CHEMISTRY LETTERS, pp. 2077-2078, 1991.

Intramolecular Photochemistry of 3-Alkynyloxy-2-pyridones and Isomerization of the Photoadduct to Tricyclic β-Lactam

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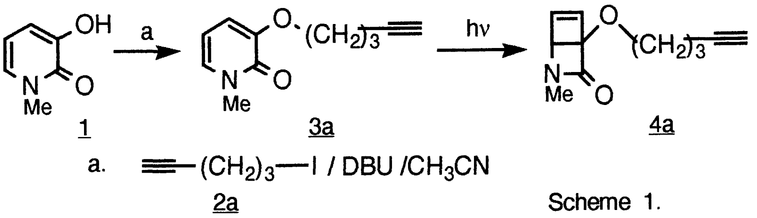
Sensitized photoreaction of 3-(5-ethoxycarbonyl-4-pentynyloxy)-2-pyridone gave a [2+2]cycloadduct across 3,4-bond of the 2-pyridone. The adduct was thermally derived to a new tricyclic β-lactam.

2-Pyridones is one of typical heterocyclic α,β,γ,δ-unsaturated carbonyl compounds, and the photoreactions with unsaturated substances are very interested in possibilities of peri-, site- and regio-selective cycloadditions,1) ring-expansion,2) and valence isomerizations of the adducts.3) One of the photo[2+2]adducts was also derived to a natural compound4) and valence isomers of 2-pyridones may become synthons of β-lactam antibiotics of fourth-generation5) and of a potent inhibitor of infectivity of immuno-deficiency virus.6) The objective of the present research is to induce a multicyclized new hetero-compounds by intramolecular photoadditions of 2-pyridones possessing triple bonds at the side-chains and to derive the adduct to a tricyclic new β-lactam. Photochemical reactivity of this typical one may be also cleared.

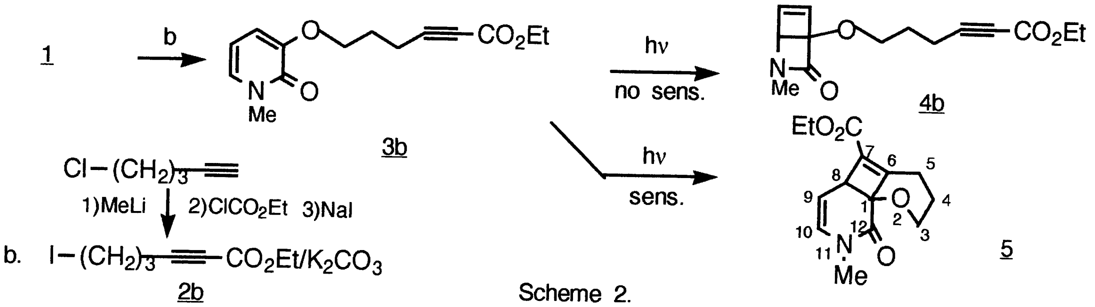
Thus, 1-methyl-3-(4-pentynyloxy)-2-pyridone (3a)(liq.)7) was prepared from 3-hydroxy-1-methyl-2-pyridone (1) as shown in Scheme 1 in 82% yield. Irradiations of 3a (8 mol m^{-3}) in acetonitrile with high-pressure mercury lamp through a Pyrex vessel were carried out in both cases of presence of benzophenone (8 mol m^{-3}) and not. They however gave no cycloadduct. Only when benzophenone was absent, a Dewar-type valence-isomer (4a)(liq.)7) of 3a was formed in 57% yield. From suggestion of our previous report,3) 3-(5-ethoxycarbonyl-4-pentynyloxy)-1-mehtyl-2-pyridone (3b)(mp 65 °C)7) was sequentially prepared in 49% yield from a reaction of 1 with ethyl 6-iodo-2-



Scheme 1.

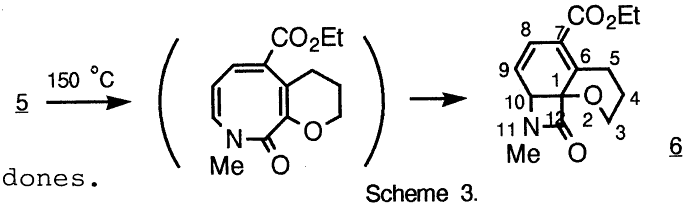
hexynoate (2b)(liq.)$^{7)}$ as shown in Scheme 2, and 3b was similarly irradiated in the presence or absence of benzophenone. Under the former conditions, 3b gave an intramolecular cycloadduct (5)(liq., 25% yield)$^{8)}$ across 3,4-positions of 2-pyridone, and under the latter conditions, 3b gave a valence-isomer 4b (liq., 50% yield)$^{7)}$.

The intramolecular photoaddition is inferred to be a triplet reaction and need some electronic attraction between the two parts.



Scheme 2.

The next step is intended isomerization. 5 was then heated at 150 °C to give a tricyclic β-lactam (6)(liq.)$^{9)}$ in 52% yield via two valence-isomerizations as shown in Scheme 3. The new β-lactam 6 showed good analytical and spectral ($\nu_{N-C=O}$ 1760 cm^{-1} etc.) data. This is also the first example of valence-isomerization of adducts across the 3,4-positions of 2-pyridones.



Scheme 3.

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7) Reasonable analytical and spectral data were obtained.

8) 5 [^{1}H-NMR ($CDCl_3$) δ 1.31 (Me, t), 1.82 (1H, m), 2.00 (1H, m), 2.47 (1H, m), 2.90 (1H, m), 3.07 (Me, s), 3.44 (1H, dd), 3.92 (1H, m), 4.22 (2H, q), 4.90 (1H, td), 5.26 (1H, dd), 5.90 (1H, d)]

9) 6 [^{1}H-NMR ($CDCl_3$) δ 1.33 (Me, t), 1.95 (2H, m), 2.68 (1H, m), 2.86 (Me, s), 3.54 (1H, m), 3.91 (1H, m), 3.95 (1H, d), 4.27 (2H, q), 4.51 (1H, m), 5.96 (1H, dd), 6.60 (1H, d)]

(Received July 31, 1991)