ACTA CHEMICA SCANDINAVICA 23 (1969) 2733–2740

Reactions between Azolium Salts and Nucleophilic Reagents

I. Bromo-1,2,3-Triazolium Salts as Brominating Reagents

MIKAEL BEGTRUP and PALLE ANKER KRISTENSEN

Polyteknisk Læreanstalt, Organisk-kemisk Laboratorium, Bygning 201, Lyngby, Denmark

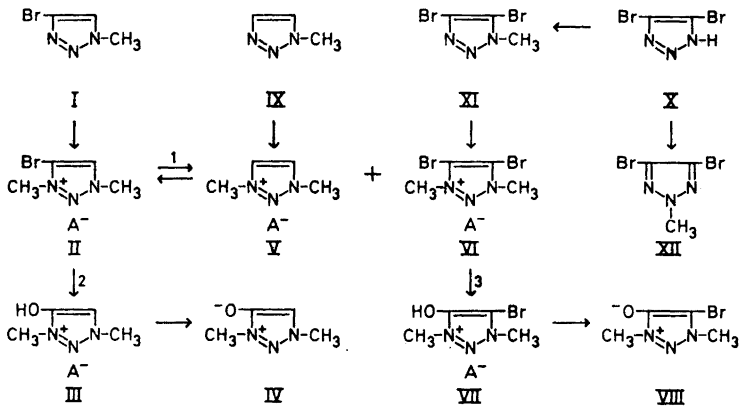
Bromo-substituted quaternary 1,2,3-triazolium salts are strong bromination reagents in basic solution. Thus 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) reacts to give 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) and 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) as primary products; again, (VIc) brominates (Vc) and an equilibrium mixture of the three salts is finally formed. Concurrently, (IIc) and (VIc) yield 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV) and the 5-bromo derivative (VIII) *via* nucleophilic attacks by hydroxide ion. The ratio between the velocity constants of the two substitution reactions determines the product distribution in the overall reaction.

It was found previously that heating of 1,3-dimethyl-4-bromo-1,2,3-triazolium chloride (IIa) with 1 N aqueous sodium hydroxide in a sealed tube at 100° for 16 h yielded 27 % of 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII).[1] The structure of (VIII) was proved by bromination of 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV).[1] (VIII) was also formed by methylation of 1-methyl-5-bromo-4-hydroxy-1,2,3-triazole.[2]

The formation of the bromo-triazolio-oxide (VIII) from the bromo-triazolium salt (IIa) involves an oxidation; therefore, a reduction must simultaneously have taken place. As no hydrogen could be detected after opening of the sealed tube, water has not been reduced, and it seemed likely that the oxidizing agent was the starting material itself. In order to identify the reduced products, the reaction has now been reinvestigated with 1,3-dimethyl-4-bromo-1,2,3-triazolium toluenesulfonate (IIc) as the starting material. This salt was prepared in 91 % yield by heating a mixture of 1-methyl-4-bromo-1,2,3-triazole (I) and methyl *p*-toluenesulfonate to 100° for 3 h.

Heating of the bromo-triazolium tosylate (IIc) with 1 N aqueous sodium hydroxide at 100° for 3 h gave a 40 % yield of 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII) and, in addition, 43 % of 1,3-dimethyl-1,2,3-triazolium salt (V) as a mixture of the tosylate and the bromide. This was passed through an ion exchange resin saturated with bromide ions, and in this way converted

Scheme 1



a: A=Cl b: A=Br c: A=p-$CH_3C_6H_4SO_3$

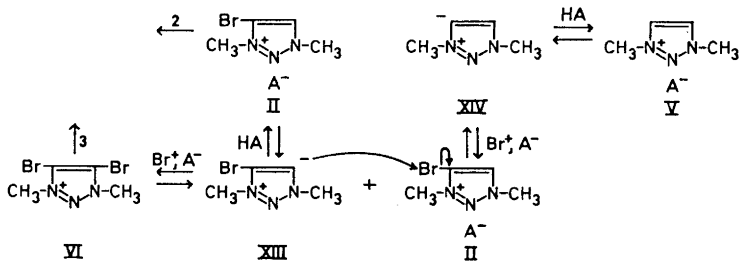
to the pure bromide (Vb). The structure of (Vb) was proved by independent synthesis from 1-methyl-1,2,3-triazole (IX). Since 1-substituted 1,2,3-triazoles are quaternized in the 3-position,[1,3,4] the salt formed in 98 % yield by heating 1-methyl-1,2,3-triazole (IX) with methyl tosylate to 100° for 3 h, must be 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) which was subsequently converted to the corresponding bromide (Vb) by ion exchange. The salt so formed was identical with the bromide previously prepared from the bromo-triazolium salt (IIc).

As a third product of the reaction of bromo-triazolium salt (IIc) with hydroxyl ions, 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV) was isolated in 12 % yield. (IV) is probably formed by proton abstraction from the intermediate (III), which is available from the starting material by simple nucleophilic substitution.

Ring protons in several azolium salts have been replaced by deuterium under mild conditions.[5-9] Similarly, the ring protons in (II) and (V) are replaced by deuterium, when the salts are dissolved in deuterium oxide at room temperature. [For (IIc) $T_{\frac{1}{2}}^{34°}=23$ min at pD=7.0, phosphate buffer; and for (Vc) $T_{\frac{1}{2}}^{34°}=13$ min at pD=9.9, borate buffer]. Both (II) and (V) exchange rapidly in 1 N sodium hydroxide. This indicates that in aqueous solution the salt (V) is in equilibrium with the 'ylide' (XIV) (Scheme 2) which is expected to show appreciable stability. Similarly, (II) is in equilibrium with (XIII). (In addition to the two aromatic protons, the six alkyl protons of (V) could also be replaced, as shown by NMR-spectra, but this necessitated heating with a suspension of barium oxide in deuterium oxide to 100° for 5 h.

1,3-Dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) was stable when heated to reflux in acid or neutral aqueous solution, but when the salt was dissolved in 1 N aqueous sodium hydroxide at room temperature, a mixture of the starting material (IIc), 1,3-dimethyl-1,2,3-triazolium tosylate (Vc),

Scheme 2



a: A=Cl b: A=Br c: A=p-$CH_3C_6H_4SO_3$

and 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) was present after 3 min, as shown by NMR-spectra. The same salt mixture was formed also when (IIc) was dissolved at room temperature in water containing a catalytic amount of potassium carbonate. The rate of the reaction depended on the amount of potassium carbonate present.

The salts were identified by adding the three pure salts one by one to the solution. By this procedure, the intensities of the appropriate NMR-signals increased, but no new absorptions were detected.

The base-catalyzed self-bromination of 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) may be explained by primary formation of the 'ylide' (XIII)* which is brominated by the starting material (IIc), possibly by transfer of a bromonium ion, thereby giving the dibromo salt (VIc). Bromonium ion abstraction from (IIc) leaves the 'ylide' (XIVc) which is protonated to (Vc).

The reaction is reversible, as the dibromo salt (VIc) brominates the salt (Vc) in 1 N aqueous sodium hydroxide at room temperature, forming a mixture of the starting materials and the monobromo salt (IIc).

Therefore, when 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate is dissolved in 1 N aqueous sodium hydroxide an equilibrium between the starting material (IIc), 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc), and 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) is rapidly attained. After 3 h at room temperature, two new signals at δ 3.97 and 3.75, corresponding to 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII), appeared in the NMR-spectrum of the solution. On further standing, the signals attributable to the bromo-triazolio-oxide (VIII) increased at the expense of the salts (VIc) and (IIc). Also methyl group signals at δ 4.11 and 3.89, due to 1,3-dimethyl-1,2,3-triazolio-4-oxide (VI), appeared in the spectrum. After two weeks, only the signals due to the two main products (VIII) and (V) and the by-product (IV) were present. The course of the reaction is shown in Fig. 1.

The formation of 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV) has been rationalized above. Analogously, the formation of the bromo-triazolio-oxide (VIII) may be explained by a nucleophilic substitution of bromine by hy-

* Formally, only the resonance structure analogous to (XIV) is an ylide.

droxylic ion in the originally formed dibromo salt (VIc), giving the intermediate (VII) which on proton abstraction yields the bromo-triazolio-oxide (VIII). (VIII) is stable under the reaction conditions, and substitution of the second bromine atom does not take place.

To decide whether the course of reaction is kinetically or thermodynamically determined, the triazolio-oxide (IV) was heated to 100° for 21 h with 1 N sodium hydroxide solution saturated with sodium bromide. Equilibrium should give the bromo-triazolio-oxide (VIII) *via* the salts (III), (II), and (VI). However, the starting material was recovered unchanged indicating kinetic control in the reaction. Hence, the ratio between the products (IV) and (VIII) (or (V)) is defined by the ratio between the velocity constants of the rate limiting steps 2 and 3.

In order to prove the proposed mechanism, 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) was prepared from 4,5-dibromo-1,2,3-triazole (X) which with diazomethane, gave 35 % of 1-methyl-4,5-dibromo-1,2,3-triazole (XI) in addition to 46 % of 2-methyl-4,5-dibromo-1,2,3-triazole (XII). From the former, the dibromo salt (VIc) was prepared in 87 % yield with methyl tosylate. (VIc), when heated with 1 N aqueous sodium hydroxide to 100° for 3 h, afforded 83 % of 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII). At room temperature, the conversion of (VIc) to (VIII) was complete after one week. The reaction was followed in NMR (Fig. 2) and was shown to be first order with respect to triazolium salt.

The proposed overall mechanism was confirmed when 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) with *N*-bromoacetamide in 1 N aqueous sodium hydroxide at room temperature in three weeks produced 71 % of 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII). Possibly by a bromonium ion mechanism, the starting material (Vc) is brominated to the dibromo salt (VIc) *via* the monobromo salt (IIc). The dibromo salt is then converted to the bromo-triazolio-oxide (VIII) by substitution and proton abstraction.

EXPERIMENTAL

Thin layer and column chromatography were carried out as described previously.[10] NMR-spectra were obtained on Varian A-60 or HA 100 instruments. Position of signals are given in ppm (δ-values) relative to DSS. Deuterium oxide was used as a solvent. Melting points are uncorrected.

1,3-Dimethyl-1,2,3-triazolium bromide (Vb). A mixture of 1-methyl-1,2,3-triazole[11] (IX) (0.86 g) and methyl *p*-toluenesulfonate (1.90 ml) was heated to 100° for 3 h. After cooling to room temperature, the crystal cake was crushed with 3 portions of ether (10 ml) and recrystallized from methanol-ether. Yield 2.57 g (98 %) of 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) as colourless crystals, m.p. 129—131°. (Found: C 48.96; H 5.75; N 15.77; S 12.05. Calc. for $C_{11}H_{15}N_3O_3S$: C 49.06; H 5.62; N 15.60; S 11.91).

The tosylate (Vc) (0.67 g), dissolved in water, was passed through a column of Amberlite IRA 400 (14 ml), regenerated with 1 N hydrobromic acid. The eluate was evaporated to dryness, and the residue was recrystallized from methanol-ether yielding 0.38 g (87 %) of 1,3-dimethyl-1,2,3-triazolium bromide (Vb) as colourless crystals, m.p. 177—179°. (Found: C 27.01; H 4.67; N 23.73; Br 44.75. Calc. for $C_4H_8N_3Br$: C 26.99; H 4.53; N 23.61; Br 44.90).

1,3-Dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc). In the same way a mixture of 1-methyl-4-bromo-1,2,3-triazole[11] (I) (1.28 g) and methyl tosylate by heating to 100° for 3 h gave, after ether washing and recrystallization from methanol-ether, 2.50 g (91 %) of 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) as colourless crystals,

m.p. 182—184°. Further recrystallization did not raise the melting point. (Found: C 37.82; H 4.18; N 12.00; S 9.18; Br 23.09. Calc. for $C_{11}H_{14}N_3O_3SBr$: C 37. 94; H 4.06; N 12.07; S 9.21; Br 22.95).

1-Methyl-4,5-dibromo-1,2,3-triazole (XI) and 2-methyl-4,5-dibromo-1,2,3-triazole (XII). 4,5-Dibromo-1,2,3-triazole[12] (X) (4.62 g), dissolved in methanol (50 ml), was methylated with diazomethane using the procedure described previously.[10] Removal of the solvent left 4.65 g of a crude product which was extracted 4 times with 20 ml of boiling hexane. The residue was recrystallized two times from ether-hexane at dry ice temperature, thereby giving 1.38 g (28 %) of 1-methyl-4,5-dibromo-1,2,3-triazole (XI) as colourless crystals, m.p. 115—116°. Further recrystallization did not raise the melting point. (Found: C 15.10; H 1.42; N 17.25; Br 66.11. Calc. for $C_3H_3N_3Br_2$: C 14.96; H 1.25; N 17.45; Br 66.34). The hexane extract contained 2.99 g of crude 2-methyl-4,5-dibromo-1,2,3-triazole (XII), m.p. 56—60° which was purified by column chromatography on silica gel (30 g), using hexane-ether 10:1 as the eluent. The first fraction contained 2.25 g (46 %) of pure 2-methyl-4,5-dibromo-1,2,3-triazole (XII) as colourless crystals, m.p. 65—66°. (Litt. m.p.[12] 66.5—67.5°). After collection of the first fraction, the column was eluted with ether yielding a second fraction which contained 0.32 g (7 %) of the 1-methyl isomer (XI) as colourless crystals, m.p. 114—115°.

1,3-Dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc). A mixture of 1-methyl-4,5-dibromo-1,2,3-triazole (XI) (1.32 g) and methyl tosylate (1.20 ml) was heated to 100° for 3 h. The crystal cake which had formed was crushed with 3 portions of ether (5 ml) and recrystallized from methanol-ether yielding 2.05 g (87 %) of 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) as colourless crystals, m.p. 187°. Further recrystallization did not raise the melting point. (Found: C 31.06; H 3.25; N 9.94; S 7.60; Br 37.40. Calc. for $C_{11}H_{13}N_3O_3SBr_2$: C 30.93; H 3.07; N 9.84; S 7.51; Br 37.41).

1,3-Dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) and sodium hydroxide. 1. Preparative experiment. 1,3-Dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) (503 mg) and 1 N aqueous sodium hydroxide (1.70 ml) were heated to reflux for 3 h. The solvent was removed *in vacuo*, and the residue was extracted 5 times with boiling chloroform (10 ml). The chloroform was removed, leaving 379 mg of a colourless, crystallizing oil which was extracted 4 times with boiling ethyl acetate (5 ml). As shown by NMR-spectra, the residue consisted of 1,3-dimethyl-1,2,3-triazolium bromide (Vb) and a minor amount of the corresponding tosylate (Vc). The residue was dissolved in water and passed through 4 ml of Amberlite IRA 400 regenerated with 1 N hydrobromic acid. Removal of water and recrystallization from methanol-ether yielded 110 mg (43 %) of pure 1,3-dimethyl-1,2,3-triazolium bromide (Vb) as colourless crystals, m.p. 174—175°. The IR-spectrum was identical with that of the material prepared as described above from 1-methyl-1,2,3-triazole. From the ethyl acetate extract, the solvent was removed leaving 138 mg of a yellow, crystallizing oil. From this, the bromo-triazolio-oxide (VIII) could be isolated by several recrystallizations from ethyl acetate-ether at —78°. The best method, however, was purification by chromatography on silica gel (20 g), using methanol as an eluent. The first fraction contained 113 mg (40 %) of 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII) as colourless crystals, m.p. 137—140°. One recrystallization from ethyl acetate-ether (1 ml—10 ml) at —78° raised the melting point to 141°. Melting point, IR- and NMR-spectra were identical with those of the material prepared by bromination of 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV),[1] or prepared by methylation of 1-methyl-5-bromo-4-hydroxy-1,2,3-triazole.[2] The second fraction to leave the column contained 20 mg (12 %) of 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV) as a colourless, crystallizing oil, m.p. 80—93°. Melting point, IR- and NMR-spectra were identical with those of the material described previously.[11]

2. Spectroscopic and kinetic experiments. A. 1,3-Dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) (32 mg) was dissolved in 1 N aqueous sodium hydroxide (0.50 ml). A 60 MHz NMR-spectrum of the solution showed two absorptions at δ 4.27 and 4.33. The mixture was acidified with hydrochloric acid (all triazolium salts and triazolio-oxides are stable in acid solution) and the solvent was removed *in vacuo*. The residue was dissolved in deuterium oxide. A 60 MHz NMR-spectrum showed the same two CH_3-signals as before and two aromatic signals at δ 8.46 and 8.63. A 100 MHz NMR-spectrum, obtained in the frequency sweep mode with DSS as the lock signal, showed that actually four CH_3-signals were present at δ 4.27_0, 4.32_7, 4.33_3, and 4.34_6. To identify these signals, the 3 pure salts (Vc), (IIc) and (VIc) were added one after the other to the mixture; the

signals at δ 4.32$_7$ and 8.46 were due to 1,3-dimethyl-1,2,3-triazolium tosylate (Vc), the signals at δ 4.27$_0$, 4.34$_6$, and 8.63 to the starting material (IIc), and the signal at δ 4.33$_3$ to 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc).

B. 1,3-Dimethyl-4-bromo-1,2,3-tirazolium tosylate (IIc) (322 mg) was dissolved in 1 N aqueous sodium hydroxide (5.50 ml), and the solution was allowed to stand at room temperature. Samples were taken at intervals. The samples were acidified with hydrochloric acid, the solvent was then removed *in vacuo*, the residue was dissolved in deuterium oxide, and NMR-spectra were obtained. The composition of the samples was not altered by this procedure.

As before, the mixture of the salts (VIc), (Vc), and (IIc) was observed immediately. After 3 h, two CH_3-signals due to 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII) could be detected at δ 3.75 and 3.97. With time, this signals grew at the expense of those corresponding to the monobromo (IIc) and the dibromo salt (VIc). After 7 h, two new CH_3-signals due to 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV) appeared at δ 3.89 and 4.11. After 2 weeks, only the signals due to the bromo-triazolio-oxide (VIII), the triazolio-oxide (IV), and the 1,3-dimethyl-1,2,3-triazolium salt (V) were present. The results are given in Fig. 1.

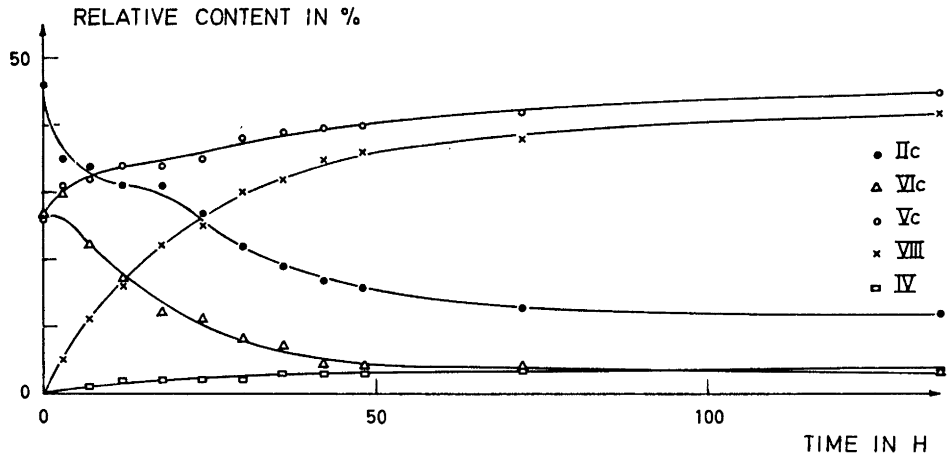


Fig. 1. The conversion of 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc) into 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV), its 5-bromo-derivative (VIII), and 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) *via* 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc).

1,3-Dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) and sodium hydroxide. 1. Preparative experiment. 1,3-Dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) (102 mg) and 1 N aqueous sodium hydroxide (0.60 ml) were heated to reflux for 3 h. The solvent was removed *in vacuo*, and the residue was extracted 5 times with boiling chloroform (10 ml). Evaporation of the chloroform yielded 43 mg of crude product which was recrystallized from ethyl acetate-ether at −78°, giving 38 mg (83 %) of 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII) as colourless crystals, m.p. 140°. IR- and NMR-spectra were identical with those of the material described above.

2. Spectroscopic experiments. 1,3-Dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) (208 mg) was dissolved in 1 N aqueous sodium hydroxide (3.50 ml), and the mixture was allowed to stand at room temperature. Samples were taken at intervals. The samples were acidified, the solvent was removed, the residue was dissolved in deuterium oxide, and NMR-spectra were obtained. After half an hour, 2 CH_3-signals at δ 3.78 and 4.00 due to 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII), could be detected. In the course of time these signals grew at the expense of those corresponding to the starting

material (VIc). After one week, only the signals due to the bromo-triazolio-oxide (VIII) were present. The course of the reaction is shown in Fig. 2. The reaction was first order in dibromo salt (VIc).

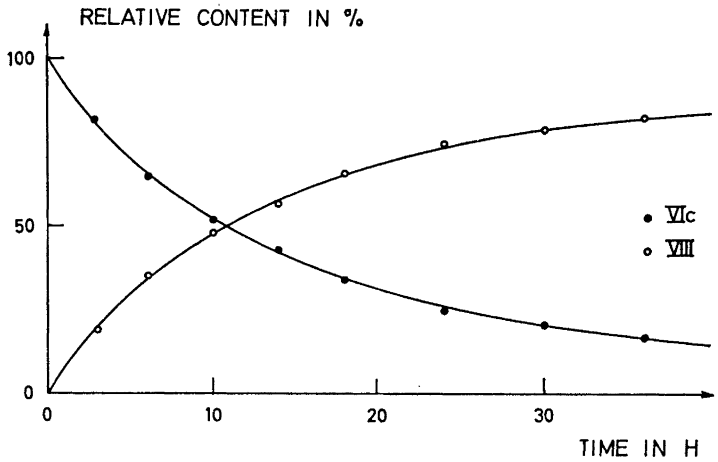


Fig. 2. The conversion of 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) into 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII).

1,3-Dimethyl-1,2,3-triazolium tosylate (Vc), 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc), and sodium hydroxide. A mixture of 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) (15 mg) and 1,3-dimethyl-4,5-dibromo-1,2,3-triazolium tosylate (VIc) (24 mg) was dissolved in 1 N aqueous sodium hydroxide (0.50 ml); the solution was allowed to stand 20 min at room temperature. Then, hydrochloric acid was added in excess, and the solvent was removed *in vacuo*. The residue was dissolved in deuterium oxide. A 100 MHz NMR-spectrum of this solution showed signals at δ 4.34_2 and 8.46 due to the starting material (Vc), at δ 4.34_8 due to the starting material (VIc), and at δ 4.27_4, 4.35_8, and 8.63 due to 1,3-dimethyl-4-bromo-1,2,3-triazolium tosylate (IIc). The ratio was 3:3:4. The presence of (IIc) was proved by NMR by adding the pure material to the solution.

Attempt to equilibrate 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV) and its 5-bromo derivative (VIII). A mixture of 1,3-dimethyl-1,2,3-triazolio-4-oxide (IV) (88 mg), sodium bromide (1.00 g), and 1 N aqueous sodium hydroxide (2.5 ml) was heated to reflux for 21 h. The solvent was removed *in vacuo*, and the residue was extracted with chloroform (5×10 ml). Evaporation of the chloroform yielded 51 mg (58 %) of the starting material (IV) as a colourless crystallizing oil which was identified by IR- and NMR-spectra. No signals due to the bromo-triazolio-oxide (VIII) could be detected in the NMR-spectrum.

1,3-Dimethyl-1,2,3-triazolium tosylate (Vc) and N-bromoacetamide. A mixture of 1,3-dimethyl-1,2,3-triazolium tosylate (Vc) (484 mg) and *N*-bromoacetamide (578 mg) was dissolved in 1 N aqueous sodium hydroxide (8.00 ml). The mixture was allowed to stand at room temperature for 3 weeks; then, the solvent was removed *in vacuo*, and the residue was extracted 5 times with boiling chloroform (10 ml). Removal of the chloroform left 298 mg of crude product. Recrystallization from ethyl acetate-ether at $-78°$ yielded 244 mg (71 %) of the 1,3-dimethyl-5-bromo-1,2,3-triazolio-4-oxide (VIII) as colourless crystals, m.p. 141°. Melting point, IR-, and NMR-spectra were identical with those of the material described above.

The authors are indebted to civilingeniør S. Refn for the infrared spectra. Microanalyses were performed by Dr. A. Bernhardt.

REFERENCES

1. Begtrup, M. and Pedersen, C. *Acta Chem. Scand.* **20** (1966) 1555.
2. Begtrup, M. and Pedersen, C. *Acta Chem. Scand.* **23** (1969) 1091.
3. Gompper, R. *Chem. Ber.* **90** (1957) 382.
4. Wiley, R. H. and Moffat, J. *J. Am. Chem. Soc.* **77** (1955) 1703.
5. Hafferl, W., Lundin, R. and Ingraham, L. L. *Biochemistry* **2** (1963) 1298.
6. Haake, P. and Miller, W. B. *J. Am. Chem. Soc.* **85** (1963) 4044.
7. Olofson, R. A., Thompson, W. R. and Michelman, J. S. *J. Am. Chem. Soc.* **86** (1964) 1865.
8. Olofson R. A. and Landesberg J. M. *J. Am. Chem. Soc.* **88** (1966) 4263.
9. Staab, H. A., Irngartinger, H., Mannschreck, A. and Wu, M.-T. *Ann.* **695** (1966) 55.
10. Begtrup, M. and Pedersen, C. *Acta Chem. Scand.* **19** (1965) 2022.
11. Pedersen, C. *Acta Chem. Scand.* **13** (1959) 888.
12. Hüttel, R. and Welzel, G. *Ann.* **593** (1955) 207.

Received February 14, 1969.