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PHOTOCHEMICAL BEHAVIOUR OF 1-PHENYL-2,2-DIMETHOXY-2(N-ALKOXYCARBONYLAMINO)-DIAZOETHANES.(*)

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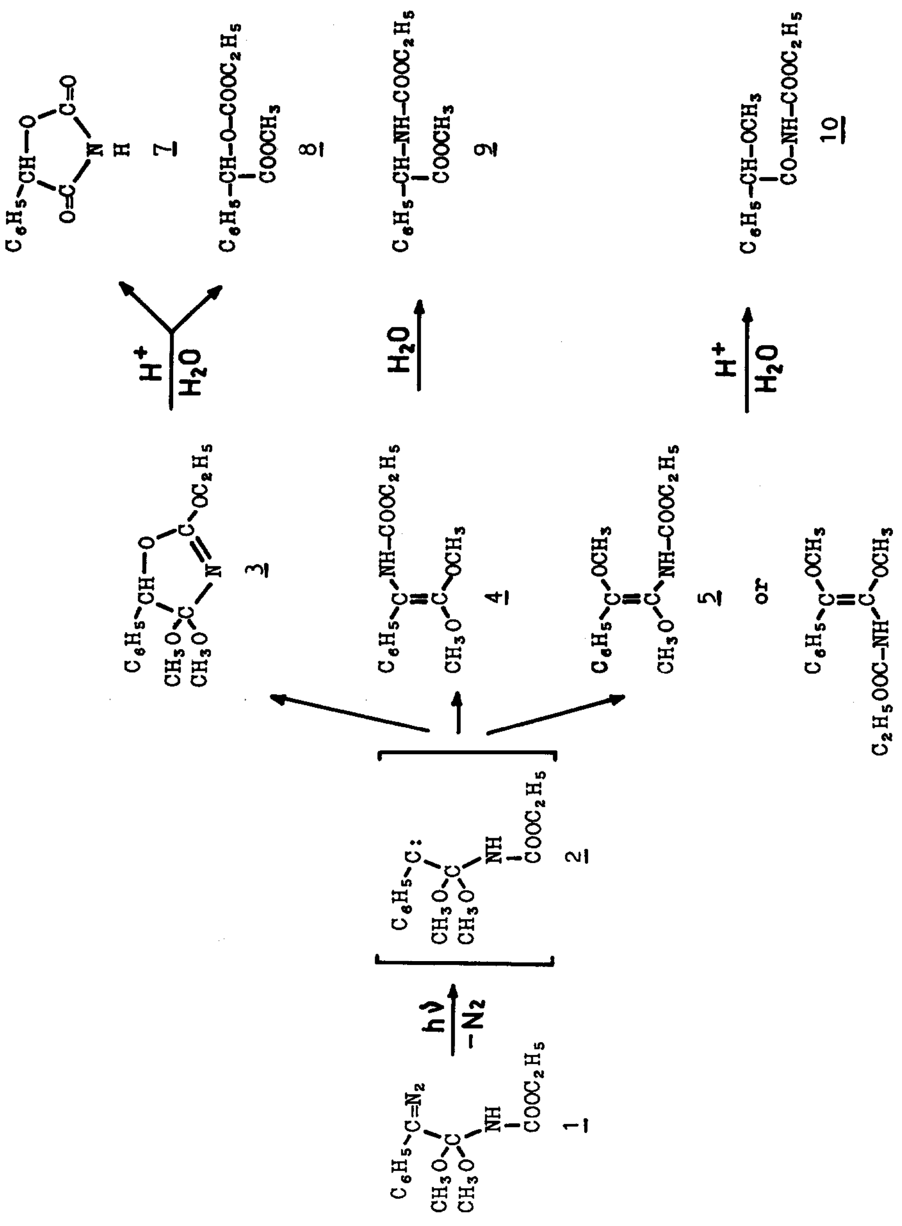
The photolysis of 2,2-diethoxy-diazoethane has been extensively studied; this compound decomposes to diethoxymethyl-carbene which rearranges to cis and trans 1,2-diethoxyethylene and ketene diethylacetal[1].

Recently we reported the synthesis and some chemical properties of the title diazoethanes[2,3], first examples of diazoamide acetals. We have now investigated the photolysis of 1-phenyl-2,2-dimethoxy-2(N-ethoxycarbonylamino)-diazoethane 1 which gave Δ^2-oxazoline 3 as the major product, ketene acetal 4 and ketene O,N-acetal 5 or 6 as the minor products.

A 2% solution of 1 in cyclohexane was degassed by bubbling nitrogen through it. The solution was then photolyzed with a high-pressure mercury lamp (Hanovia 450 W) placed in a water-cooled quartz immersion well with a pyrex filter sleeve. The reaction was complete in 2.30 hr when nitrogen ceased to evolve and the orange solution became colorless. After removal of the solvent on a rotatory evaporator, IR spectrum (CCl_4) of the reaction mixture revealed the presence of $\rangle NH$ (3385 cm^{-1}), -COOR (1750-1720 cm^{-1}) and of $\rangle C{=}C\langle$ (1637 cm^{-1}) functions in addition to Δ^2-oxazoline $\rangle C{=}N-$ function (1661 cm^{-1}). NMR spectrum (CCl_4) showed the presence of oxazoline 3[3,4]; moreover exhibited a slightly broadened signal centered at τ 4.04 (NH of 4 and 5 or 6) and three singlets at τ 6.18,


1
hν
−N₂
2
3
4
5
or
6
H⁺
H₂O
H₂O
H⁺
H₂O
7
8
9
10

6.36, 6.47 (methoxyl groups of 4 and 5 or 6; the area of the singlet at τ 6.36 equals about[5] the sum of the areas of the one at τ 6.18 and 6.47, the relative areas of the signals at τ 4.04 and 6.36 are about[5] 1:3).

The composition of the reaction mixture, presumed on the basis of IR and NMR spectra, was confirmed by chromatographic methods and chemical data. Al_2O_3 chromatography allowed the isolation of oxazoline 3 (∼40%) and ester 9 (∼16%), the latter was evidently formed by hydrolysis of 4 during the separation procedure, as observed in similar cases[6,3]. No evidence was obtained, by Al_2O_3 chromatography, to support the presence in the reaction mixture of ketene O,N-acetal 5 or 6[7]; however its presence was confirmed by the results obtained from mild acid hydrolysis of the crude reaction mixture followed by chromatography on silica gel. In this way it was possible to isolate amide 10 (∼5%; from 5 or 6) in addition to oxazolidine-2,4-dione 7 and ester 8 (from oxazoline 3), ester 9 (∼16%; from ketene acetal 4).

No spectral evidence was obtained to support the 1-ethoxycarbonyl-2,2-dimethoxy-3-phenylaziridine presence in the reaction mixture, however it is possible that 9 is partly formed by hydrolysis from this compound.

The photolysis, in the above conditions, of 1-phenyl-2,2-dimethoxy-2(N-isopropoxycarbonylamino)-diazoethane[8] also gave the corresponding Δ^2-oxazoline[8] as the main product.

REFERENCES and NOTES

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[1] W. Kirmse and M. Buschhoff, Ber. 100, 1491 (1967).

[2] R. Scarpati and M.L. Graziano, Tetrahedron Letters, 1971, 2085.

[3] R. Scarpati and M.L. Graziano, Tetrahedron Letters, 1971, 4771.

[4] Identification was made possible by comparison with NMR spectrum of the pure compound.

[5] The determination of the areas cannot be rigorous owing to the presence of the methylenes quartets of the esters 4 and 5 or 6 in same region of the spectrum.

[6] R. Scarpati, M.L. Graziano and R.A. Nicolaus, Gazz. Chim. Ital. **100**, 665 (1970).

[7] It is to be noted that amide 10, which is evidently formed by hydrolysis of 5 or 6 during the Al_2O_3 chromatography, could not be isolated as it in its turn undergoes hydrolysis in contact with this adsorbent.

[8] The compound gave satisfactory elemental analysis; IR and NMR spectra are consistent with the proposed structure.