REACTION OF DIKETENE WITH CARBENES AND NITRENES

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The reaction of diketene with carbenes and nitrenes was examined.

The photoreaction of diketene with ethyl diazoacetate and diazoacetone in the presence of benzophenone gave ethyl 5-oxo-4-oxaspiro[2.3]hexane-1-carboxylate (1a) and 1-acetyl-5-oxo-4-oxaspiro[2.3]hexane (1b), respectively. Similarly, the reaction of diketene with 2-diazoesters such as ethyl 2-diazo-3-oxobutyrate, ethyl 2-diazo-3-oxohexanoate and di-tert-butyl diazomalonate, followed by treatment with methanolic hydrogen chloride gave β-keto adipates, and/or furan derivatives.

The similar reaction of diketene with α-diazoalkylphosphonates and α-diazoalkylphosphine oxide gave the corresponding 5-oxo-4-oxaspiro[2.3]hexane derivatives (1c-h) in good yields. Compound (1a) reacted with anilines to give the acetoacetanilides which, on treatment with conc. sulfuric acid, cyclized to 2-quinolones. Compound (1a) reacted with carbonyl reagents such as phenylhydrazine and hydroxylamine to afford pyrrazolin-3-one and isoxazolin-5-one, respectively.

Reaction of 1 with phenols, amidine and o-phenylenediamine gave coumarins, pyrimidine and 1,5-benzodiazepin-2-ones, respectively.

Reaction of diketene with dichlorocarbene obtained by thermolysis of phenyl(trichloromethyl)mercury gave 1,1-dichloro-5-oxo-4-oxaspiro[2.3]hexane in good yield.

The reaction of diketene with aroyl azides or ethyl azidoformate under irradiation afforded 1-substituted-4-hydroxy-2-pyrrolinones.