CHEMISTRY LETTERS, pp. 697-698, 1978. Published by the Chemical Society of Japan

STUDIES ON KETENE AND ITS DERIVATIVES (XCI)[1] REACTION OF DIKETENE WITH ACYL AZIDES

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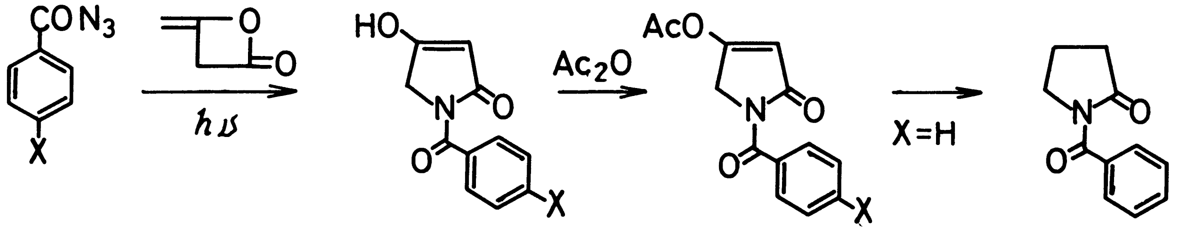
Photoreaction of diketene with benzoyl azide (1a) gave 1-benzoyl-4-hydroxy-3-pyrrolin-2-one (2a). Similarly, diketene reacted with p-anisoyl azide (1b), p-chlorobenzoyl azide (1c), and p-toluoyl azide (1d) to give the corresponding 1-aroyl-4-hydroxy-3-pyrrolin-2-ones (2b,c and d).

Most reactions of diketene fall into the category of addition reactions with concomitant opening of the β-lactone ring to give acetoacetyl derivatives or cyclic (mostly heterocyclic) compounds.[2,3] On the other hand, only a few reactions involve the olefinic double bond keeping the β-lactone ring intact. For instance, homolytic addition of thiols to diketene gives γ-alkylthio-β-lactones.[4] Similarly, β-butyrolactone is obtained by catalytic reduction of diketene.[5] Previously, we have reported such modal reactions of diketene to give the spiro compounds.[6] The present communication reports the photoreaction of acyl azides with diketene to give the pyrrolinone derivatives (2), which are presumably produced *via* the spiro intermediates (8).

When benzoyl azide (1a)[8] was allowed to react with diketene under irradiation, 1-benzoyl-4-hydroxy-3-pyrrolin-2-one (2a), was obtained in 17% yield, mp 180° (decomp.).[7] Heating of compound (2a) with acetic anhydride gave a 92% yield of 4-acetoxy-1-benzoyl-3-pyrrolin-2-one (3a), mp 133°, which, on catalytic reduction, was converted to 1-benzoyl-2-pyrrolidone (4), mp 89—90°, undepressed on admixture with an authentic sample prepared according to the literature (lit, mp 91°).[9] Hydrolysis of compound (2a) gave N-acetonylbenzamide (5), mp 83° (lit, mp 85°).[10] Methanolysis of (2a) afforded methyl 4-benzamidoacetoacetate (6), $PhCONHCH_2COCH_2CO_2CH_3$, as colorless leaves (from cyclohexane - $CHCl_3$), mp 88°.

Similarly, photoreaction of diketene with p-anisoyl azide (1b), p-chlorobenzoyl azide (1c), and p-toluoyl azide (1d)[8] gave rise to 1-(p-anisoyl)-, mp 181° (decomp.) (2b), 1-(p-chlorobenzoyl)-, mp 175° (decomp.) (2c), and 1-(p-toluoyl)-4-hydroxy-3-pyrrolin-2-one, mp 168.5° (decomp) (2d), which were acetylated with acetic anhydride giving the corresponding 4-acetoxy derivatives (3b,c and d).

Concerning the formation of these products (2), the most likely pathway is elucidated as follows: that is, the nitrene intermediates produced on photolysis of aroyl azides (1), add to the C=C double bond of diketene giving the spiro compounds (8) as intermediates, ring transformation of which would give the products (2).



1 2 3 4

a : X = H
b : X = OMe
c : X = Cl
d : X = Me

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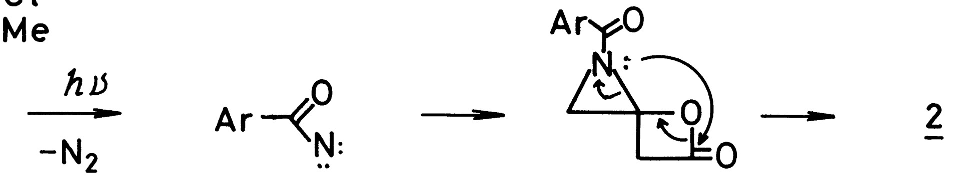

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Acknowledgment: In part, this work was supported by a Grant-in-Aid from the Ministry of Education and this is gratefully acknowledged.

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(Received April 28, 1978)