

SHORT COMMUNICATIONS

The Photochemical Reactions of Several Mesoionic Compounds

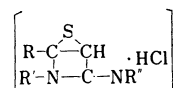
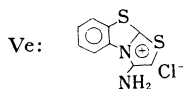
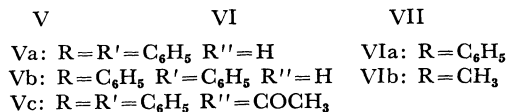
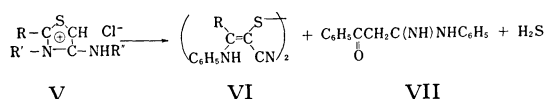
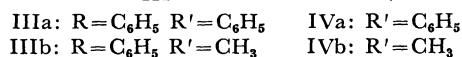
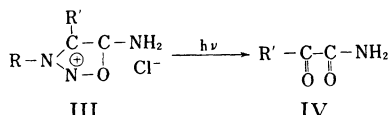
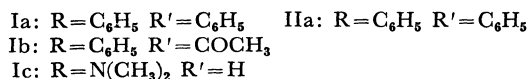
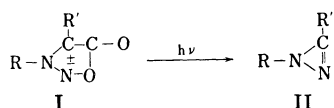
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(Received March 30, 1970)

Since interest in the photochemistry of mesoionic compounds is increasing,¹⁻³ we wish now to report a part of the results of our studies of this subject, which are going on in our laboratory.

The irradiation of a dioxan solution of 3,4-diphenylsydnone (Ia) in a Pyrex vessel under nitrogen and with a high-pressure mercury lamp (100 W, 30 hr) gave white plates (yield, 15%; mp 119–120°C [UV λ_{\max} (dioxan) 298 m μ (ϵ



VIII

7660); IR ν (KBr) 3050, 1595, 1493, 1455, 1439, 775, 756, 700, 693 cm⁻¹; NMR $\tau_{\text{Me}_4\text{Si}}$ (CDCl₃) 1.75–1.95(2H), 2.30–2.50(3H), 2.50–2.70(5H); Mass spectra M⁺, m/e 194 (11%)] whose spectral characteristics are consistent with its formulation as 1,3-diphenyldiazirine (IIa). This reaction seems to proceed by a mechanism analogous to that of the photolysis of 3-phenylsydnone.¹⁾ The irradiation of Ib and Ic gave seven and fourteen products respectively; those products were only detected with vpc and were not isolated.

The irradiation of an aqueous solution of IIIa and IIIb for 20–40 hr gave IVa (yield, 9%; white needles with a mp of 79–81°C [UV λ_{\max} (EtOH) 253 and 357 m μ (ϵ 10500 and 1300); IR ν (KBr) 3440, 3300(w), 3210, 1695, 1660, 1240 cm⁻¹; NMR $\tau_{\text{Me}_4\text{Si}}$ (CDCl₃) 1.6–1.8(2H), 2.3–2.6(3H), 2.8–3.2(1H), 3.7–4.1(1H)] and IVb (yield, 8%; white prisms with a mp of 120–123°C [IR ν (KBr) 3400, 3280(w), 3200, 1730, 1680, 1360 cm⁻¹]) respectively.

The irradiation of an aqueous solution of Va for 6 hr gave VIa ((C₁₅H₁₁N₂S)₂, yield, 23%; yellow needles with a mp of 230–231°C [UV λ_{\max} (EtOH) 265, 325 and 385 m μ (ϵ 23400, 18500 and 15300); IR ν (KBr) 3300, 3250, 2180, 1580, 1545 cm⁻¹; mol wt (in DMF) 444.7]), VII (yield, 70%; white needles with a mp of 165–166°C [UV λ_{\max} (EtOH) 235 and 333 m μ (ϵ 12000 and 24600); IR ν (KBr) 3480, 3310, 3190, 1680, 1600 cm⁻¹; Mass spectra M⁺, m/e 238 (63%)]), and H₂S, which was removed in a stream of N₂ and which was characterized by reaction with lead(II) acetate. The irradiation of an aqueous solution of Vb gave VIb (yield, 12%; mp 215–216.5°C [UV λ_{\max} (EtOH) 275, 295 and 355 m μ (ϵ 15700, 12200 and 17800); IR ν (KBr) 3220, 2180, 1560, 1540 cm⁻¹]) and H₂S. These results show that the photolyses of thiazone imine derivatives most likely proceed *via* bicyclic intermediates (VIII). However, the irradiation of Vc in an aqueous solution gave no detectable products and resulted in the recovery of the starting material, while the irradiation of Vd gave only a resinous oil. No change was observed by the irradiation of Ve in an aqueous solution.

1) C. U. Krauch, J. Kuhls and H.-J. Piek, *Tetrahedron Lett.* **1966**, 4043.

2) R. M. Moriarty, J. M. Kliegman and R. B. Desai, *Chem. Commun.*, **1967**, 1255.

3) R. M. Moriarty and R. Mukherjee, *Tetrahedron Lett.*, **1969**, 4627.