Reaction of *N*-Methoxypyridazinium Salts with Hydroxide Ion: Formation of Vinyl Diazomethanes

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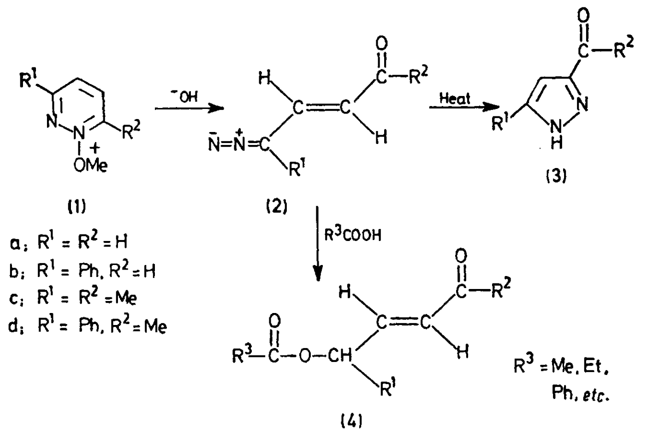
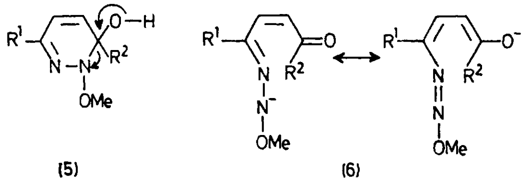
Summary Reaction of *N*-methoxypyridazinium salts with hydroxide ion results in ring-opening to give vinyl diazomethanes in high yields.

In connection with studies on *N*-alkoxypyridinium salts,[1,2] we were interested in the reaction of *N*-alkoxypyridazinium salts (**1**) with bases, and recently reported[3] that the reaction of these salts with cyanide ion afforded β-ethynylacrylonitriles.

We now report that ring-opening of the salts (**1**) by hydroxide ion causes the formation of vinyl diazomethanes. This is the first example of the isolation of a diazo-compound in the reaction of pyridazines, although the intermediacy of diazo-compounds has been observed before.[4]

The salts (**1**), prepared from pyridazine *N*-oxides with dimethyl sulphate, were treated with KOH in water at 0—5 °C for *ca.* 5 min, followed by extraction with ether. Evaporation of the extract *in vacuo* at below room temperature yielded vinyl diazomethanes (**2**) in 70—90% yield. The aldehyde compounds (**2a, b**) were stable and when





purified by column chromatography on alumina gave as a yellow liquid: (**2a**) m/e 96 (M^+) and 68 ($M - N_2$); ν (liq.) 2080 ($C{=}N_2$) and 1648 (C=O) cm^{-1}; δ (CCl_4) 5·18 (1H, d, 1-H), 5·83 (1H, dd, 3-H), 7·03 (1H, dd, 2-H), and 9·32 (1H, d, 4-H), $J_{1,2}$ 9·0, $J_{2,3}$ 16·0, and $J_{3,4}$ 7·5 Hz; (**2b**) m/e 172 (M^+) and 144 ($M - N_2$); ν (liq.) 2030 ($C{=}N_2$) and 1658 (C=O) cm^{-1}; δ(CCl_4) 5·95 (1H, dd, 3-H), 7·58 (1H, d, 2-H), 7·3 br (5H, Ph-H), and 9·59 (1H, d, 4-H), $J_{2,3}$ 16·0 and $J_{3,4}$ 7·5 Hz. However the acetyl compounds (**2c,d**) were relatively unstable and decomposed during separation.

These spectral data are consistent with the proposed structure (**2**), which was also confirmed by the following chemical studies.

αβ-Unsaturated diazoalkanes are known[5] to undergo an intramolecular 1,3-dipolar cycloaddition, resulting in the formation of pyrazoles. The diazo-compounds (**2**) thus obtained were heated in benzene to give pyrazole-3-aldehydes[6] (**3a,b**) and 3-acetylpyrazoles[7] (**3c,d**) in 60—80% yield, respectively. The compounds (**2**) also reacted readily with carboxylic acids, such as acetic acid in ether at a low temperature, to give the corresponding esters (**4**) in a moderate yield.

A possible mechanism for the formation of the diazo-compound (**2**) involves the nucleophilic addition of hydroxide ion to the pyridazine ring and subsequent ring fission of the 1,6-dihydro-compound (**5**) to the ring-opened intermediate (**6**), followed by elimination of the methoxy group. The assignment of a *trans* geometry to the olefin function in the diazo compound (**2**) is indicated by an H–H coupling constant of 16 Hz. Formation of the *trans* compound might be explained by postulation of the enolate rather than the keto form as the predominant form of the intermediate (**6**) in alkaline solution, analogous to that observed in pyridines.[1]

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