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CYCLOADDITION OF DIOXOPYRROLINES WITH OLEFINS

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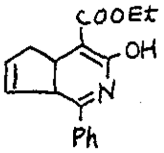
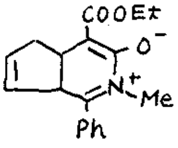
Thermal and photo-cycloaddition reactions of several 2,3-disubstituted Δ^2-pyrroline-4,5-diones (dioxopyrrolines) with olefins were investigated. Diels-Alder reaction of dioxopyrrolines with butadiene was found to give four different types of adducts as follows. 3-Phenyl-dioxopyrroline (1) gave a normal Diels-Alder adduct (2). On the other hand, 2-phenyl-3-ethoxycarbonyl-dioxopyrroline (3) afforded 1,2-adduct, 1-phenyl-3,4-dioxo-5-ethoxycarbonyl-7-vinyl-1,5,7,cis-bicyclo[3,2,0]-2-azabicycloheptane (4), which on heating rearranged into hydroindol derivative (5) in a [1,3]sigmatropic manner. 4 also was obtained by photocycloaddition of 3 with butadiene. 1-Phenyl-2-ethoxycarbonyl-3-benzoyl-dioxopyrroline (6) gave 1,4-diphenyl-2,3-dioxo-6-vinyl-7-ethoxycarbonyl-2,3,6,7,7a-pentahydropyrano[4,3-b]pyrrole (7), which by [3,3]sigmatropic manner rearranged to hydroindol derivative (8). 2-Methyl-3-ethoxycarbonyl-dioxopyrroline (9) is equilibrated with its enol form (10). The mixture gave only the Diels-Alder adduct (11) derived from the enol form. The presence of phenyl group at C_2-possition of dioxopyrroline markedly decreased its reactivity as a dienophile.

Photochemical generation of 2-hydroxy-4,5-dihydropyridines was observed by cycloaddition of 3 with olefins. Cyclopentadiene, cyclopentene and trimethylsilyoxycyclopent-1-ene afforded as a major product dihydropyridines (12), (13) and (14) respectively. The corresponding N-methyl derivative obtained from the corresponding N-methyldioxopyrroline and cyclopentadiene was found to be a novel meso-ionic compound (15). The mechanism of formation of dihydropyridines is now under investigation.



12 R=H
13 R=H, 2H instead of double bond
14 R=$OSiMe_3$, 2H instead of double bond



15