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THE ADDITION OF O-ARYLHYDROXYLAMINES TO DIMETHYL ACETYLENEDICARBOXYLATE

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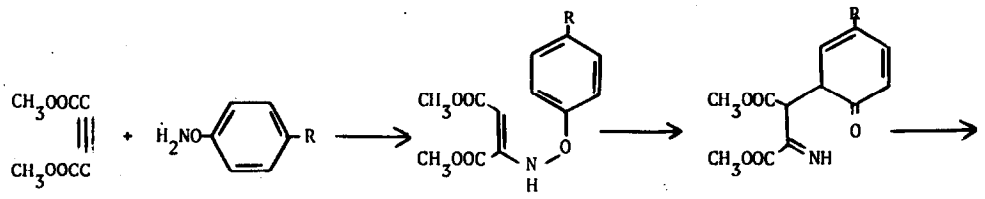
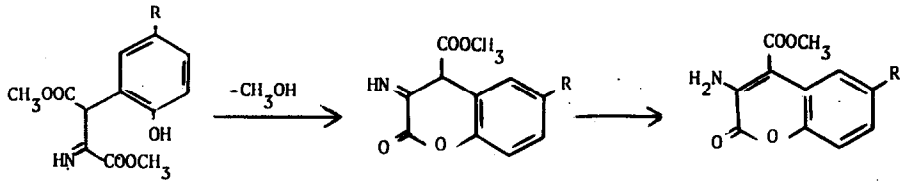
During a study on hetero-Cope rearrangements of hydroxylamine derivatives we tried the title reaction as a possible route to O-aryl-N-vinylhydroxylamines. The products were however identified as 3-amino-4-carbomethoxycoumarins (IV). Their formation can be rationalized on the basis of the following mechanism:



I II III V



VI VII IV

a, R = H
b, R = CH_3
c, R = NO_2

The addition yielded the expected O-aryl-N-(1,2-dicarbomethoxyvinyl)hydroxylamines (III) which rearranged spontaneously to the dienones V. Aromatization (VI) and lactonization gave IV.

Compounds IVa (m.p. 150°, 80%) and IVb (m.p. 120°, 70%) precipitated immediately on mixing ethanolic or ethereal solutions of I and II[1,2] at -30°. The structural assignments are based on analytical and spectral (IR, NMR, MS) data and chemical reactivity which were in accord with structures IV and excluded other possibilities.

In the reaction of I with IIc[3] the coumarin IVc (m.p. 227-228°, 10%) was only a minor product. The main product (m.p. 56°, 50%) was identified as O-(4-nitrophenyl)oxime of dimethyl oxalacetate (VIII). The formations of IVc and VIII are competitive as VIII could not be transformed to IVc under the reaction conditions. However, reflux of VIII in methanolic HCl gave IVc quantitatively.

We have previously reported the rearrangements of O-aryl[4,5] and O-vinyloximes[6] which required either acid catalysis or high temperatures. On the basis of the present results it can be safely concluded that these harsh conditions served only for the tautomerization of the oximes, while the rearrangement step is spontaneous, as can be expected from the big difference in bond energies between the cleaved and the formed bonds and the polarity of the N-O bond.

Further work on the synthetic utilization of the reaction is in progress.

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