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ON THE PHOTOCHEMISTRY OF AN AMINO-ACRYLOPHENONE DERIVATIVE

Albert Padwa* and Robert Gruber
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York, 14214

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Although intramolecular 1,2-shifts of hydrogen or alkyl groups have not been unequivocably confirmed in monoradical reactions[1], their occurrence has been ambly demonstrated in 1,3-diradicals[2-5]. These results suggest that an important driving force which provides for stabilization of the transition state for rearrangement is the formation of a structure in which all electrons are paired. Recent work by Griffin and coworkers on the photocyclization of propenes indicates that 1,2-alkyl migrations may also be induced from an excited state of an olefin.[6,7] In this paper, we report on some aspects of a related photoreaction of a β-amino substituted ketoolefin and its significance relative to the current photochemical literature.

Irradiation of 2-[α-(N-t-butylamino)benzyl]acrylophenone(I) in aqueous dioxane at 25° with ultraviolet light for 3 hr. afforded in excellent yield (75%) a product whose structure was demonstrated to be dibenzoylethane (II). The formation of II from I may be rationalized on the assumption that the excited state of I undergoes photocyclization to an amino-substituted cyclopropane followed by a subsequent ground-state opening of the three-membered ring. The 1,2-hydrogen shift postulated in this reaction is analogous to that observed by Griffin in the photochemical interconversion of propenes and cyclopropanes.[6,7]

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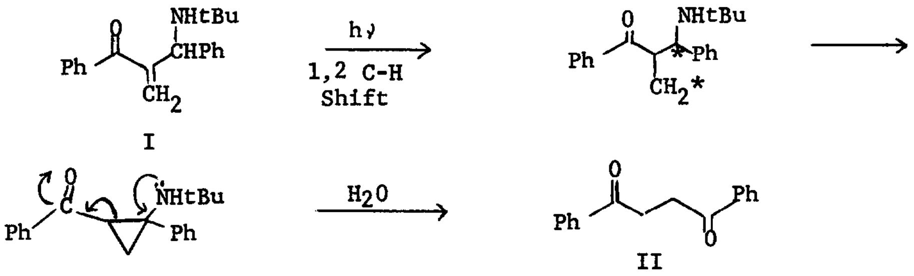
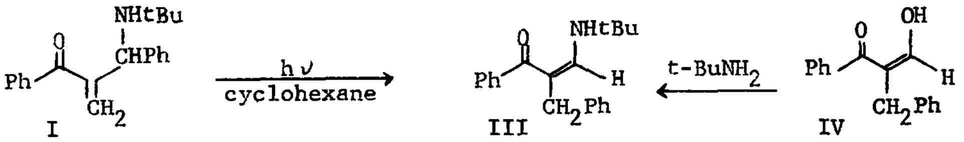
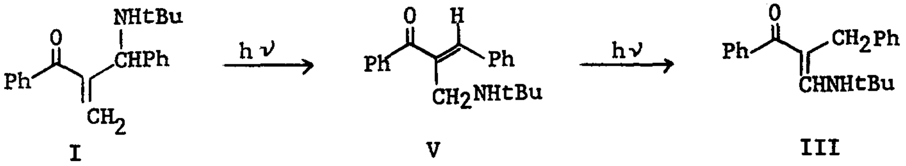
* Fellow of the Alfred P. Sloan Foundation



The reaction course proved to be dramatically different when the irradiation was carried out in cyclohexane as solvent. In this case, the major product isolated (84%) was identified as 1-phenyl-2-benzyl-3-t-butylamino-2-propenone (III), m.p. 136-137°, on the basis of the chemical and physical data cited. The elemental analysis of this component (Anal. Calcd. for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.81; H, 7.84; N, 4.78) indicates that it is an isomer of I. The infrared spectrum of III was characterized by a series of sharp bands at 3.12, 6.13, 6.60, 7.60, 8.13, 10.41 and 14.32 u. The ultraviolet spectrum in 95% ethanol has a maximum at 306 mu (ϵ 32,300). The mass spectrum of III showed the molecular ion at m/e 293 and major peaks at m/e 237 and 236 which correspond to the loss of isobutylene and a t-butyl group. The most striking feature in the nmr spectrum of III is the existence of two chemically distinct signals for the t-butyl (τ 9.02, 8.71) and benzyl (τ 6.52, 6.28) hydrogens in the ratio of 3:1. All the experimental data points towards rotation about the C-C double bond and the establishment of a cis-trans isomerization as the process responsible for the observed nmr spectrum.[8] As expected, the spectrum is simplified upon heating and, at 86°, the rotational barrier is overcome. The free energy of activation for the isomerization (ΔG = 13.5 Kcal/mole) at the temperature of coalescence (tc) was calculated in the usual way from the maximum chemical shift separation of the signals and from tc using the Eyring equation.[9] Structure III was further confirmed by its unequivocal synthesis from IV and t-butylamine.



At first glance one might be tempted to conclude that the formation of III from I proceeds via a 1,3-phenyl shift and that the polarity of the solvent exerts a profound effect on the migratory aptitude of the phenyl group. Careful monitoring of the photochemical rearrangement however, indicated that III is not a primary photoproduct. Subsequent experimentation has established that trans-α[(N-t-butylamino)methyl] chalcone (V) is, in fact, the initial photoproduct. Our conclusion that V is an intermediate in the conversion of I to III is supported by the observation that V is rapidly converted to III upon



irradiation. Variation of the photolysis time allowed for maximization of the concentration of V to an isolable level. Cromwell has already reported on the thermal rearrangement of I to V.[10] Presumably the photolysis of I proceeds via a structurally related sequence. The formation of III upon irradiation of V is reasonably formulated as proceeding by a 1,3-hydrogen shift.

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