CYCLOADDITION OF 3-ACYL AND 3-CARBETHOXY-Δ^2-PYRROLIN-4,5-DIONES WITH OLEFINS

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Cycloaddition of 2-phenyl-3-carbethoxy-Δ^2-pyrrolin-4,5-dione (I) and N-phenyl-2-carbethoxy-3-benzoyl-Δ^2-pyrrolin-4,5-dione (II) with olefins was investigated.

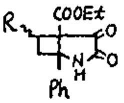
Photocycloaddition of I with olefins gave corresponding 1,2-adduct (III) in moderate yield. While styrene and cyclopentadiene gave dihydroazatropolone derivatives (IV) and (V), respectively, as major product. V on treatment with potassium hydroxide formed an azatropolone (VI). Dihydroazatropolone was proved to be formed by photo-ring fission of four membered ring of 1,2-adduct. This is, we believe, the first case of azatropolone synthesis.

Heating of II with olefins gave corresponding pyrano-pyrrole derivatives (VII). This reaction was found to proceed thermally in a concerted [4+2] manner with regio- and stereospecificity.

In reactions of II with butadienes, two types of [4+2] cycloaddition were observed. One is a formation of pyrano-pyrrole (VII) (Path A), where butadiene behaved as a dienophile and II as a diene. The other gave a usual Diels-Alder product (VIII) (Path B), where butadiene and pyrrolindione acted as 4π and 2π systems respectively. Heating of II with butadiene at 100° gave VIII and in a ratio of 4:1. VII is an adduct of type A and VIII is of type B. While 1-acetoxy, 1-suphenyl and 1-trimethylsilyloxybutadienes afforded only type B adduct (VIII) respectively.

In spite of the fact that VII rearranged by [3,3] sigmatropic manner into VIII on heating above 120°, thermally controlled experiments indicated that path A and path B in cycloaddition reaction occur competitively, the product ratio being mainly depending on species of dienes used.

Sigmatropic sifts were also observed. III (R=$-CH=CH_2$) rearranged to IX at 160-180°. This [1,3] sigmatropic shift proceeds with retention of stereochemistry at migrating cabon. VII (R=$-CH=CH_2$) rearranged to VIII at 160° in a [3,3] sigmatropic manner. The similar sigmatropic sift was observed in a norbornadine adduct (X), which afforded at 160° a cyclopropane derivative (XI). This rearrangement is a [3,4] sigmatropic *shift in a formal sense.*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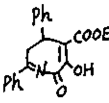
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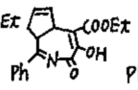
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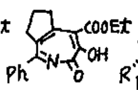
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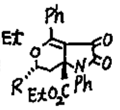
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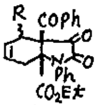
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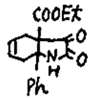
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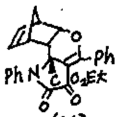
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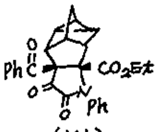
(XI)