

## Studies on Methylated 1,2,3-Triazoles. III

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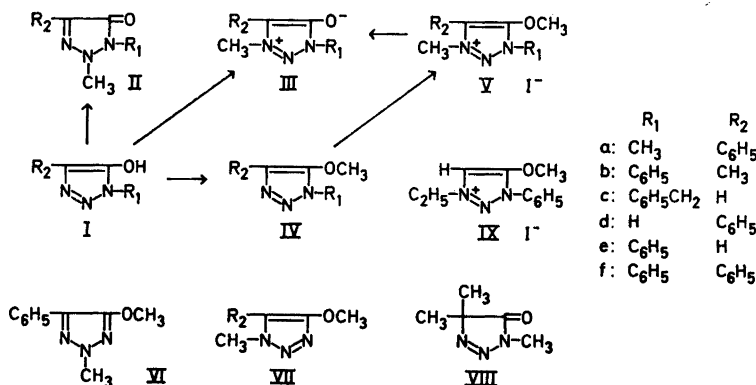
The methylation of a number of 5-hydroxy-1,2,3-triazoles with diazomethane has been investigated. The methylation of 1-substituted 1,2,3-triazoles gives a mixture of the *O*-methylated product (IV) and two *N*-methylated compounds (II) and (III). Methylation of 4-phenyl-5-hydroxy-1,2,3-triazole (Id) gives three *O*-methylated compounds (IV), (VI), and (VII), and a *N*-methylated product (III). The *O*-methylated compounds (IV) were all rearranged to the *N*-methylated products (III) when treated with methyl iodide. The rearrangement was shown to proceed *via* the quaternary salt (V).

In previous papers<sup>1,2</sup> it was shown that methylation of 1-methyl-5-hydroxy-1,2,3-triazole with diazomethane gives a mixture of 1-methyl-5-methoxy-1,2,3-triazole and 1,3-dimethyl-1,2,3-triazolio-4-oxide. In the present paper the methylation of a number of 5-hydroxy-1,2,3-triazoles with diazomethane is described.

Treatment of 1-methyl-4-phenyl-5-hydroxy-1,2,3-triazole (Ia) with diazomethane gave a mixture of three compounds which were separated by chromatography on silica gel columns. The major product, obtained in 42 % yield, is assumed to be 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa) as it shows no carbonyl group absorption in infrared. A second compound, isolated in 23 % yield, had a carbonyl absorption at 1630–1660  $\text{cm}^{-1}$ . This product is assumed to be 1,2-dimethyl-4-phenyl-1,2,3-triazolone-5 (IIa), a type of compound which was not formed by methylation of 1-methyl-5-hydroxy-1,2,3-triazole or its 4-carbomethoxy derivative.<sup>1</sup> A third product had a carbonyl absorption at 1630  $\text{cm}^{-1}$  and since this low value was also found in the infrared spectrum of 1,3-dimethyl-1,2,3-triazolio-4-oxide<sup>2</sup> this product is believed to be 1,3-dimethyl-5-phenyl-1,2,3-triazolio-4-oxide (IIIa). As described below its structure was confirmed through its formation by treatment of 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa) with methyl iodide.

By a similar procedure methylation of 1-phenyl-4-methyl-5-hydroxy-1,2,3-triazole (Ib) gave three products. 1-Phenyl-4-methyl-5-methoxy-1,2,3-triazole (IVb) was obtained in 12 % yield and showed no carbonyl absorption. 1-Phenyl-2,4-dimethyl-1,2,3-triazolone-5 (IIb) (25 % yield) had a carbonyl

band at  $1675\text{ cm}^{-1}$  whereas 1,5-dimethyl-3-phenyl-1,2,3-triazolio-4-oxide (IIIb) (62 % yield) had its carbonyl absorption at  $1640\text{ cm}^{-1}$ . The structure of (IIIb) is verified through its formation from the reaction of (IVb) with methyl iodide (see below). The structure of (IIb) (or the other 1,2-disubstituted triazolones) has not been proved directly. However, the only other product that could conceivably arise from the methylation of (Ib) would be the *C*-methylated compound (VIII), and the NMR spectrum of (IIb) (Table 1) shows that the two methyl groups are quite different and that one of them has its signal at  $\delta\ 3.22$  corresponding to an *N*-methyl group.



The methylation of 1,4-diphenyl-5-hydroxy-1,2,3-triazole (Ic) gave the methoxy compound (IVc), 1,4-diphenyl-2-methyl-1,2,3-triazolone-5 (IIc), and 1-methyl-3,5-diphenyl-1,2,3-triazolio-4-oxide (IIIc). Structures were assigned to the latter two compounds on the basis of their infrared spectra which showed carbonyl absorption at  $1672$  and  $1633\text{ cm}^{-1}$ , respectively. Scarpati *et al.*<sup>3</sup> obtained only two products from this reaction, namely the methoxy compound (IVc) and the 3-methylated derivative (IIIc) to which they assigned the structure (IIIc).

Methylation of 1-benzyl-5-hydroxy-1,2,3-triazole (Ic) also gave three products. The methoxy derivative (IVc) was identified through its infrared spectrum which showed no carbonyl absorption. Its structure was confirmed by synthesis from 1-benzyl-5-chloro-1,2,3-triazole and sodium methoxide. The two other products obtained by methylation of (Ic) were 1-benzyl-2-methyl-1,2,3-triazolone-5 (IIc) and 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc) showing carbonyl absorptions at  $1660$  and  $1646\text{ cm}^{-1}$ , respectively.

Finally, the methylation of 4-phenyl-5-hydroxy-1,2,3-triazole (Id) with diazomethane was studied. By a series of chromatographic separations four products were isolated from this reaction. Two of these products were identical with compounds described above, namely 1,3-dimethyl-5-phenyl-1,2,3-triazolio-4-oxide (IIIa) and 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa). The two other products could not be identified with certainty; none of them showed carbonyl bands in infrared and they must therefore be 2-methyl-5-phenyl-4-methoxy-1,2,3-triazole (VI) and 1-methyl-5-phenyl-4-methoxy-1,2,3-

triazole (VIIa). In analogy with the results obtained by methylation of 4-hydroxy-1,2,3-triazole<sup>1</sup> it may be assumed that the product obtained in highest yield (60 %) is the 2-methylated derivative (VI). The fifth isomer, 1,2-dimethyl-4-phenyl-1,2,3-triazolone-5 (IIa), could not be detected.

It was described previously<sup>2</sup> that treatment of 1-methyl-5-methoxy-1,2,3-triazole with methyl iodide in chloroform gave 1,3-dimethyl-1,2,3-triazolio-4-oxide in high yield. In this reaction 1,3-dimethyl-4-methoxy-1,2,3-triazolium iodide was shown to be an intermediate. The methoxy compounds described above have now been treated with methyl iodide, and in all cases they were rearranged to the triazolio oxides (III) by this treatment. Thus a solution of 1-benzyl-5-methoxy-1,2,3-triazole (IVc) in deuteriochloroform with added methyl iodide was kept at room temperature in an NMR sample tube, and spectra were taken at intervals. After a few hours the signals of a compound assumed to be 1-methyl-3-benzyl-4-methoxy-1,2,3-triazolium iodide (Vc) appeared in the spectrum and at the same time the signals of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc) also appeared. The signals of the latter compound grew at the expense of those corresponding to 1-benzyl-5-methoxy-1,2,3-triazole and the triazolium salt. Integration of the spectra gave the composition of the mixture at various intervals as shown in Fig. 1. After three weeks, 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc) could be isolated in 91 % yield. When 1-benzyl-5-methoxy-1,2,3-triazole was boiled with methyl iodide for 3 h, a 72 % yield of (IIIc) was obtained. The quaternary salt (Vc) apparently loses methyl iodide very easily and could therefore not be isolated.

Reaction of 1-methyl-4-methoxy-1,2,3-triazole<sup>1,2</sup> (VIIc) with benzyl iodide in deuteriochloroform at room temperature took a course very similar to that of the reaction described above. NMR spectra showed that the quaternary salt (Vc) was formed as an intermediate which decomposed with the formation of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc) and methyl iodide. After three weeks the NMR spectrum also showed that *ca.* 2 % of 1,3-dimethyl-1,2,3-triazolio-4-oxide was present in the reaction mixture

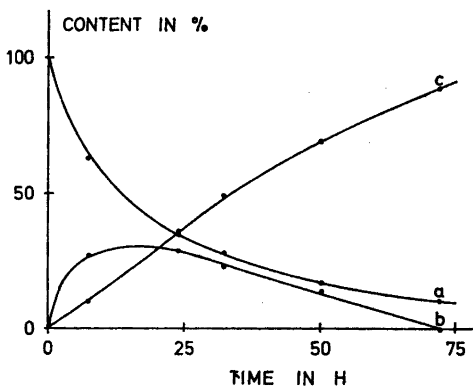


Fig. 1.

formed by reaction of 1-methyl-4-methoxy-1,2,3-triazole with the methyl iodide liberated.<sup>2</sup> 1-Methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc) was isolated in 55 % yield. The formation of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc) from the methoxytriazoles (Ic) and (VIIc) proves that (IIIc) is a 1,3-disubstituted triazole since this is the only product that could be formed from both these methoxytriazoles.

In the same way 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa), when treated with methyl iodide in deuteriochloroform at room temperature, gave the triazolio oxide (IIIa) as seen from the NMR spectra (Table 1). However, in this case no quaternary salt (Va) could be detected as an intermediate, probably because it is too unstable to accumulate in sufficient quantities. When (IVa) was boiled with methyl iodide for three hours a quantitative yield of (IIIa) could be isolated.

1-Phenyl-4-methyl-5-methoxy-1,2,3-triazole (IVb) behaved in the same way yielding the triazolio oxide (IIIb) when treated with methyl iodide. No quaternary salt could be detected as an intermediate.

Finally the reaction of 1-phenyl-5-methoxy-1,2,3-triazole (IVe) with methyl and ethyl iodide was studied. (IVe) was prepared from 1-phenyl-5-chloro-1,2,3-triazole and sodium methoxide.

Treatment of 1-phenyl-5-methoxy-1,2,3-triazole (IVe) with methyl iodide proceeded as described above. After *ca.* 10 h the signals of 1-methyl-3-phenyl-1,2,3-triazolio-4-oxide (IIIe) appeared in the NMR spectrum and after two

Table 1. NMR spectra (in deuteriochloroform) and infrared absorption of carbonyl groups.

Compound	Infrared cm <sup>-1</sup>	NMR $\delta$ -values		
		CH	CH <sub>2</sub>	CH <sub>3</sub>
1-Methyl-4-phenyl-5-methoxy-triazole				3.90 3.85
1-Phenyl-4-methyl-5-methoxy-triazole				3.95 2.44
1,4-Diphenyl-5-methoxy-triazole				3.75
1-Benzyl-5-methoxy-triazole		7.10	5.32	3.90
1-Phenyl-5-methoxy-triazole		7.24		4.02
2-Methyl-5-phenyl-4-methoxy-triazole				4.10 4.08
1-Methyl-5-phenyl-4-methoxy-triazole				4.09 4.03
1,3-Dimethyl-5-phenyl-triazolio-4-oxide	1630			4.00 3.72
1,5-Dimethyl-3-phenyl-triazolio-4-oxide	1640			3.90 2.25
1-Methyl-3,5-diphenyl-triazolio-4-oxide	1633			4.07
1-Methyl-3-benzyl-triazolio-4-oxide	1646	6.66	5.20	3.80
1-Methyl-3-phenyl-triazolio-4-oxide	1627	6.78		3.94
1-Ethyl-3-phenyl-triazolio-4-oxide	1658	6.79	4.28	1.60
1,2-Dimethyl-4-phenyl-triazolone-5	1630-60			3.55 3.52
1-Phenyl-2,4-dimethyl-triazolone-5	1675			3.22 2.29
1,4-Diphenyl-2-methyl-triazolone-5	1672			3.38
1-Benzyl-2-methyl-triazolone-5	1660	7.14	5.18	3.51
1-Methyl-3-benzyl-4-methoxy-triazolium iodide		8.92	5.51	4.34 4.28
1-Ethyl-3-phenyl-4-methoxy-triazolium iodide		9.51	4.70	3.45 1.50

weeks the signals of the methoxy compound (IVe) had disappeared. No other signals were seen at any time. The 1-methyl-3-phenyl-1,2,3-triazolio-4-oxide (IIIe) could be isolated in quantitative yield; its structure was confirmed by its infrared spectrum which showed a strong carbonyl absorption at  $1627\text{ cm}^{-1}$ .

Reaction of 1-phenyl-5-methoxy-1,2,3-triazole with ethyl iodide led to the formation of 1-ethyl-3-phenyl-1,2,3-triazolio-4-oxide which was isolated in 74 % yield together with a small amount of (IIIc) formed from the methyl iodide liberated in the reaction. NMR spectra taken in the course of the reaction showed, besides the signals of the methoxy compound (IVe) and the triazolio oxide, another set of signals which probably represents 1-ethyl-3-phenyl-4-methoxy-1,2,3-triazolium iodide (IX). This compound, although too unstable to be isolated, is apparently more stable than the methyl analogue (Vc) which could not be detected. The integrated NMR spectra showed that a maximum of 12 % of (IX) was present after a reaction time of 1350 h.

Whereas 1,3-dimethyl-1,2,3-triazolio-4-oxide reacted with methyl iodide to give 1,3-dimethyl-4-methoxy-1,2,3-triazolium iodide,<sup>2</sup> none of the 1,3-substituted triazolio oxides (III) described in the present paper yielded quaternary salts (V) when treated with methyl iodide. Neither did any of the 1,2-substituted triazolones (II) react with methyl iodide.

#### EXPERIMENTAL

Thin layer and column chromatography was carried out as described previously.<sup>1</sup> NMR spectra were obtained on a Varian A-60 instrument. Position of signals are given in ppm ( $\delta$ -values) relative to tetramethylsilane. Deuteriochloroform was used as a solvent.

*1-Phenyl-5-methoxy-1,2,3-triazole (IVe)*. 1-Phenyl-5-chloro-1,2,3-triazole<sup>4</sup> (2.0 g) was dissolved in a solution of sodium (0.26 g) in methanol (8 ml). The solution was kept for 72 h at room temperature, the solvent was then evaporated and the residue was extracted with methylene chloride. Evaporation of the solvent gave 1.68 g of crude product which was chromatographed on a column of silica gel using ether as eluent.

The first fraction to come off the column contained 402 mg of unchanged chloro compound. The second fraction gave 618 mg (40%) of 1-phenyl-5-methoxy-1,2,3-triazole as colourless crystals, m.p.  $49^\circ$ . (Found: C 61.08; H 5.19; N 24.22. Calc. for  $\text{C}_9\text{H}_9\text{N}_3\text{O}$ : C 61.70; H 5.18; N 23.98).

*1-Benzyl-5-chloro-1,2,3-triazole*. Methyl diazomalonate *N*-benzylamide<sup>5</sup> (2.0 g) was mixed with phosphorus pentachloride (2.6 g) and heated to  $80^\circ$  for 3 h. The phosphorus oxychloride was then removed *in vacuo* and the residue was treated with ice (10 g). The mixture was extracted with methylene chloride, the solution was dried and filtered through activated carbon. Removal of the solvent left 2.4 g of crude 1-benzyl-4-carboxy-5-methoxy-5-chloro-1,2,3-triazole as a red oil. This product was dissolved in methanol (5.0 ml) containing potassium hydroxide (0.54 g) and the solution was kept for 24 h at room temperature. The precipitated potassium salt was then filtered off, dissolved in water and acidified with conc. hydrochloric acid. On cooling 1-benzyl-4-carboxy-5-chloro-1,2,3-triazole precipitated as colourless crystals, m.p.  $126^\circ$ , yield 0.80 g (38 %).

The acid was decarboxylated by heating to the melting point for 5 min, thereby giving an oil which crystallized on cooling, m.p.  $41^\circ$ . Recrystallization from hexane gave the pure 1-benzyl-5-chloro-1,2,3-triazole, m.p.  $42^\circ$ . (Found: C 55.65; H 4.42; N 21.49; Cl 18.53. Calc. for  $\text{C}_9\text{H}_8\text{N}_3\text{Cl}$ : C 55.84; H 4.17; N 21.70; Cl 18.32).

*1-Benzyl-5-methoxy-1,2,3-triazole (IVc)*. To 1-benzyl-5-chloro-1,2,3-triazole (185 mg) was added a solution of sodium (23 mg) in methanol (1.0 ml) and the mixture was heated to  $120^\circ$  for 16 h in a sealed tube. The methanol was then evaporated, the residue was extracted with methylene chloride and the solution was filtered through activated carbon. Removal of the methylene chloride gave a red oil (156 mg) which was extracted several

times with ether. The ether extract was purified by column chromatography using ether as eluent thereby giving 112 mg (62 %) of 1-benzyl-5-methoxy-1,2,3-triazole as colourless crystals, m.p. 58–62°. Recrystallization from ethyl acetate-hexane gave the pure product, m.p. 63°. (Found: C 63.13; H 5.67; N 21.80. Calc. for  $C_{10}H_{11}N_3O$ : C 63.49; H 5.87; N 22.21).

### Methylations

Methylations were carried out by adding excess of distilled ethereal diazomethane to a cooled solution of the hydroxytriazole in methanol. The mixture was then kept over night at room temperature and the solvent was evaporated with a stream of air leaving a crude product which was worked up as described in the following.

*1-Methyl-4-phenyl-5-hydroxy-1,2,3-triazole (Ia)*. Methylation of 1-methyl-4-phenyl-5-hydroxy-1,2,3-triazole<sup>6</sup> (1.0 g) gave a colourless oil which gave two spots on thin layer chromatography. The product was put on a column of silica gel. Elution with ethyl acetate gave 457 mg (42 %) of 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa), m.p. 53–56°. Recrystallization from hexane gave the pure product, m.p. 58°. (Found: C 63.65; H 6.06; N 22.01. Calc. for  $C_{10}H_{11}N_3O$ : C 63.47; H 5.87; N 22.21).

Elution of the column with methanol gave a hygroscopic oil which was dried *in vacuo* over calcium chloride. The product was shown by NMR spectroscopy to consist of a mixture of two isomeric compounds in a 1:1 proportion. 247 mg of this mixture was put on a 20 × 20 cm plate covered with a 1 mm thick layer of silica gel PF<sub>254</sub> (Merck). Elution 10 times with benzene-ether (4:1) separated the two compounds. The fast running fraction gave 96 mg (23 %) of 1,2-dimethyl-4-phenyl-1,2,3-triazolone-5 (IIa) as a colourless oil which crystallized on standing, m.p. 115–116°. Recrystallized from ethyl acetate-hexane, m.p. 120°. (Found: C 63.78; H 6.05; N 22.12).

Elution of the slow running fraction gave 100 mg (24 %) of 1,3-dimethyl-5-phenyl-1,2,3-triazolio-4-oxide (IIIa) as colourless crystals, m.p. 85–86°. After two recrystallizations from ethyl acetate-hexane the melting point was 60°. The compound is very hygroscopic. (Found: C 63.34; H 6.02; N 22.03).

*1-Phenyl-4-methyl-5-hydroxy-1,2,3-triazole (Ib)*. Methylation of 263 mg of this compound<sup>6</sup> gave 286 mg of crude product which was put on a column of silica gel. Elution with ethyl acetate gave 110 mg of a yellow oil which was separated into two fractions by preparative thin layer chromatography using benzene-ether (4:1) as eluent (the plate was eluted four times). The fast running fraction gave 35 mg (12 %) of 1-phenyl-4-methyl-5-methoxy-1,2,3-triazole (IVb), m.p. 61°. Two recrystallizations from ethyl acetate-hexane did not change the melting point. (Found: C 63.76; H 6.06; N 22.11. Calc. for  $C_{10}H_{11}N_3O$ : C 63.47; H 5.87; N 22.21).

The slower moving fraction gave 71 mg (25 %) of 1-phenyl-2,4-dimethyl-1,2,3-triazolone-5 (IIb), m.p. 56°. After two recrystallizations from ethyl acetate-hexane the m.p. was 70°. (Found: C 63.70; H 5.85).

Elution of the silica gel column with methanol gave 176 mg (62 %) of 1,5-dimethyl-3-phenyl-1,2,3-triazolio-4-oxide (IIIb), m.p. 85–87°. Recrystallization from ethyl acetate-hexane raised the m.p. to 88–90°. The compound is very hygroscopic, and a correct analysis could therefore not be obtained. (Found: C 62.60; H 5.93; N 21.33).

*1,4-Diphenyl-5-hydroxy-1,2,3-triazole (If)*. Methylation of 115 mg of (If)<sup>6</sup> gave 175 mg of a mixture which was separated into three fractions by preparative thin layer chromatography, eluting once with benzene-ether (4:1).

The first fraction gave 59 mg (48 %) of 1,4-diphenyl-5-methoxy-1,2,3-triazole (IVf), m.p. 86–87°. Two recrystallizations from ethyl acetate-hexane did not change the m.p. (recorded<sup>3</sup> m.p. 88–90°). (Found: C 72.01; H 5.40. Calc. for  $C_{15}H_{13}N_3O$ : C 71.70; H 5.22; N 16.72).

The second fraction contained 15 mg (12 %) of 1,4-diphenyl-2-methyl-1,2,3-triazolone-5 (IIc), m.p. 136–137°. Two recrystallizations from ethyl acetate-hexane gave the pure product, m.p. 141°. (Found: C 71.58; H 5.40).

The third fraction gave 36 mg (30 %) of 1-methyl-3,5-diphenyl-1,2,3-triazolio-4-oxide (IIIc), m.p. 127–130°. After two recrystallizations the m.p. was 130° (recorded<sup>3</sup> 135–136°). (Found: C 71.67; H 5.34; N 16.48).

*1-Benzyl-5-hydroxy-1,2,3-triazole (Ic)*. Methylation of 264 mg of (Ic)<sup>7</sup> gave 299 mg of crude material which was chromatographed on a column of silica gel (30 g). Elution

with tetrahydrofuran gave two fractions and a third fraction was obtained by elution with methanol.

The first fraction to come off the column gave 69 mg (24 %) of 1-benzyl-5-methoxy-1,2,3-triazole (IVc), m.p. 61–63°. After recrystallization from hexane the product melted at 64°. It was identical with the material described above.

The second fraction after rechromatography on a column of silica gel using tetrahydrofuran as eluent gave 25 mg (10 %) 1-benzyl-2-methyl-1,2,3-triazolone-5 (IIc) as a colourless oil which could not be induced to crystallize. (Found: C 63.25; H 5.99; N 22.12. Calc. for  $C_{10}H_{11}N_3O$ : C 63.47; H 5.87; N 22.21).

The third fraction gave 159 mg (56 %) of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc), m.p. 76–79°. The product was recrystallized from ethyl acetate-hexane, m.p. 88°. It was very hygroscopic. (Found: C 62.90; H 5.73; N 21.61).

*4-Phenyl-5-hydroxy-1,2,3-triazole (Id)*. Methylation of 4-phenyl-5-hydroxy-1,2,3-triazole <sup>6,8</sup> (215 mg) gave 273 mg of crude product as a colourless oil. This product was separated into two fractions by chromatography on a column of silica gel using ethyl acetate-methanol (1:1) as eluent.

The slow moving fraction consisted of 44 mg (18 %) of pure 1,3-dimethyl-5-phenyl-1,2,3-triazolio-4-oxide (IIIa), identical with the material described above.

The fast moving fraction was rechromatographed using ether as eluent thereby giving three fractions. The first fraction to come off the column consisted of 149 mg (60 %) of colourless crystals, m.p. 30°. Recrystallization from hexane did not change the m.p. The compound showed no carbonyl absorption in infrared and it is probably 2-methyl-4-phenyl-5-methoxy-1,2,3-triazole (VI). (Found: C 63.56; H 5.99; N 22.12. Calc. for  $C_{10}H_{11}N_3O$ : C 63.47; H 5.87; N 22.21).

The second fraction gave 18 mg (7 %) of colourless crystals, m.p. 62°. Two recrystallizations raised the m.p. to 79°. The product showed no carbonyl absorption in infrared and is probably 1-methyl-5-phenyl-4-methoxy-1,2,3-triazole (VII). (Found: C 63.63; H 6.01; N 22.13).

The third fraction gave 12 mg (5 %) of colourless crystals, m.p. 59°. Mixed melting point and infrared spectra showed that this product was identical with the 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa) described above.

## Rearrangements

*Reaction of 1-benzyl-5-methoxy-1,2,3-triazole (IVc) with methyl iodide*. 1-Benzyl-5-methoxy-1,2,3-triazole (110 mg) was dissolved in a mixture of deuteriochloroform (0.2 ml) and methyl iodide (0.3 ml). The solution was kept at room temperature and NMR spectra were taken at intervals (Fig. 1). After 3 weeks the solvents were removed and the residue was separated into two fractions by column chromatography using methanol as eluent. The first fraction gave a few mg of a red oil which was not investigated further. The second fraction gave 101 mg (91 %) of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc), m.p. 88–90°. Infrared and NMR spectra showed that the product was identical with the material described above.

In another experiment 1-benzyl-5-methoxy-1,2,3-triazole (140 mg) was heated under reflux with 2 ml of methyl iodide for 3 h. Removal of the solvent and recrystallization from ethyl acetate-hexane gave 100 mg (72 %) of (IIIc), m.p. 95°.

*Reaction of 1-methyl-4-methoxy-1,2,3-triazole (VIIc) with benzyl iodide*. 1-Methyl-4-methoxy-1,2,3-triazole (61 mg) and benzyl iodide (132 mg) was kept in deuteriochloroform (0.5 ml) for 3 weeks. The solvent was then removed and the mixture was chromatographed on a column using methanol as eluent. Two fractions were obtained. The first fraction consisted of 14 mg of a red oil. The second fraction gave 56 mg (55 %) of 1-methyl-3-benzyl-1,2,3-triazolio-4-oxide (IIIc), m.p. 95°.

*Reaction of 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa) with methyl iodide*. 1-Methyl-4-phenyl-5-methoxy-1,2,3-triazole (46 mg) was dissolved in methyl iodide (0.4 ml) in an NMR sample tube and the solution was kept at room temperature while spectra were taken at intervals. The signals of 1,3-dimethyl-5-phenyl-1,2,3-triazolio-4-oxide (IIIa) appeared after 2 h and after 190 h 47 % of this compound was formed as seen from the integrated spectrum. No signals corresponding to a quaternary salt (Va) could be seen.

In another experiment 55 mg of 1-methyl-4-phenyl-5-methoxy-1,2,3-triazole (IVa) was boiled for 3 h with 2 ml of methyl iodide. Removal of the solvent left a quantitative yield of (IIIa), m.p. 60°.

*Reaction of 1-phenyl-4-methyl-5-methoxy-1,2,3-triazole (IVb) with methyl iodide.* 1-Phenyl-4-methyl-5-methoxy-1,2,3-triazole (37 mg) was dissolved in a mixture of methyl iodide (0.2 ml) and deuteriochloroform (0.5 ml). The integrated NMR spectra showed that equal amounts of methoxy compound and triazolium oxide were present after 300 h. No quaternary compound could be seen in the spectra. After 10 weeks the mixture was worked up and yielded 26 mg (70 %) of 1,5-dimethyl-3-phenyl-1,2,3-triazolium-4-oxide (IIIb) with m.p. 53–56°. The product was identical with the material described above.

*Reaction of 1-phenyl-5-methoxy-1,2,3-triazole (IVd) with methyl iodide.* 1-Phenyl-5-methoxy-1,2,3-triazole (55 mg) was dissolved in deuteriochloroform (0.5 ml) and methyl iodide (0.2 ml) and the solution was kept at room temperature. After 268 h the NMR spectrum showed only the signals corresponding to 1-methyl-3-phenyl-1,2,3-triazolium-4-oxide (IIIId). No quaternary salt could be seen in the spectra at any time. Removal of the solvent after 2 weeks left a quantitative yield of (IIIId), m.p. 89–91°. The product was recrystallized from ethyl acetate-hexane, m.p. 104°; it is very hygroscopic. (Found: C 58.86; H 5.43; N 22.88. Calc. for  $C_9H_9N_3O$ : C 61.70; H 5.18; N 23.98).

*Reaction of 1-phenyl-5-methoxy-1,2,3-triazole (IVd) with ethyl iodide.* 1-Phenyl-5-methoxy-1,2,3-triazole (66 mg) was dissolved in ethyl iodide (0.1 ml) and deuteriochloroform (0.4 ml). After 3 weeks the NMR spectrum showed that the mixture contained 53 % of methoxytriazole (IVd) and 35 % of triazolium oxide. Besides, another set of signals corresponding to a 12 % content of 1-ethyl-3-phenyl-4-methoxy-1,2,3-triazolium iodide (IX) was present. The signal of methyl iodide could also be seen.

After 8 weeks the mixture was chromatographed on a column using methanol as eluent. Two fractions were obtained. The first fraction gave a few mg of 1-methyl-3-phenyl-1,2,3-triazolium-4-oxide (IIIId). The second fraction gave 51 mg (74 %) of 1-ethyl-3-phenyl-1,2,3-triazolium-4-oxide, m.p. 63°. Recrystallization from ethyl acetate-hexane did not raise the m.p. The compound is very hygroscopic (Found: C 63.28; H 6.00; N 22.12. Calc. for  $C_{10}H_{11}N_3O$ : C 63.47; H 5.87; N 22.21).

The authors are indebted to cand. pharm. I. Krogh Andersen for the infrared spectra. Microanalyses were performed by Dr. A. Bernhardt.

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Received November 28, 1966.