14 days. The solvent was removed, and the residue was extracted as above. The crude product was purified by preparative TLC, eluting twice with ethyl acetate-chloroform (1 : 1). The upper zone (R_F-value 0.28) contained 37 mg (14 %) of 1,2-dimethyl-4-methoxy-1,2,3-triazol-5-one

(XXIVa) as a yellow oil. Recrystallization from ether gave colourless crystals, m.p. 57 – 58°. (Found: C 42.12; H 6.47; N 29.24. Calc. for $C_5H_9N_3O_3$: C 41.94; H 6.33; N 29.36). The lower zone (R_F-value 0.14) contained 193 mg (54 %) of 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa) as colourless crystals, m.p. 93 – 96°. Recrystallization from ether raised the melting point to 96 – 97°. IR- and NMR-spectra were identical with those of the material described above.

1,2-Dimethyl-4,5-dibromo-1,2,3-triazolium fluorosulfonate (XIIa) and 1,2-dimethyl-1,2,3-triazolium fluorosulfonate (IIa). (XIIa) (385 mg), (IIa) (231 mg), and 1 N sodium methoxide (3.45 ml) were kept at room temperature for 14 days. The mixture was worked up as before. The ethyl acetate extract contained 262 mg of a yellow oil. An NMR-spectrum indicated the presence of 1,2-dimethyl-4-bromo-1,2,3-triazol-5-one (XXVa) and traces of the 4-methoxy-triazol-5-one (XXIVa). The compounds were identified by adding, one by the other, the pure substances to the solution. The NMR-spectrum showed no absorptions at lower field than δ 5. Consequently, the triazolone (IXa) or the triazolio-oxide (VIIIa) is not present in the product.

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