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SPECIFIC CYCLODIMERISATION OF SOME 1,3-OXAZOL-2-ONE SYSTEMS IN THE PRESENCE OF SULPHURIC ACID

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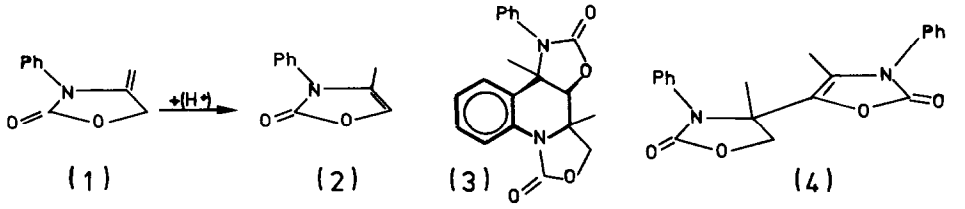
Substituted 4-methylene-1,3-oxazolidin-2-one (1) is known to undergo isomerisation reaction to substituted 4-methyl-Δ^4-1,3-oxazolin-2-one (2) in several reaction media with particular ease[1-3]. However, previous results have shown that the formation of (2), via acid catalytic isomerisation of (1), is directly related to the reaction procedure used[1,2] and may provide two additional by-products[2]. In the course of isomerisation of various 1,2-oxazol-2-one derivatives, we found that increasing the acid catalysts (H_2SO_4) concentration (1) also gives the tetrahydroquinoline dimer (3), as a novel condensed heterocyclic derivative, as well as the well-known dimerisation product of similar precursors[4,5] i.e., compound (4). Further,the specific formation of the cyclodimers (3) and (4) depends on the solvent used, the first is



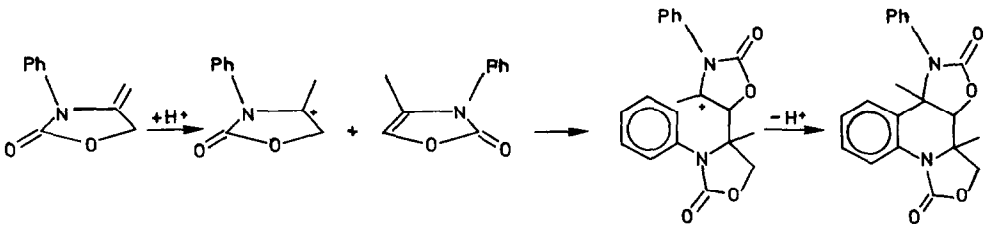
(1) (2) (3) (4)

formed in nearly quantitative yield in neat sulphuric acid solution and the latter dimeric isomer in ethereal solution with the addition of a small catalytic amount of the same acid.

Conversion of (1) into the dimer (3) takes place in concentrated sulphuric acid, the dimer (3), m.p. 290-291°C, is the only product formed and the reaction is complete within 2h at room temperature with 98% yield. The product is identified from its spectra: the mass spectrum of (3) shows an intense molecular ion at m/e 350 ($C_{20}H_{18}N_2O_4$) which represents also the base peak of the spectrum, thus indicating the high stability of the molecule to fragmentation under electron impact. The remaining features of the mass spectrum of (3) [peak at m/e 335,

291, 247, 231, 216, 202, 187, 172, 158, 144, 130, 119] are in agreement with the assigned structure[3,6]; the n.m.r. spectrum [$\delta(D_2SO_4$, 60 MHz), 8,0-6,5 (m, 9 H, ArH), 5,25 (s, 1 H, 3-CH), 5,17 and 4,67 (dd, 1 H and H, J_{gem}9, CH_2), 2,00 (s, 3 H, 4-CH_3), and 1,52 p.p.m. (s, 3 H, 2-CH_3)] and the i.r. spectrum [ν_{max}(Nujol) 1954 and 1739 cm^{-1} (CO)] are consistent with structure (3).

Treatment of (1) with H_2SO_4 in dry ether affords exclusively compound (4), m.p. 137-136°C, in excellent yield (95%). The mass spectrum of (4) shows peaks at m/e 350 (M^+, $C_{20}H_{18}N_2O_4$, 45%), 335, 231 (100%), 214, 202, 176, 175, 158, 119, 118, 91, 77, which reveal marked differences with the fragmentation pattern of the isomeric compound (3), although confirming the presence of the 1,3-oxazolidine moiety[3,6]. The n.m.r. spectrum [$\delta(CDCl_3)$, 7,0-7,6 (m, 10 H, ArH), 4,71 and 4,27 (dd, 1H and 1H, J_{gem}9, CH_2), 1,77 (s, 3 H, allyl-CH_3), and 1,72 p.p.m. (s, 3 H, CH_3)] and the i.r. spectrum [ν_{max}(Nujol) 1760 and 1735 (CO)] provide clear evidence for structure (4), which is also expected in accordance with previous reports on similar systems[4,5] .



(1) (5) (2) (6) (3)

These experimental results suggest that the dimerisation reaction of (1) leading to (3) and (4) proceeds via a carbonium ion (5) formed at position 4 which then adds to the isomerised compound (2) to yield (3) by electrophilic cyclisation or (4) by proton elimination, through the intermediate (6), according to the reaction conditions. The involvement of (2) in the reaction path from (1) to (3) is confirmed by the formation of (3) using compound (2) as precursor and following the same procedure described above . Thus, it is feasible for the dimerisation process to be controlled by the appropriate choice of the reaction media, leading to a unique product.

Detailed studies of the dimerisation reaction described above are in hand and will be reported elsewhere.

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