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PHOTOLYSIS OF Δ^2-TETRAZOLINES: FORMATION OF DIAZIRIDINES

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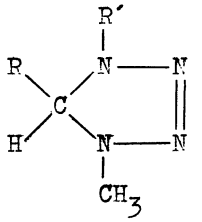
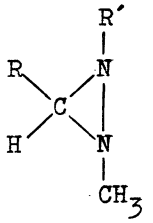
UV-irradiation of Δ^2-tetrazolines (1) resulted in the elimination of nitrogen molecule to afford 1,2,3-trisubstituted diaziridines (2). This procedure constitutes a novel method of formation of diaziridines, especially 1-aryldiaziridines, in yields of preparative value.

In a previous paper from our laboratory the preparation of Δ^2-tetrazolines (1) utilizing sodium borohydride reduction of 1,4,5-trisubstituted tetrazolium iodides was described.[1] The compounds (1) were found to be fairly stable to heat, but upon heating over 120°C 1a, for example, decomposed into N-benzylideneemethylamine and methyl azide. No elimination of nitrogen molecule was observed.



1



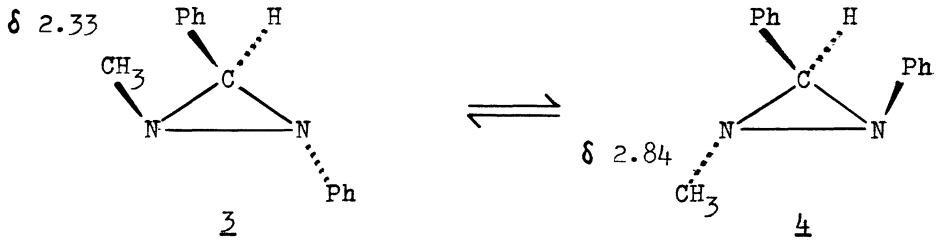
2

a) R : Ph, R′: CH_3
b) R : CH_3, R′: Ph
c) R : Ph, R′: Ph

In the present communication we wish to report the photolysis of 1 in dichloromethane giving diaziridines (2) in fairly good yield, which is the first instance of photochemical elimination of nitrogen molecule from 1 forming diaziridines.[2]

The following experimental description for the reaction of 1c[3] may be regarded typical. A solution of 1c (244 mg; 1.0 mmole) in dichloromethane (20 ml) was irradiated under nitrogen atmosphere for 20 hr by means of high-pressure Hg arc at room temp., the residue was distilled utilizing Kugelrohr (Büchi) apparatus (98-101°C /0.25 mmHg) to give 2c (132 mg; 0.63 mmole) in 62% yield. Spectral data established the diaziridine structure. MS: Found: M^+, 210.1131. Calcd for $C_{14}H_{14}N_2$: M^+, 210.1157, IR: (neat) 3030m, 1600s, 1490s, 760m, 750m, 690s cm^{-1}. However, 2c was proved to be a mixture of two stereoisomers since NMR spectrum of 2c has two singlet signals at δ 2.33 and 2.84 ppm assignable to N-methyl protons.[4] Just after the irradiation the ratio of these signals determined on the crude reaction mixture was observed to be 3:2, but after the above-mentioned distillation the ratio became almost 1:1, and this ratio did not alter by prolonged heating at the same temperature. These results can be interpreted by assuming that 2c is a mixture of 3 and 4 which are in thermal equilibrium.[5]

Photolysis of other tetrazolines (1a,b)[1] was conducted similarly and results obtained are summarized in Table 1. As expected, 2a was a single substance.



3 ⇌ 4

Table 1 Properties of Diaziridines (2)#

	δ (ppm) of NMR (CCl_4)						bp (°C/mmHg)	yield (%)
	N-CH_3	N-CH_3	N-Ph	C-Ph	C-CH_3	C-H		
2a	2.03(s)	2.53(s)		7.29(s)		3.37(s)	65-68/2	16
2b	2.58(s) 2.60(s)		6.8-7.3(m)		1.48(d) 0.94(d)	2.86(q) 2.94(q)	68-71/2	71
2c	2.33(s) 2.84(s)		6.6-8.0(m)			4.02(s) 3.83(s)	98-101/0.25	62

All new compounds gave satisfactory analyses.

In conclusion we feel that aforementioned photochemistry of 1 is extremely useful for preparation of 2, since 1-aryldiaziridines has been proved highly difficult to prepare by conventional methods,[2] and only scanty examples are scattered in the literature.[8] The mechanistic aspects of the formation of 2 will be the subject of a further report.

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REFERENCES

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2) For pertinent reference for diaziridines: E. Schmitz, Advances in Heterocyclic Chemistry, Vol 2, Academic Press, New york (1963) p. 83.

3) New compound prepared from 1,5-diphenyl-4-methyltetrazolium iodide and $NaBH_4$ according to the published method (Ref. 1) giving correct analysis, mp 112°C. NMR δ (ppm) 2.97(s, 3H), 5.28(s, 1H), 6.8-7.6(m, 10H). MS: Found: M^+, 238.1214. Calcd for $C_{14}H_{14}N_4$: M^+, 238.1218.

4) To date GLC separation of stereoisomers has been unsuccessful since the sample clearly decomposed at the injection port at 150°C.

5) The exact structures of 3 and 4 are still open to discussion,[6] but we assign them tentatively as shown by an analogy with the reported results on oxaziridines.[7]

6) The cis structure with respect to N-N bond of diaziridine has been ruled out. A. Mannschreck, R. Radeglia, E. Gründemann, and R. Ohme, Chem. Ber., 100, 1778 (1967).

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