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A NOVEL PHOTOREDUCTION PRODUCT OF BENZOPHENONE N-BENZHYDRYLIMINE

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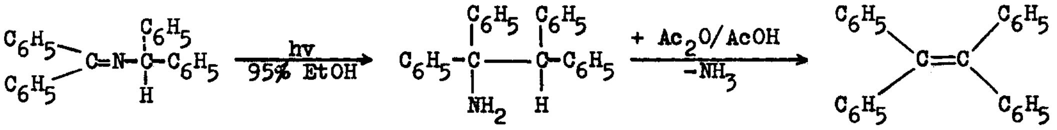
Photoreduction of benzophenone N-alkylimines to benzhydryl alkylamines[1], photodimerisation and photoreductive dimerisation of benzaldimines to 1,3-diazetidine system[2] and to N,N'-dialkyl-1,2-diaryl-1,2-diaminoethane[3,4] respectively have been reported. The present study has shown the presence of 1,1,2,2-tetraphenyl ethylamine as one of the photoreduction products of benzophenone N-benzhydrylimine.

Benzophenone N-benzhydrylimine(I) (λ_{max}^{EtOH} 252 nm, ε, 1.85×10^4) was prepared by the method of Rahman and Farooq[5]. A solution (2.7×10^{-5}M) of I in 95% ethanol was irradiated with pyrex-filtered light from a 450-W medium pressure Hanovia lamp for 7 hr. A white solid mp 186-7°(yield 22%) was obtained from the irradiated solution. TLC analysis of the mother liquor indicated two other products besides the unreacted imine, I.

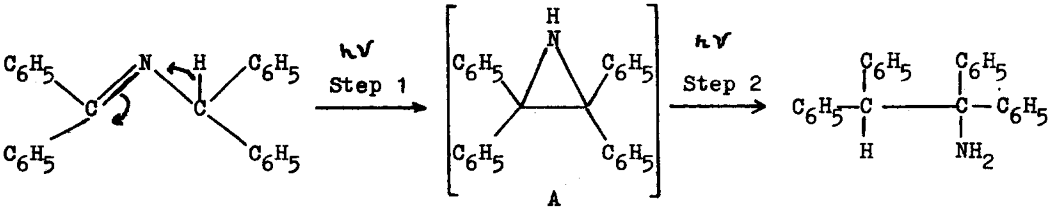


I II III

Anal (%) calcd. for $C_{26}H_{23}N$: C, 89.39; H, 6.59; N, 4.01. Found: C, 88.88; H, 6.96; N, 4.66. Molecular weight = 349. The mass spectrum showed intense peaks at m/e 182 (90%) and 167 (63%). This fragmentation is characteristic of α-(c-c) cleavage in amines[6]. The other peaks are at m/e 349(M$^+$) 4%, 332(M$^+$-NH$_3$) 2%, 272(M$^+$-C_6H_5) 11%, 152, 34%; 105(M$^+$-ϕ_3CH) 60% and 90(M$^+$-ϕ_3CNH) 9.5%. uv end absorption. ir ($CHCl_3$ cm^{-1}) 3400m, 3335w (νN-H), 1600s, 1585m, 1492s, 1445s, 1335m, 1315w, 1150m, 1080s, 1030m, 960b, 900m, 860b. nmr (60MH$_z$, $CDCl_3$, δ values): 7.20(m, 20H, C_6H_5), 5.30(s, 1H, ϕ_2CH) and 2.20(broad s, 2H, NH$_2$, exchangeable).

From the above data, the photoproduct is assigned a structure, 1,1,2,2-tetraphenyl ethylamine(II). This is further supported as II undergoes elimination readily on refluxing with Ac_2O/glacial AcOH to give tetraphenyl ethylene(III), which was identical (mixed mp and ir spectra) with an authentic sample.

From the analogy of the photocyclisation of phenylpropenes to phenyl cyclopropanes[7], it is expected that the imine I would give rise to the 2,2,3,3-tetraphenyl aziridine intermediate (Step 1), which would form II (Step 2) by the photochemical reductive ring opening process in a way analogous to the photochemical reduction of substituted imines[1].



I II

The characterisation of the other two photoproducts and the studies on the confirmation of the proposed mechanism are in progress.

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