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PHOTOCHEMICAL REACTION OF N-ACYLSYDNONE IMINES

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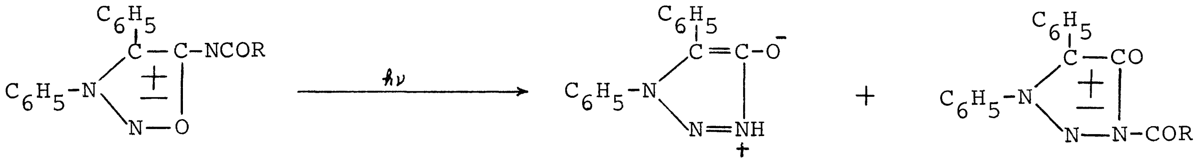
Irradiation of a benzene-ethanol solution of N-acyl-3,4-diphenylsydnone imine afforded 1,5-diphenyl-4-hydroxy-1,2,3-triazole and anhydro-3-acyl-1,5-diphenyl-4-hydroxy-1,2,3-triazolium hydroxide. Irradiation of N-acylsydnone imine in the presence of dimethyl acetylenedicarboxylate yielded an addition product.

As part of our continuing interest in photochemical reaction of mesoionic compounds, we reported[1,2] the photolysis of sydnones. In this paper, we describe the photochemical reaction of N-acylsydnone imines.

Irradiation of a benzene-ethanol (14:1) solution of N-acetyl-3,4-diphenylsydnone imine (I) in a Pyrex vessel under nitrogen and with a high pressure mercury lamp (100W, 9 hr) yielded 1,5-diphenyl-4-hydroxy-1,2,3-triazole (II) (yield 10%; mp 211-213°C; NMR τ(DMSO-d_6) 2.4-2.75 (m, 10H), -0.67 (s,1H)) and anhydro-3-acetyl-1,5-diphenyl-4-hydroxy-1,2,3-triazolium hydroxide (III) (yield 11%; mp 150-151°C; Found: C, 68.62; H, 4.74; N, 15.24%. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.80; H, .69; N, 15.05%; UV λ_{max}(EtOH) 247 mμ (ε 11300); IR ν(KBr) 3050, 1790, 1770, 1610, 1370, 1190, 770, and 700 cm^{-1}; NMR τ($CDCl_3$) 7.7 (s, 3H), 2.6-2.75 (m, 10H); mass spectrum M^+ m/e 279 (4%), m/e 43 (54%, CH_3CO), m/e 77 (79%, C_6H_5), m/e 180 (base peak, $C_6H_5C{=}NC_6H_5$), m/e 236 (78%, M^+-CH_3CO)). Structure of II was confirmed by mixed melting point measurement with an authentic sample which was prepared by treating I with methanolic potassium hydroxide.[3] Treatment of III with methanolic potassium hydroxide afforded II at room temperature. Irradiation of N-benzoyl-3,4-diphenylsydnone imine (IV) under the same conditions afforded II (yield 35%) and anhydro-3-benzoyl-1,5-diphenyl-4-hydroxy-1,2,3-triazolium hydroxide (V) (yield 2%; mp 179-180°C; Found: C, 73.81; H, 4.35; N, 12.33%. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31%; UV λ_{max}(EtOH) 235 mμ (ε 28400); IR ν(KBr) 1760, 1610, 1370, 1250, 1235, 1055, 760, and 700 cm^{-1}; Mass spectrum of IV did not show a molecular ion peak but strong peaks at m/e 105 (base peak, C_6H_5CO) and at m/e 180 (85%, $C_6H_5C{=}NC_6H_5$)).

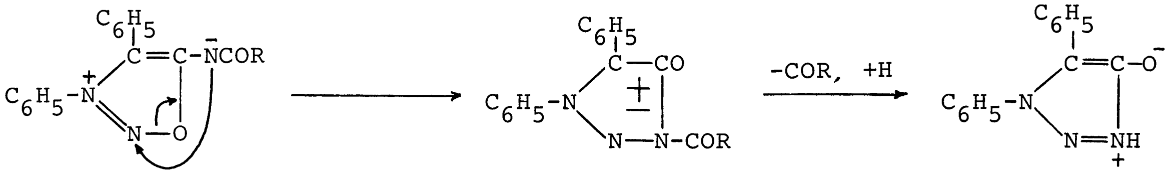


I: R=CH_3
IV: R=C_6H_5

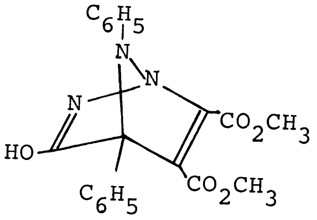
II

III: R=CH_3
V: R=C_6H_5

These results showed that in the photochemical reaction of N-acylsydnone imines rearrangement preferentially occurred to the nitrile imine formation which predominated in the photolysis of sydnones,[1,2,4] as shown below.



1,3-Dipolar cycloaddition of sydnones under irradiation has been reported.[1,2,4] The photochemical reaction of sydnone in the presence of dimethyl acetylenedicarboxylate (VI) afforded the addition products of nitrile imines derived from sydnones and VI. However, irradiation of I in the presence of VI yielded II, III, and a crystalline adduct, $C_{20}H_{17}N_3O_5$ (II:VI=1:1)(yield 3.6%; mp 110-111°C; Found: C, 63.30; H, 4.55; N, 11.37%. Calcd for $C_{20}H_{17}N_3O_5$: C, 63.32; H, 4.52; N, 11.08%; IR ν(KBr) 3425, 1730, 1665, 1595, 1280, 755, and 690 cm^{-1}). The structure of the adduct was supposed to be dimethyl 3-hydroxy-4,7-diphenyl-1,2,7-triazabicyclo[2,2,1]heptane-5,6-dicarboxylate (VII), though not conclusive. Irradiation of IV under the same conditions afforded II and V, and the adduct was not detected. Treatment of II with VI did not afford the adduct in the dark.



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