# Reactions Between Azolium Salts and Nucleophilic Reagents

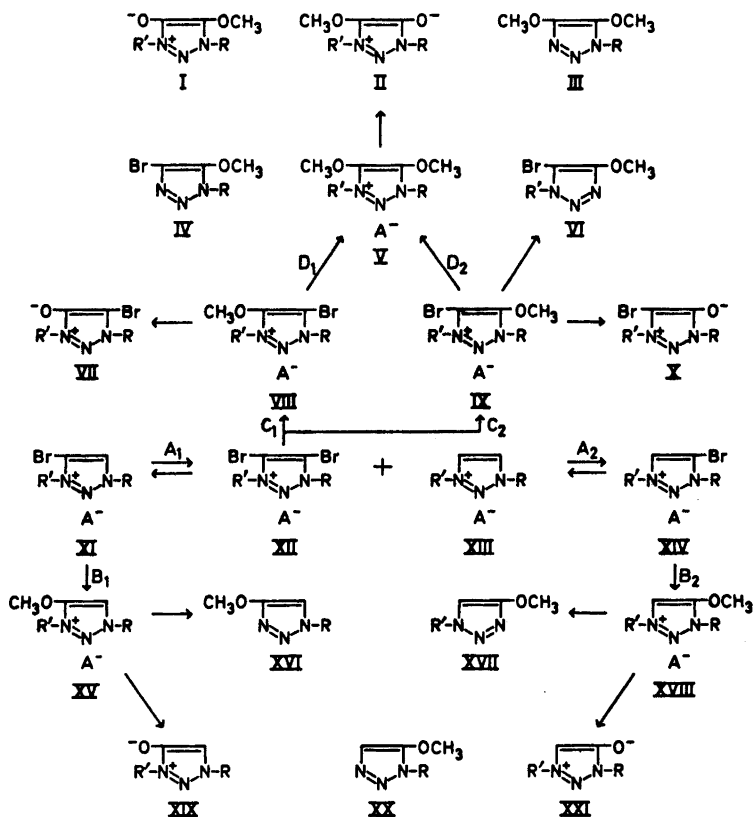## V. 1,3-Disubstituted 1,2,3-Triazolium Salts and Sodium Methoxide

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1-Methyl-3-benzyl-monobromo-1,2,3-triazolium salts (XIb) or (XIVb), when dissolved in sodium methoxide, produce an equilibrium mixture also containing the dibromo (XIIb), and the unsubstituted salt (XIIIb). The bromo salts undergo nucleophilic substitution *via* the routes $B_1$, $B_2$, and $C_2$ (Scheme 1). Non-brominated triazolium salts (XIII), upon reaction with $N$-bromoacetamide and sodium methoxide, react similarly to the dibromo derivative (XII), or to a mixture of the latter and the monobromo compounds, (XI) and (XIV). The base-catalyzed deuterium exchange rates of the heteroaromatic protons in triazolium salts provide information about their relative reactivity as halonium ion acceptors or donors, and apparently thereby about their reactivity towards nucleophilic overall displacement of halogen. In many cases, predictions as to product distribution thereby become possible. Dealkylation of methoxytriazolium salts has been studied, and the relative tendencies of various alkyl groups to undergo detachment are discussed.

In a previous paper,[1] the reactions between 1,3-dimethyl-1,2,3-triazolium salts and sodium methoxide were described. Here, the corresponding reactions of some unsymmetrically substituted 1,2,3-triazolium salts with sodium methoxide are reported. In aqueous sodium hydroxide, 1-benzyl-3-methyl-4-bromo-1,2,3-triazolium tosylate (XIb) and 1-methyl-3-benzyl-4-bromo-1,2,3-triazolium tosylate (XIVb) equilibrate *via* the dibromo (XIIb) and the unsubstituted compound (XIIIb).[2]

After treatment of (XIb) or (XIVb) with 1 N sodium methoxide in methanol, seven products were isolated in addition to the bromine-free salt (XIIIb) (Scheme 1 and Table 1). Of these, 1-benzyl-3-methyl-1,2,3-triazolio-4-oxide (XIXb) and 1-benzyl-4-methoxy-1,2,3-triazole (XVIb) arise by $O$- and $N$-demethylation, respectively, of the methoxy salt (XVb), formed by displacement on (XIb) (route $B_1$). Analogously, 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (XXIb) and 1-methyl-4-methoxy-1,2,3-triazole (XVIIb) arise from the salt (XVIIIb), formed from (XIVb) (route $B_2$). No bromo-triazolio-oxides were detected, but 1-methyl-4-methoxy-5-bromo-1,2,3-triazole (VIb) was

2

Scheme 1

I    II    III

IV    V    VI

D₁    V    D₂

VII    VIII    IX    X

C₁    C₂

A₁    XI    XII    +    XIII    A₂    XIV

B₁    B₂

XV    XVI    XVII    XVIII

XIX    XX    XXI

|   | R | R' |
|---|---|---|
| a | $CH_3$ | $CH_3$ |
| b | $CH_2C_6H_5$ | $CH_3$ |
| c | $CH_2C_6H_5$ | $CH_2C_6H_5$ |
| d | $C_6H_5$ | $CH_3$ |

$A^- = p\text{-}CH_3C_6H_4SO_3^-$, when not otherwise stated

isolated, the latter arising from the methoxy-bromo salt (IXb), formed from (XIIb) (route $C_2$). No products derived from the isomeric methoxy-bromo compound (VIIIb) were detected (route $C_1$), for reasons to be discussed later. The ratio between products formed *via* routes $B_1$ and $B_2$, as well as routes $C_1$ and $C_2$, was about 8.4 (Table 1). This is in contrast to the reaction with hydroxide ions, which did not at all lead to products formed *via* routes $B_1$ or

*Table 1.* Reactions of 1,2,3-triazolium salts with sodium methoxide.

| Starting material | Mechanism route | % | Intermediate methoxy-tri-azolium salt | Triazolio-oxide (leaving group $O\text{-}CH_3$) | % | Methoxy triazole (leaving group $R-N_3$) | % | Methoxy triazole (leaving group $R-N_1$) | % | Other products |
|---|---|---|---|---|---|---|---|---|---|---|
| (XIa)[c] | B | 100 | (XVa) | (XIXa) | 100 | (XVIa) | 0 | (XXa) | 0 | |
| | C | 0 | (VIIIa) | | | | | | | |
| (XIb) | B₁ | 26 | (XVb) | (XIXa) | 22 | (XVIa) | 4 | (XXa) | 0 | (XIIIb) 29 % |
| | B₂ | 20 | (XVIIIb) | (XXIb) | 15 | (XVIIb) | 5 | (XXb) | 0 | 1-benzyl-4-bromo-triazole 6 % |
| | C₁ | 0 | (VIIIb) | | | | | | | 1-benzyl-triazole 6 % |
| | C₂ | 5 | (IXb) | (Xb) | 0 | (VIb) | 5 | (IVb) | 0 | |
| | D₁+D₂ | 0 | (Vb) | | | | | | | |
| (XIVb) | B₁ | 21 | (XVb) | (XIXb) | 18 | (XVIa) | 3 | (XXa) | 0 | (XIIIb) 37 % |
| | B₂ | 17 | (XVIIIb) | (XXIb) | 12 | (XVIIb) | 5 | (XXb) | 0 | 1-benzyl-4-bromo-triazole 5 % |
| | C₁ | 0 | (VIIIb) | | | | | | | 1-benzyl-triazole 5 % |
| | C₂ | 5 | (IXb) | (Xb) | 0 | (VIb) | 5 | (IVb) | 0 | |
| | D₁+D₂ | 0 | (Vb) | | | | | | | |
| (XIIIb)[a] | B₁ | 10 | (XVb) | (XIXb) | 10 | (XVIb) | 0 | (XXa) | 0 | |
| | B₂ | 12 | (XVIIIb) | (XXIb) | 12 | (XVIIb) | 0 | (XXb) | 0 | |
| | C₁ | 0 | (VIIIb) | | | | | | | |
| | C₂ | 26 | (IXb) | (Xb) | 0 | (VIb) | 26 | (IVb) | 0 | |
| | D₁+D₂ | 0 | (Vb) | | | | | | | |
| (XIIIc)[a] | B | 34 | (XVc) | (XIXc) | 9 | (XVIc) | 20 | (XXc) | 5 | 1-benzyl-4-bromo-triazole 27 % |
| | C | 0 | (VIIIc) | | | | | | | 1-benzyl-triazole 6 % |
| (XIIId)[a] | B₁ | 8 | (XVd) | (XIXd) | 8 | (XVId) | 0 | | | |
| | B₂ | 27 | (XVIIId) | (XXId) | 27 | | | (XXd) | 0 | |
| | C₁ | 4 | (VIIId) | (VIId) | 4 | (IVd) | 0 | | | |
| | C₂ | 19 | (IXd) | (Xd) | 19 | | | (IVd) | 0 | |
| | D₁+D₂ | 16 | (Vd) | (Id) | 0 | (IIId) | 0 | | | |
| | | | | (IId) | 16 | | | | | |
| (XIIId)[b] | B₁ | 27 | (XVd) | (XIXd) | 27 | (XVId) | 0 | | | |
| | B₂ | 58 | (XVIIId) | (XXId) | 58 | | | (XXd) | 0 | |
| | C | 0 | | | | | | | | |
| (XIIa)[c] | C | 71 | (VIIIa) | (VIIa) | 71 | (IVa) | 0 | (VIa) | 0 | (XIXa) 5 % |
| | D₁+D₂ | 16 | (Va) | (Ia) | 16 | (IIIa) | 0 | (IIIa) | 0 | |
| (XIIb) | C₁ | 0 | (VIIIb) | | | | | | | (XIXb) 32 % |
| | C₂ | 27 | (IXb) | (Xb) | 0 | (VIb) | 27 | (IVb) | 0 | (XXIb) 12 % |
| | D₁+D₂ | 0 | (Vb) | | | | | | | (XVIb) 10 % |

[a] With *N*-bromoacetamide added (molar ratio 1:2.5). [b] With *N*-bromoacetamide added (molar ratio 1:1).
[c] Data have been published previously [1] but are shown here for comparison.

$B_2$.[2] As found for dimethyl-triazolium salts,[1] halogenation of the unsubstituted salt (XIIIb) with the dibromo salt (XIIb) is faster than the substitution of (XIIb); this is faster than the substitution of the monobromo compounds (XIb) or (XIVb), which again is faster than the selfhalogenation of (XIb) or (XIVb). Furthermore, 1-benzyl-1,2,3-triazole and 1-benzyl-4-bromo-1,2,3-triazole were isolated, probably formed by dequaternization of the salts (XIIIb) and (XIb). In fact, thermal dequaternization of (XIIIb, $A^- = I^-$) has been reported by Gompper.[3]

Treatment of the pure dibromo salt (XIIb) with sodium methoxide yielded 1-methyl-4-methoxy-5-bromo-1,2,3-triazole (VIb), formed via route $C_2$ (Table 1). No bromo-triazolio oxide (XVIIb) or compounds formed by demethylation of the isomeric methoxy-bromo compound (VIIIb) (route $C_1$) were found. Additional isolated reaction products were: 1-benzyl-4-methoxy-1,2,3-triazole (XVIb), 1-benzyl-3-methyl-1,2,3-triazolio-4-oxide (XIXb), and 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (XXIb), most likely formed via the monobromo compounds (XIb) and (XIVb), which, in turn, may arise from reduction of the starting material (XIIb) by methoxide ions.[1] Another obvious possibility is that the dibromo salt (XIIb) initially gives the bromo-methoxy salts (VIIIb) and (IXb), and that these, like (VIIIa),[1] are able to oxidize methoxide ions.

Similarly, 1,3-disubstituted triazolium salts (XIII), and $N$-bromo-acetamide, in a molar ratio of 1:2.5, reacted to the dibromo compounds (XII) in the presence of methoxide (Table 1). Again, 1-methyl-3-phenyl-1,2,3-triazolium tosylate (XIIId), $N$-bromoacetamide, and sodium methoxide afforded a mixture of 1-methyl-3-phenyl-5-bromo-1,2,3-triazolio-4-oxide (Xd), 1-phenyl-3-methyl-5-bromo-1,2,3-triazolio-4-oxide (VIId), 1-methyl-3-phenyl-1,2,3-triazolio-4-oxide (XXId), 1-phenyl-3-methyl-1,2,3-triazolio-4-oxide (XIXd), and 1-methyl-3-phenyl-5-methoxy-1,2,3-triazolio-4-oxide (IId) (Table 1). The structure of the latter product followed from its spectroscopical characteristics. Thus, the NMR-spectrum showed two $CH_3$-signals identified by the $J_{^{13}C-H}$ coupling constants to be an $O-CH_3$ signal and an $N-CH_3$ signal, respectively.[4] The IR-spectrum showed an absorption at 1650 cm$^{-1}$, characteristic of 1,2,3-triazolio-oxides.[4,5] Furthermore, (IId) reacted as a 1,3-dipole with dimethyl acetylenedicarboxylate to give 1-*methyl*-3,4-dimethoxycarbonyl-5-methoxy-pyrazole, whereas the isomeric methoxy-triazolio-oxide (Id) should give the corresponding 1-*phenyl*-pyrazole.[6] The bromo-oxides (VIId) and (Xd) may be formed by demethylation of the salts (VIIId) and (IXd), arising by substitution of the dibromo salt (XIId) or by bromination of the methoxy compounds (XVd) or (XVIIId).* (IId) may arise by demethylation of the dimethoxy compound (Vd), formed by substitution of the bromo-methoxy compound (VIIId) and/or (IXd).

In the molar ratio 1 : 1, 1,3-disubstituted 1,2,3-triazolium salts (XIII) and $N$-bromoacetamide reacted similarly to a mixture of the monobromo compounds (XI) and (XIV). Thus, (XIIId), $N$-bromoacetamide, and sodium methoxide afforded a mixture of the isomeric triazolio-oxides (XXId) and (XIXd) besides uncharged starting material (Table 1). No bromo-triazolio-

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* The formation of the bromo-triazolio-oxides (VIId) and (Xd) by bromination of the triazolio-oxides (XIId) and (XXId) may be excluded, since (XIXd) and (XXId) do not react with $N$-bromoacetamide under the conditions of the reaction.

oxides (VIId) or (Xd) could be detected, a fact which is easily rationalized by assuming that any dibromo compound (XIId) formed halogenates unchanged (XIIId) before substitution occurs and that interhalogenation of the monobromo compounds (XId) and (XIVd) is slower than substitution. 1,4-Dimethyl-3-phenyl-1,2,3-triazolium tosylate (XXIIb) and 1-phenyl-3,4-dimethyl-1,2,3-triazolium tosylate (XXIIa) reacted sluggishly with N-bromoacetamide and sodium hydroxide.[2] With N-bromoacetamide and sodium methoxide, however, 1-phenyl-3,5-dimethyl-1,2,3-triazolio-4-oxide (XXVb) and 1,5-dimethyl-3-phenyl-1,2,3-triazolio-4-oxide (XXVa) were obtained in high yield at room temperature (Scheme 2). The smooth reaction with sodium

Scheme 2



| | R | R' | R'' |
|---|---|---|---|
| a | CH$_3$ | C$_6$H$_5$ | CH$_3$ |
| b | C$_6$H$_5$ | CH$_3$ | CH$_3$ |
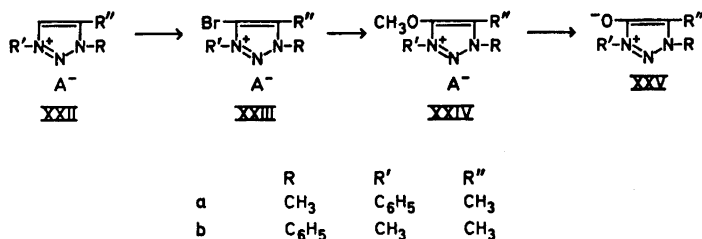
methoxide may be due to faster substitution of the intermediate bromo compounds by methoxide ions. The above-mentioned experiments demonstrate the synthetic value of the preparation of triazolio-oxides from unsubstituted triazolium salts and N-bromoacetamide.

Returning to the final products (XIX) and (XVI), or (XXI) and (XVII), formed from the methoxy compound (XV), or (XVIII) by demethylation, it appears unlikely that an equilibrium should exist between the dimethylated products, e.g. (XIX) and (XVI), and the methoxy compound, e.g. (XV). Consequently, the observed product distribution reflects the relative aptitude for group detachment. The results summarized in Table 1 indicate that the most labile group in methoxy-triazolium salts, unsubstituted in 5-position, is normally the O-methyl group, followed by N-benzyl groups adjacent to an O-methyl group. (In fact, the 3-benzyl group of the 1,3-dibenzyl-4-methoxytriazolium salt (XVc) is more labile than the O-methyl group.) Then follow: an N-methyl group adjacent to an O-methyl group, an N-benzyl group at 1-position, and, finally, an N-methyl group at 1-position. Introduction of bromine at 5-position makes an N-benzyl group at 1-position more labile than an O-methyl group. An O-methyl group adjacent to an N-phenyl group is more labile than an O-methyl group adjacent to an N-methyl group.

The methoxy compounds (XV) and (XVIII) are therefore intermediates in the formation of the final products (XIX), (XVI), (XXI), and (XVII). The halogenation of the unsubstituted salt (XIII) by the dibromo compound (XII) is fast, compared with the substitution of the monobromo compounds (XI) and (XIV). The ratio between products formed via B$_1$ and B$_2$ (Table 1)

may therefore provide information about the relative reactivity of the halogen atoms of (XI) and (XIV) towards substitution, most likely proceeding according to the addition-elimination mechanism shown in Scheme 3.[2] As suggested by the previously reported exchange rates,[2] the transition state leading to an ylide with a negative charge adjacent to an $N$-benzyl group is 1.2 times more stable than that carrying the negative charge adjacent to an $N$-methyl group. Consequently, the transition state involved to give (XXVIb) is expected to be about 1.2 times more stable than that corresponding to (XXVIIb). Hence, the ratio between the rates of substitution of (XI) and (XIV) could be expected to be 1.2, as is indeed the fact. This ratio is reversed, however, when 1-methyl-3-benzyl-triazolium tosylate (XIIIb) is treated with $N$-bromoacetamide and sodium methoxide. The bromonium ion acceptor properties of 1,2,3-triazolium salts have been shown previously to be proportional to the deuterium exchange rates of the heteroaromatic protons.[2] Consequently, bromination in the 4-position of (XIIIb), giving (XIVb), should be 1.2 times faster than the bromination in the 5-position with formation of (XIb). If the bromination of the unsubstituted salt (XIIIb) by $N$-bromoacetamide is slow, compared with the substitution of the monobromo compounds (XIb) and (XIVb), the ratio between the products formed *via* the routes $B_1$ and $B_2$ should be reversed as observed. In fact, it was shown by NMR-spectra that bromination of (XIIIa) by $N$-bromoacetamide is slow, compared with substitution of the bromo compound (XIa), thus confirming the above predictions.

According to the exchange rates of the heteroaromatic protons of (XIIId)[1] and the discussion above, the calculated ratio between products formed *via* route $B_1$ and $B_2$ is 0.42, when 1-methyl-3-phenyl-1,2,3-triazolium tosylate (XIIId) is treated with $N$-bromoacetamide (molar ratio 1 : 1) and sodium methoxide. The experimentally found ratio was 0.45.

Since substitution of the dibromo compounds (XII) probably proceeds as shown in Scheme 3, the ratio between products formed *via* the routes

Scheme 3



R and R', see Scheme 1
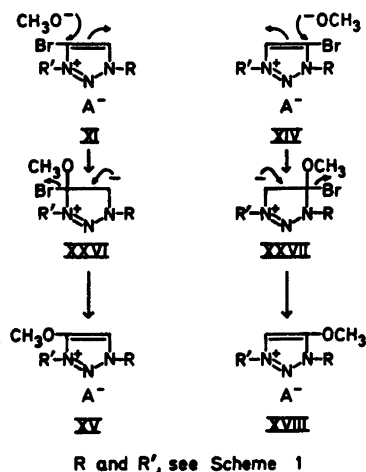
$C_1$ and $C_2$ can be expected to be equal to the ratio between the exchange rates of the heteroaromatic protons in the corresponding unsubstituted salt (XIII). However, further substitution of the intermediate bromo-methoxy salts, (VIII) and (IX), competes with demethylation, giving rise to the dimethoxy compound (V) which, in its turn, undergoes demethylation to, e.g., (II). Consequently, competition between demethylation and substitution of the bromo-methoxy compounds may influence the ratio of products formed via the routes $C_1$ and $C_2$. When unsubstituted triazolium salts (XIII) and N-bromoacetamide are used as starting materials, brominations to give (XI) or (XIV) may be slow, compared with substitution to give (XV) and (XVIII). Consequently, (VIII) and (IX) may be formed, at least in part, by bromination of (XV) and (XVIII), respectively, and the relative rates of the bromination reactions may influence the ratio between the bromo-triazolio-oxides or bromo-methoxy-triazoles formed. As a consequence, predictions as to the product ratio are normally not possible. In the methyl-phenyl-triazolium salt series the ratio is 0.21 (Table 1). In the methyl-benzyl-triazolium salt series, no reactions via the path $C_1$ are observed, for the following reasons. The intermediate bromo-methoxy compound (IXb) is expected to undergo dequaternization much faster than the isomeric salt (VIIIb). Conceivably, (VIIIb) would rather undergo substitution, leading to the dimethoxy compound (Vb), which, however, was not observed, as were not its expected dialkylation products (Ib), (IIb), (IIIa), or (IIIb). In contrast to other 1,2,3-triazolio-4-oxides, (IId) is not very stable (see above). (Ib) and (IIb) might be even less stable, decomposing under the conditions of the reaction. (Dimethoxy-1,2,3-triazoles, such as (IIIa) or (IIIb), have not yet been isolated.)

On the basis of the few substrates studied, the above results suggest that the relative reactivity of halogen atoms of mono- or dihalo-1,2,3-triazolium salts towards substitution by methoxide ions is approximately inversely proportional to the exchange rates of the ring protons of the corresponding unsubstituted salts. In addition, the available data indicate that when unsubstituted 1,2,3-triazolium salts are treated with N-bromoacetamide and methoxide, the ratio between the nucleophilic substitution products is approximately proportional to the exchange rates of the ring protons of the starting materials. No predictions can normally be made about the ratio between products formally derived from dibromo-compounds (XII). Further experiments will be necessary to unequivocally prove the proposed relationship between exchange rates and reactivity towards nucleophilic substitution, which, on the other hand, may apply to other azolium salts and nucleophilics as well.

<div align="center">EXPERIMENTAL</div>

*1-Benzyl-3-methyl-4-bromo-1,2,3-triazolium tosylate (XIb) and sodium methoxide.* (XIb)[2] (772 mg) and 1 N sodium methoxide (5.90 ml) were heated to reflux for 3 h. The solvent was removed cautiously (some of the products are rather volatile), and the residue was extracted 5 times with boiling chloroform (10 ml). Cautious removal of the chloroform left an oil, which was extracted 4 times with boiling ethyl acetate (5 ml). This left a crystalline residue, which was dissolved in water and passed through Amberlite IRA 400 (4 ml), regenerated with 1 N hydrobromic acid. Removal of the water afforded 132 mg (29 %) of 1-methyl-3-benzyl-1,2,3-triazolium bromide (XIIIb, $A^- = Br^-$), m.p.

184°. IR- and NMR-spectra were identical with those of the material described previously.[2] From the ethyl acetate extract the solvent was removed cautiously. This left a red oil (271 mg), which was chromatographed on silica gel (15 g), using benzene-ether (4 : 1) as an eluent. The first fraction contained 26 mg (6 %) of 1-benzyl-4-bromo-1,2,3-triazole, m.p. 64 — 67°. Recrystallization from ether-hexane raised the melting point to 74°. Melting point, IR-, and NMR-spectra were identical with those of the material described previously.[2] The second fraction contained 17 mg (5 %) of 1-methyl-4-methoxy-5-bromo-1,2,3-triazole (VIb) as colorless crystals, m.p. 96 — 103°. Recrystallization from ether with cooling in dry ice raised the melting point to 104°. Melting point, IR-, and NMR-spectra were identical with those of the material described previously.[7] The third fraction contained 14 mg (4 %) of 1-benzyl-4-methoxy-1,2,3-triazole (XVIb) as colorless crystals, m.p. 50 — 51°. IR- and NMR-spectra proved the identity with the material described previously.[7] The next fraction contained 14 mg (5 %) of 1-benzyl-1,2,3-triazole as a colorless oil. IR- and NMR-spectra were identical with those of an authentical sample.[2] The next fraction contained 10 mg (5 %) of 1-methyl-4-methoxy-1,2,3-triazole (XVIIb) as a colorless oil, identical with the material described previously. The column was then eluted with ethyl acetate (ca. 80 ml). This gave a fraction containing 6 mg of a colorless oil. An NMR-spectrum indicated the presence of several compounds, which were not identified further. Finally, the column was eluted with ethyl acetate-methanol (1 : 1). This gave 126 mg of a mixture of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (XXIb) and 1-benzyl-3-methyl-1,2,3-triazolio-4-oxide (XIXb). The two compounds could not be separated by chromatographic methods. They were identified by NMR-spectra, adding one by the other the pure substances [5,4] to the solution. This indicated the ratio between (XXIb) and (XIXb) to be 0.68, corresponding to 15 and 22 % yield, respectively.

*1-Methyl-3-benzyl-4-bromo-1,2,3-triazolium tosylate (XIVb) and sodium methoxide.* Similarly, (XIVb) [2] (628 mg) and 1 N sodium methoxide (4.80 ml) were heated to reflux for 3 h and worked up as described above. This gave 134 mg (37 %) of 1-methyl-3-benzyl-1,2,3-triazolium bromide (XIIIb, $A^- = Br^-$), m.p. 178 — 179°, 16 mg (5 %) of 1-benzyl-4-bromo-1,2,3-triazole, 13 mg (5 %) of 1-methyl-4-methoxy-5-bromo-1,2,3-triazole (VIb), 9 mg (3 %) of 1-benzyl-4-methoxy-1,2,3-triazole (XVIb), 12 mg (5 %) of 1-benzyl-1,2,3-triazole, and 8 mg (5 %) of 1-methyl-4-methoxy-1,2,3-triazole (XVIIb). All compounds were identified through melting points, IR-, and NMR-spectra as above. Finally, a mixture of 1-methyl-3-benzyl-1,2,3-triazolio-oxide (XXIb) and the isomeric triazolio-oxide (XIXb) (245 mg) was obtained. The ratio between (XXIb) and (XIXb) was 0.75, as shown by NMR. This corresponds to 12 and 18 % yield, respectively.

*1-Methyl-3-benzyl-4,5-dibromo-1,2,3-triazolium tosylate (XIIb) and sodium methoxide.* Similarly, (XIIb) [2] (245 mg) and 1 N sodium methoxide (1.60 ml) were heated to reflux for 3 h and worked up as described above. No 1-methyl-3-benzyl-1,2,3-triazolium salt (XIIIb) was observed. The first fraction from the chromatographical separation on 15 g of silica gel contained 9 mg of colorless oil, which was not identical with 1-benzyl-4-bromo-1,2,3-triazole. The NMR-spectrum was very similar to that of this compound. Signals corresponding to 2 protons at $\delta$ 5.60, 5 protons at $\delta$ 7.36, and 1 proton at $\delta$ 7.44 were present. Consequently, the compound may be 1-benzyl-5-bromo-1,2,3-triazole. However, the structure was not proved. The following fractions contained 25 mg (27 %) of 1-methyl-4-methoxy-5-bromo-1,2,3-triazole (VIb) and 9 mg (10 %) of 1-benzyl-4-methoxy-1,2,3-triazole (XVIb). The compounds were identified through melting points, IR-, and NMR-spectra as above. Finally, a mixture of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (XXIb) and the isomeric triazolio-oxide (XIXb) (41 mg) was obtained. The ratio between (XXIb) and (XIXb) was 0.38, as shown by NMR. This corresponds to 12 and 32 % yield, respectively.

*1-Methyl-3-benzyl-1,2,3-triazolium tosylate (XIIIb), N-bromoacetamide, and sodium methoxide.* (XIIIb) [2] (762 mg), N-bromoacetamide (763 mg), and 1 N sodium methoxide (9.00 ml) were kept at room temperature for 14 days and worked up as described for the reaction between 1-benzyl-3-methyl-4-bromo-1,2,3-triazolium tosylate and sodium methoxide. No starting material (XIIIb) was observed. The first fraction from the chromatographical separation on 30 g of silica gel contained 47 mg of a brown oil, which was not identified further. The following fractions contained 110 mg (26 %) of 1-methyl-4-methoxy-5-bromo-1,2,3-triazole (VIb) and 20 mg (5 %) of 1-benzyl-4-methoxy-1,2,3-triazole (XVIb). The compounds were identified through melting points, IR-, and NMR-spectra as above. Finally, a mixture of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (XXIb)

and the isomeric triazolio-oxide (XIXb) (92 mg) was obtained. The ratio between (XXIb) and (XIXb) was 1.2, as shown by NMR. This corresponds to 12 and 10 % yield, respectively.

*1-Methyl-3-phenyl-1,2,3-triazolium tosylate (XIIId), N-bromoacetamide, and sodium methoxide. A.* (XIIId)[2] (378 mg), N-bromoacetamide (158 mg) (molar ratio 1 : 1), and 1 N sodium methoxide (5.10 ml) were kept at room temperature for 14 days. The solvent was then removed and the residue extracted with boiling chloroform (5 × 10 ml). Removal of the chloroform gave an oil. TLC and NMR-spectra indicated that neither (VIId) nor (Xd) were present. The oil was purified by preparative TLC (two 40 × 20 cm plates, 1 mm layer of Merck silica gel $pF_{254}$) using acetone as eluent (4 elutions). The fraction with high $R_F$-value contained 116 mg (58 %) of 1-methyl-3-phenyl-1,2,3-triazolio-4-oxide (XXId), m.p. 87 – 90°. Recrystallization from ethyl acetate-hexane with cooling in dry ice raised the melting point to 95 – 98°. IR- and NMR-spectra were identical with those of the material described previously.[5] The other fraction contained 54 mg (27 %) of 1-phenyl-3-methyl-1,2,3-triazolio-4-oxide (XIXd), m.p. 154 – 158°. Recrystallization from ether as described below for 1,4-dimethyl-3-phenyl-1,2,3-triazolio-4-oxide gave colorless crystals, m.p. 160 – 162°. Melting point, IR-, and NMR-spectra proved the identity with the material described previously.[2]

*B.* Similarly, (XIIId) (522 mg), N-bromoacetamide (544 mg) (molar ratio 1 : 2.5), and 1 N sodium methoxide (7.00 ml) were kept at room temperature for 14 days and worked up as described above. The first fraction from the chromatographical separation on silica gel (20 g), using ethyl acetate as eluent, contained 76 mg (19 %) of 1-methyl-3-phenyl-5-bromo-1,2,3-triazolio-4-oxide (Xd) as colorless crystals, m.p. 84 – 89°. Recrystallization from ethyl acetate-ether raised the melting point to 106 – 108°. Melting point, IR-, and NMR-spectra were identical with those of the material described previously.[2] The next fraction contained 52 mg (16 %) of 1-methyl-3-phenyl-5-methoxy-1,2,3-triazolio-4-oxide (IId) as an oil, which was dissolved in ethyl acetate and filtered through activated carbon. Removal of the solvent left a colorless oil which could not be induced to crystallize. The material is very hydroscopic and a correct analysis could therefore not be obtained. (Found: C 55.70; H 5.59. Calc. for $C_{10}H_{11}N_3O_2$: C 58.53; H 5.40.) The NMR-spectrum showed an $NCH_3$ group signal at $\delta$ 3.81 ($J_{13C-H}=144$ Hz) and an $OCH_3$ group signal at $\delta$ 4.22 ($J_{13C-H}=150$ Hz). The next fraction contained 14 mg (4 %) of 1-phenyl-3-methyl-5-bromo-1,2,3-triazolio-4-oxide (VIId) as a colorless oil, which crystallized on standing, m.p. 157 – 160°. Extraction of the material with several portions of boiling ether and removal of the solvent gave the pure compound, m.p. 164 – 167°. Melting point, IR-, and NMR-spectra were identical with those of the material described previously.[2] The column was then eluted with ethyl acetate-methanol (1 : 1). This gave 121 mg of a mixture of 1-methyl-3-phenyl-1,2,3-triazolio-4-oxide (XXId) and 1-phenyl-3-methyl-1,2,3-triazolio-4-oxide (XIXd) as a yellow oil which crystallized on standing. The two compounds were not separated. They were identified by NMR-spectra, adding one by the other the pure substances[2] to the solution. This indicated the ratio between (XXId) and (XIXd) to be 3.4, corresponding to 27 and 8 % yield, respectively.

*1,3-Dibenzyl-1,2,3-triazolium tosylate (XIIIc), N-bromoacetamide and sodium methoxide.* Similarly, (XIIIc)[2] (545 mg), N-bromoacetamide (431 mg), and 1 N sodium methoxide (7.00 ml) were kept at room temperature for 14 days and worked up as described above. The first fraction from the chromatographical separation on silica gel (20 g), using benzene-ether (4 : 1) as eluent, contained 81 mg (27 %) of 1-benzyl-4-bromo-1,2,3-triazole. Two recrystallizations from ether-hexane raised the melting point to 71 – 72°. The second fraction contained 44 mg (20 %) of 1-benzyl-4-methoxy-1,2,3-triazole (XVIc) as colorless crystals, m.p. 51 – 53°. The third fraction contained 6 mg (3 %) of 1-benzyl-1,2,3-triazole. The three products gave IR- and NMR-spectra identical with those of the compounds described previously.[2,7,8] The fourth fraction contained 17 mg of a mixture of 1-benzyl-1,2,3-triazole and 1-benzyl-5-methoxy-1,2,3-triazole (XXc). The ratio was 2, as shown by NMR, corresponding to 6 and 5 % yield, respectively. The compounds were identified by NMR by adding, one by the other, the pure substances to the solution.[8,5] The column was then eluted with acetone. This gave a minor amount of a brown oil, not identified further. Finally, the column was eluted with ethyl acetate-methanol (1 : 1). This gave 34 mg (9 %) of 1,3-dibenzyl-1,2,3-triazolio-4-oxide (XIXc) as a yellow oil, which crystallized on standing, m.p. 74 – 85°. Recrystallization from ether raised the melting point

to 90 − 91°. Melting point, IR-, and NMR-spectra proved the identity with the material described previously.[4]

*1,4-Dimethyl-3-phenyl-1,2,3-triazolium tosylate (XXIIb)*, N-*bromoacetamide, and sodium methoxide.* Similarly, (XXIIb) [2] (516 mg), N-bromoacetamide (517 mg), and 1 N sodium methoxide (5.00 ml) were kept at room temperature for 14 days and worked up as described above. The first fraction, obtained by chromatography on silica gel (25 g), using acetone as eluent, gave a minor amount of a yellow oil. An NMR-spectrum indicated that no aromatic protons were present, and the material was not identified further. Then a slow-running fraction, containing 308 mg of a brown oil, left the column. An NMR-spectrum indicated that no aromatic protons were present, and the material was not identified further. The column was then eluted with ethyl acetate-methanol (1 : 1). This gave 226 mg (79 %) of 1-phenyl-3,5-dimethyl-1,2,3-triazolio-4-oxide (XXVb) as a yellow oil, which was purified by extraction with boiling ether (7 × 10 ml). The volume of the combined extracts was reduced to *ca.* 10 ml, and the solution was cooled to − 30°. This gave 162 mg of (XXVb) as colorless crystals, m.p. 143°. Further recrystallization did not raise the melting point. Melting point, IR-, and NMR-spectra proved the identity with the material described previously.[2]

*1,5-Dimethyl-3-phenyl-1,2,3-triazolium tosylate (XXIIa)*, N-*bromoacetamide, and sodium methoxide.* Similarly, (XXIIa) [2] (380 mg), N-bromoacetamide (379 mg), and 1 N sodium methoxide (4.50 ml) were kept at room temperature for 14 days and worked up as described above. The crude product was dissolved in ethyl acetate, and the solution was filtered through activated carbon. Removal of the solvent gave 194 mg (92 %) of 1,5-dimethyl-3-phenyl-1,2,3-triazolio-4-oxide (XXVa) as colorless crystals, m.p. 79 − 81°. Recrystallization from ether, as described above for the isomeric compound (XXVb), did not raise the melting point. IR- and NMR-spectra proved the identity with the material described previously.[2]

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