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THE PHOTOCHEMISTRY OF N-SUBSTITUTED BENZALDIMINES.

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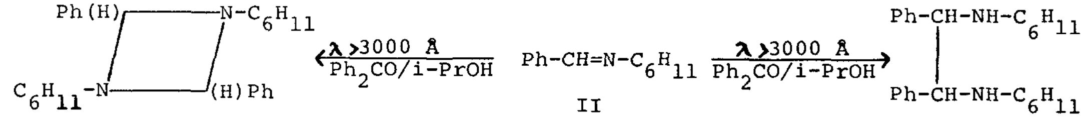
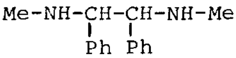
The photochemistry of benzaldimines was unknown until recently and the few published results are contradictory (1,2):



A mp 143-144° (1) (C_6H_{11}- = cyclohexyl) B mp 143-144° (2)

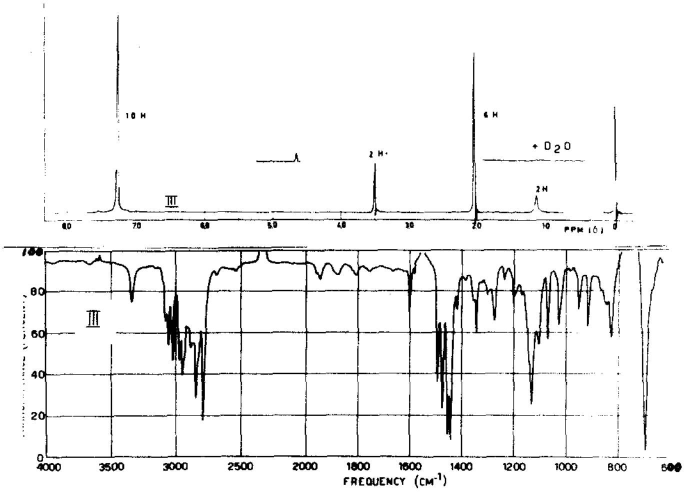
We wish to report our results for the photosensitized reaction of benzaldimines I (Ph-CH=N-Me) and II while the investigation of other derivatives is in progress.

Irradiation (λ>3000 Å) of I and II in the presence of Ph_2CO in i-PrOH gives the compounds III (mp 136.5-137°) and IV (mp 143-144°) respectively. On account of the ambiguity of the structures of photoproducts, NMR and IR spectra are reproduced for III in 10% solutions (CCl_4, IR: 0.1 mm cell). After shaking the CCl_4 solution of III with a few drops of D_2O the 1.15(δ) (2H) peak vanishes while the rest of the spectrum remains unchanged. Furthermore the IR spectrum of III shows a single band in the N-H stretching region at 3340 cm^{-1}, the intensity of which is strongly reduced in the deuterated compound and for which a new peak appears at 2490 cm^{-1}. The ratio v_{N-H}/v_{N-D} = 1.34 is in good agreement with the theoretical value of 1.37. (Deuterated III for IR spectrum was prepared by evaporation of the NMR sample, and the residue, carefully dried at 40° in vacuum, was dissolved in CCl_4.) Undoubtedly, compound III must contain a N-H group. From the evidence of the NMR, IR and Mass Spectroscopic data as well as on the basis of the elemental analysis and chemical properties, we concluded that compound III is of the following structure:


III

Me-NH-CH(Ph)-CH(Ph)-NH-Me

The Mass Spectrum *of* III *shows a* very weak M^+ peak at m/e 240 beside M^+ +1 and M^+ -1 ions. The base peak at m/e 120 ($M^+/2$) indicates the usual α (C-C) cleavage of an α branched secondary amine. The other major peaks are at m/e (%): 42(18)($M^+/2$ - C_6H_6: m*= 14.7), 118(21), 119(10), 121(6). Anal.(%). Calculated



for $C_{16}H_{20}N_2$: C 79.96, H 8.38, N 11.66. Found: C 79.87, H 8.27, N 11.80. Calculated for $C_{16}H_{18}N_2$ (cyclic structure like A): C 80.63, H 7.61, N 11.75. NMR (Me_4Si internal standard) in δ units. 7.25(10H):two phenyls. 3.50(2H):two tertiary H. 2.05(6H):two N-Me. 1.15(2H):two N-H. IR in cm^{-1}. Phenyl:3080,3060, 3025,700(v.s.),1600,1585(v.w.),1490. N-Me:characteristic C-H str. at 2790 beside other ones.

The investigation of compound IV indicated that it had the open chain meso structure B. Mass Spectrum: Very weak M^+ (m/e 376), M^+ +1 and M^+ -1 peaks. Base peak at m/e 188($M^+/2$), indicating an α cleavage similar to III. The other major peaks are at m/e (%): 106(29) ($M^+/2$ - cyclohexene:$m^* = 59.8$),189(16),18(10). NMR(δ). 7.25(10H):two phenyls. 3.90(2H):two tertiary H. Broad abs. from 0.4 to 2.35(24H):two cyclohexyls and two N-H in which the N-CH protons are assigned to the abs. from 1.90 to 2.35(2H). IR(cm^{-1}). N-H:3320, intensity of which is strongly reduced by deuteration (in the same experimental condition as III); N-D at 2460, $\nu_{N-H}/\nu_{N-D} = 1.35$. Phenyl:data identical with III. CH_2 in cyclohexyl:2925 and 2850.

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