REACTION OF 2-DIAZOCYCLOHEXANONE WITH AZODICARBOXYLIC ACID ESTERS

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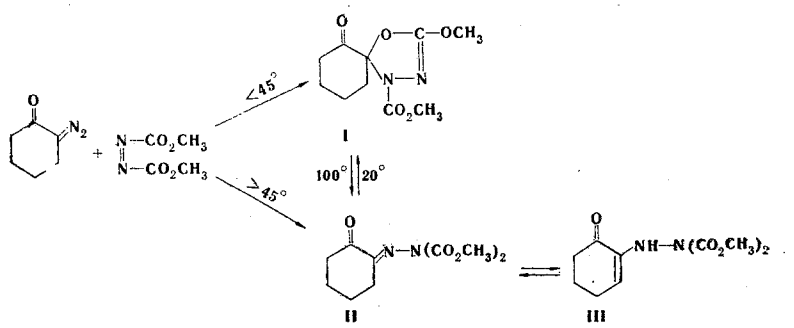
The reaction of aliphatic diazo compounds with azodicarboxylic acid esters may proceed in several directions [1], but, as a rule, α-diazo ketones in these cases give exclusively substituted α-diketone monohydrazones [2].

We have shown that 2-diazocyclohexanone reacts exothermically with azodicarboxylic acid esters. The reaction with dimethyl azodicarboxylate at no higher than 45°C gives 2-oxo-5'-methoxy-3'-carbomethoxycyclohexanespiro-2-(1,3,4-oxadiazoline) (I) in 60% yield; at higher temperatures 1,2-cyclohexanedione di(carbomethoxy)hydrazone (II) is formed along with it:



Oxadiazoline I can be quantitatively converted to hydrazone II in a few minutes by heating at 100°; the reverse conversion II→I is observed at room temperature. Conversion of I to hydrazone II is also noted on prolonged storage of solutions of I in CCl_4 or $CHCl_3$.

1,3,4-Oxadiazoline I was obtained as shiny crystals with mp 94-95°. IR spectrum (in CCl_4), ν, cm^{-1}: 1760 m, 1724 s, 1696 vs. UV spectrum ($CHCl_3$): λ_{max} 255 nm (ε 180). PMR spectrum (in $CHCl_3$): δ 1.95 (multiplet, 4H), 2.58 (multiplet, 4H), 3.80 (singlet, 3H), and 3.95 ppm (singlet, 3H).

Hydrazone II was obtained as a viscous yellow liquid. IR spectrum (in $CHCl_3$), ν, cm^{-1}: 3350 m, 3135 w, 3040 m, 1785 w, 1755 s, 1730 s, 1635 w, and 1605 w. UV spectrum ($CHCl_3$): λ_{max} 272 nm (ε 5100). PMR spectrum (in $CHCl_3$): δ 1.95 (multiplet, 4H), 2.66 (multiplet, 4H), 3.76 (singlet, 6H), 5.58 (triplet, $-CH=$), and 6.50 ppm (singlet, NH).

The appearance of absorption bands in the IR spectrum of hydrazone II at 3040-3400 cm^{-1} and the presence of weak signals at 5.58 and 6.50 ppm in its PMR spectrum constitute evidence for the possibility of a tautomeric hydrazone-enehydrazine equilibrium (II⇌III).

The results of elementary analysis of I and II are in agreement with the calculated values.

LITERATURE CITED

1. E. Fahr and K. Königsdorfer, Tetrahedron Lett., 1873 (1966).
2. E. Fahr, K. Königsdorfer, and F. Scheckenbach, Ann., 690, 138 (1965).

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