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THE ACTION OF BASE ON THE 1,3-DIMETHYLTETRAZOLIUM CATION

William P. Norris and Ronald A. Henry

Chemistry Division, Research Department, U. S. Naval Ordnance
Test Station, China Lake, California

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We wish to report on the action of base on 1,3-dimethyltetrazolium salts*,**.

In D_2O buffered to pD 4.40 (potassium acid phthalate) at 25° the 5-proton of 1,3-dimethyltetrazolium chloride (I) is half exchanged in 60 ± 5 min.***. Under more basic conditions, pD 11.15 (potassium carbonate-potassium bicarbonate buffer), I (0.95 M) in D_2O at 60°, shows

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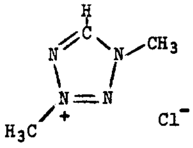
* 1,3-Dimethyltetrazolium benzenesulfonate, m.p. 72-74° after recrystallization from acetone, can be made in essentially quantitative yield from 2-methyltetrazole and methyl benzenesulfonate in refluxing toluene (prepared by Kirby Salsbury). Anal. Found: C, 42.17; H, 4.87; N, 21.94. The benzenesulfonate was converted to the chloride, m.p. 149-150°, using ion exchange resin.

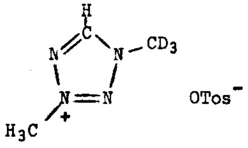
** R. A. Olofson, W. R. Thompson and J. S. Michelman, [J. Am. Chem. Soc., **86**, 1865 (1964)] report that 1,4-diethyltetrazolium p-toluenesulfonate undergoes rapid hydrogen-deuterium exchange in D_2O and reacts with base to give nitrogen and the intermediate, diethylcarbodiimide. We have observed the same behavior with 1,4-dimethyltetrazolium picrate. The latter reacts rapidly with primary and secondary amines to yield substituted guanidinium picrates and nitrogen.

*** This is in accord with the value of $t_{1/2}$ = 15 min. at pD 4.8 at 31°, for the H-D exchange of 1,3-diethyltetrazolium salt communicated to us by Dr. R. A. Olofson, Harvard University.

in addition to complete exchange of the 5-proton, exchange of the protons on the 3-methyl group with a half-life of 130 ± 10 min. The exchange rates were followed by n.m.r. In the latter reaction, under the conditions employed, the rate did not show a simple first order dependence on I. This may be due to the rather high concentrations employed. There is no detectable proton exchange on the 1-methyl group. 1-Methyl-d_3-3-methyltetrazolium p-toluenesulfonate (II) was prepared and its n.m.r. spectrum measured to establish that it was the 3-methyl group of I which was exchanging.



I



II

$H(1\text{-}CH_3)$ τ = 5.4*

$H(3\text{-}CH_3)$ τ = 5.2 $H(3\text{-}CH_3)$ τ = 5.2

$H(5\text{-}H)$ τ = -0.1

In the presence of still stronger base, 50% KOH in water, 1,3-dimethyltetrazolium benzenesulfonate cleaves to give diazomethane and potassium methylcyanamide. Diazomethane was identified by reacting it with 3,5-dinitrobenzoic acid to give the methyl ester, m.p. 107-108°. Potassium methylcyanamide was identified by isolating the methylcyanamide and comparing its infrared spectrum with that of an authentic sample (1), and by polymerizing it to the known cyclic trimer, m.p. 175-177° (1).

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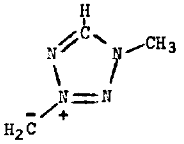
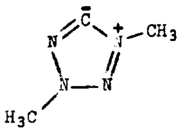
* N.M.R. measurements were made in D_2O solvent with tetramethylsilane as an external reference by Donald W. Moore.

The ylide III may be involved in the H-D exchange on the 3-methyl



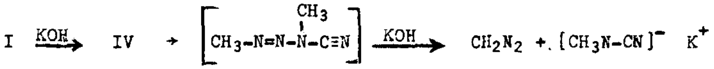
III



IV

and the ylide IV is undoubtedly involved in the H-D exchange in the 5-position.

The cleavage reaction probably proceeds via IV to 3-cyano-1,3-dimethyl-



$$\mathrm{I} \xrightarrow{\mathrm{KOH}} \mathrm{IV} \rightarrow \left[CH_3\text{-}N{=}N\text{-}\overset{CH_3}{N}\text{-}C{\equiv}N\right] \xrightarrow{\mathrm{KOH}} CH_2N_2 + [CH_3N\text{-}CN]^- \; K^+$$

triazene which is further cleaved by base to diazomethane and potassium methylcyanamide. This reaction sequence is supported by the fact that 1-methyl-3-phenyltetrazolium iodide is cleaved by potassium hydroxide to give 3-cyano-3-methyl-1-phenyltriazene, m.p. 31-33°*.

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* 3-Cyano-3-methyl-1-phenyltriazene was also prepared from benzenediazonium chloride and methylcyanamide in the presence of base.

REFERENCES

1. R. H. McKee, Am. Chem. J., 36, 211 (1906).