Tetrahedron Letters,Vol.28,No.38,pp 4397-4398,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

3a-AZAAZULENONES CONTAINING A CARBONYL GROUP IN THE 5-MEMBERED RING[1)]

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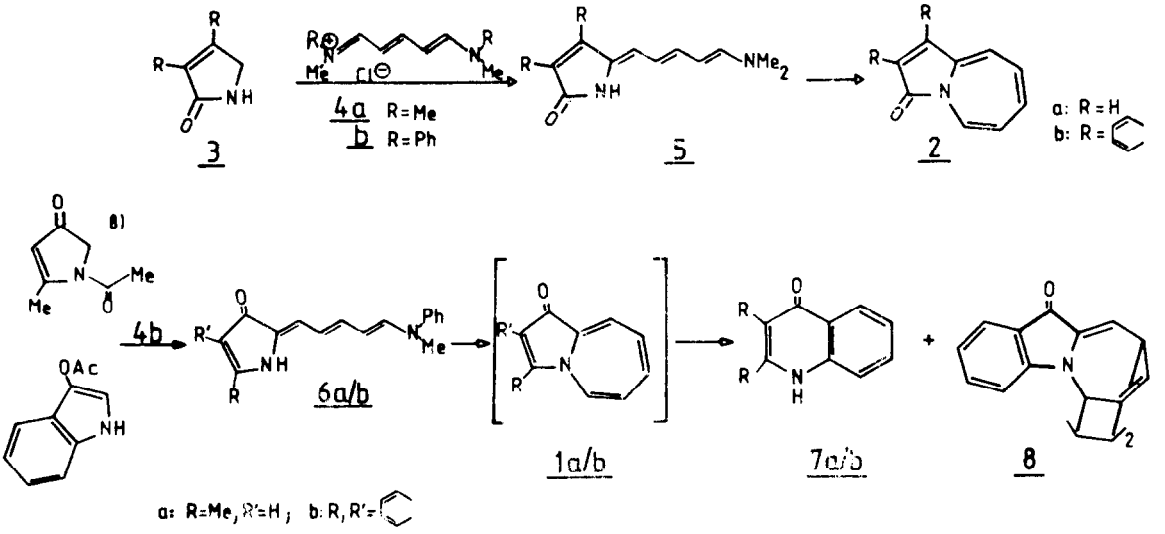
SUMMARY: A report is given on the synthesis of 3a-azaazulen-3-ones 2a and 2b. Experiments designed to prepare isomeric 3a-azaazulen-1-ones 1a/b resulted in a formation of rearranged γ-pyridone derivatives 7a/b and a dimer 8 of 1b.

3a-Azaazulenones containing carbonyl groups in the 7-membered ring have been synthesized and shown to be stable compounds[2)]. Isomers 1 and 2, however, lacking a stabilising pyrrole subunit, should be labile. Our efforts, resulting in a synthesis of 3a-azaazulen-3-one 2a as well as the benzo-derivative 2b are shown in the scheme. Condensation of Δ^3-pyrrolin-2-one 3a[3)] and the isoindole 3b[4)] with the pentamethinium salt 4a[5)] gave the enaminones 5a (26%)[6,7)] and 5b (35%)[6,7)]. 2a (5%) and 2b (2%)[6,7)] were obtained from a subsequent flash vacuum pyrolysis.

The 3a-azaazulenones are highly coloured and are extremely unstable in oxygen. The average value of the proton shifts of 2a (δ = 6,01 ppm) is 0.7-0.9 ppm to highfield, compared with the isomers which contain the carbonyl group in the 7-membered ring[2)], thus indicating a diminished diatropicity.



Attempts to obtain 3a-azaazulen-1-ones 1 analogously[8,11] are depicted in the scheme. During the thermolysis of 6a, a transient blue colour developed, which points to an intermediate 1a. An additional indication for a formation of an 3a-azaazulen-1-one 1 was obtained from the thermolysis of 6b which, besides the production of 7b, yielded the dimer 8. The dimerization of 1b, which is not allowed as a concerted reaction for symmetry reasons, could proceed in a manner similar to that of the multistep dimerization of azepines investigated earlier[9]. Rearrangements of 3a-azazulen-1-ones 1 to γ-pyridone derivatives are formally analogous to transformations of azulene into naphthalene.

ACKNOWLEDGEMENT

We are grateful to the Minister für Wissenschaft und Forschung des Landes-Nordrhein Westfalen for financial support of these investigations.

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6) Experimental conditions: 5a: $NaOCH_3$, MeOH, reflux, 4 h, 5b: NaH, DMF, 70°C, 3 h crystallized from ethanol. 2: FVP, 10^{-2} Torr, 600°C, 1 h. 2a: FVP, 10^{-2} Torr, 650°C, 1 h. Thermolysis of 6a/b: 1,2,4-Trichlorbenzone, reflux, 5-15 min. 15 and thermolysis, DMF $(OMe)_2$, reflux, 4 h 52%; quinoline, 200°C, 16 h, 42%
7) The new compounds were characterized by elemental analysis and spectra. Selected data: 2a: $CDCl_3$ δ: 4.98 (dd, 1H, J_{54} = 10.1 Hz, J_{56} = 7.6 Hz), 5.52 (dd, 2H, J_{76} = 11.4 Hz, J_{78} = 7.7 Hz), 5.72 (dd, 1H, J_{65} = 7.6 Hz, J_{67} = 11.4 Hz), 6.51 (d, 1H, J_{21} = 5.5 Hz), 6.73 (d, 1H, J_{45} = 10.1 Hz), 7.02 (d, 1H, J_{12} = 5.5 Hz). 2b: ^{1}H-NMR (300 MHz, Acetone-d_6: δ = 4.91 (dd, 1H, J_{65} = 10.3 Hz, J_{67} = 7.0 Hz), 5.56 (quin, 2H, J_{76}) 7.0 Hz, J_{78} = 11.2 Hz, J_{89} = 6.9 Hz), 6.12 (d, 1H, J_{98} = 6.9 Hz), 6.58 (d, 1H, J_{56} = 10.3 Hz), 7.61 (d, 1H, J_{43} = 7.6 Hz), 7.76 (t, 1H, J_{34} = 7.6 Hz, J_{32} = 6.8 Hz), 7.80 (t, 1H, J_{21} = 7.2 Hz, J_{23} = 6.8 Hz), 7.94 (d, 1H, J_{12} = 7.2 Hz). 7a: ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 2.41 (s, 3H, CH_3), 6.10 (s, 1H, olef-H), 7.32 (t, 1H, J_{21} = 8.0 Hz, J_{23} = 7.0 Hz), 7.42 (d, 1H, J_{12} = 8.0 Hz, 7.59 (t, 1H, J_{34} = 8.5 Hz, J_{32} = 7.0 Hz), 8.25 (d, 1H, J_{43} = 8.5 Hz). 7b: ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 7.32 (t, 2H, J_{21} = 8.25 Hz, J_{23} = 7.0 Hz), 7.38 (d, 2H, J_{43} = 8.5 Hz), 7.64 (t, 2H, J_{34} = 8.5 Hz, J_{32} = 7.0 Hz), 8.18 (br, 1H, N-H), 8.32 (d, 2H, J_{12} = 8.25 Hz). 8: NMR (300 MHz, CD_2Cl_2): δ = 2.72 (dd, 2H, J_{89} = 8.2 Hz, J_{87} = 7.5 Hz), 2.77 (d, 2H, J_{56} = 6.3 Hz), 4.59 (d, 2H, J_{98} = 8.2 Hz), 5.88 (dd, 2H, J_{78} = 7.5 Hz, J_{76} = 9.0 Hz), 6.58 (dd, 2H, J_{67} = 9.0 Hz, J_{65} = 6.3 Hz), 6.71 (d, 2H, J_{12} = 8.4 Hz), 6.75 (t, 2H, J_{34} = 8.0 Hz, J_{32} = 7.1 Hz), 7.37 (t, 2H, J_{21} = 8.4 Hz, J_{23} = 7.1 Hz), 7.45 (43, 2H, J_{43} = 8.0 Hz).
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(Received in Germany 4 June 1987)