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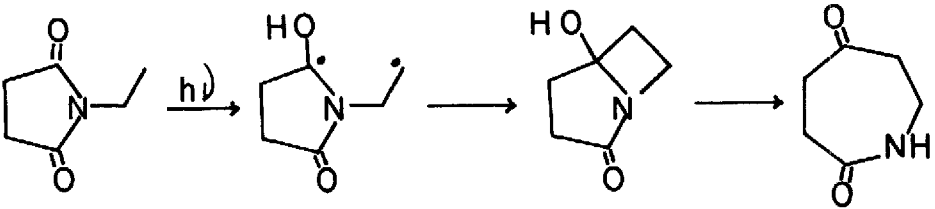
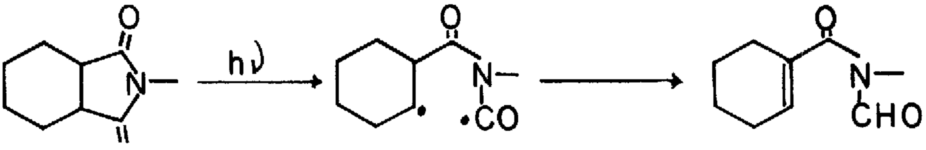
COMPETITIVE TYPE II ELIMINATIONS IN ALIPHATIC IMIDES

Paul H. Mazzocchi, William Jameson, Tomihiro Nishiyama and Ann DeCamp
Department of Chemistry
University of Maryland
College Park, Maryland 20742

SUMMARY: Aliphatic imides have been shown to undergo type II eliminations across the imide moiety in addition to those on the C-alkyl chain and α cleavage reactions.

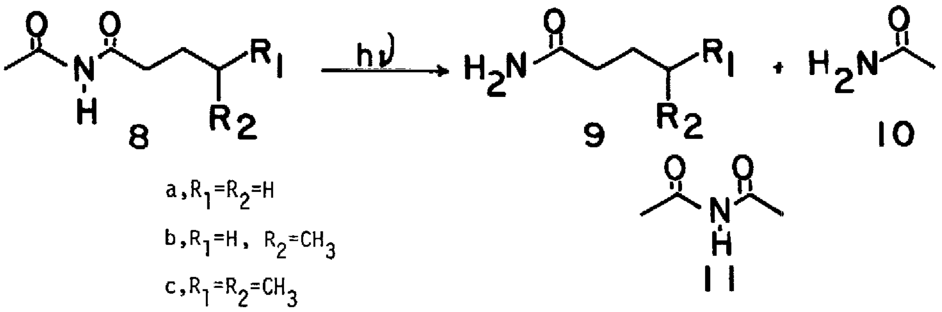
There have been several recent reports on the photochemistry of alicyclic imides[1,2,3] which indicate that these materials follow two major photodecomposition pathways. When there is a γ-H on the N alkyl group as in the succinimides 1, the major process appears to be type II abstraction to the biradical 2 which subsequently affords the ring expanded 4.[1] When the carbon α to the carbonyl group is tertiary C(O)-C cleavage becomes an important process[2,3] and leads to intramolecular hydrogen abstraction products such as 7.





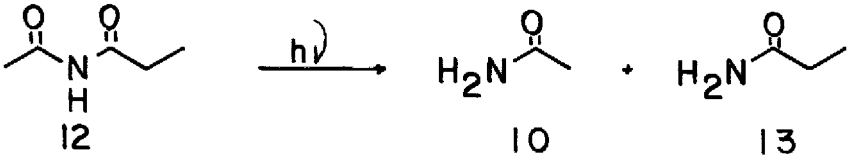
Our interest in the photochemistry of aromatic imides[4] and the observation that model amides[5] and lactams[5] did not undergo type II cleavages efficiently led us to investigate the photochemistry of a series of model alkyl imides.

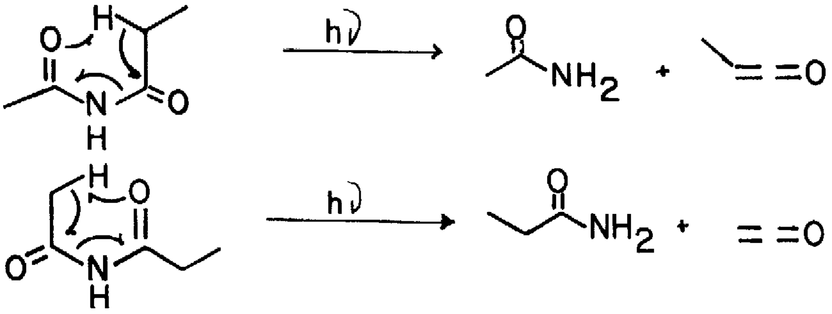
Our observation was that irradiation of t-butanol solutions of imides 8a-c gave the corresponding long chain amide 9a-c, acetamide (10) and diacetamide (11). Our initial interpretation of these results was that 11 arose from a type II process and 9 and 10 were type I products initiated by C(O)-N bond α cleavage, a reaction which has some precedent in amide, imide and urea photochemistry.



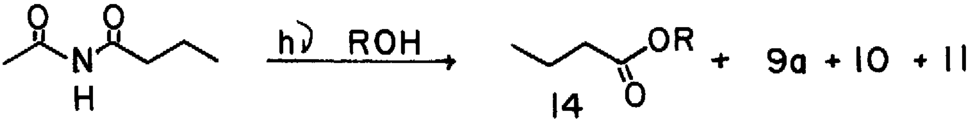
a,R_1=R_2=H
b,R_1=H, R_2=CH_3
c,R_1=R_2=CH_3

Further study of the singlet state "type I" process suggested that this analysis was probably incorrect.[6] Since it is known that the efficiencies of α cleavage reactions are a function of the stabilities of the incipient radical pair,[7] we expected that N-acetyl propionamide (12), which does not have the potential for a complicating type II process on the C-alkyl chain, would give equal yields of 10 and 13. The surprising result was that the 10/13 ratio was 1.9 and not unity as expected. The same result was obtained with 8a-c, i.e., the 10/9 ratio was always > 1.[8] The possibility of conformational factors dramatically influencing the product ratio was discounted by low temperature NMR studies which indicated that the two E,Z conformers[9] were equally populated at irradiation temperatures. These results are most consistent with reaction taking place by the alternative and unexpected type II process across the imide moiety, with 2° hydrogen abstraction (to 10) favored over 1° hydrogen abstraction (to 13).

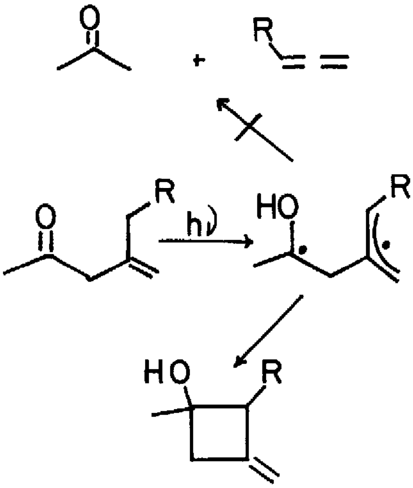


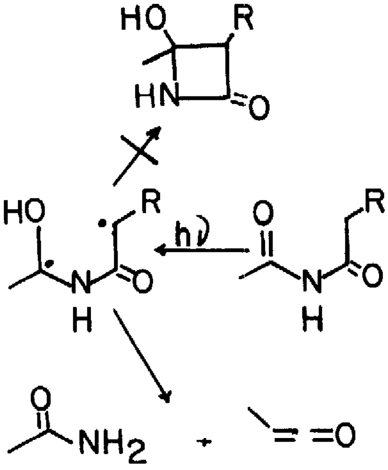


Convincing evidence for this process was obtained from a study of the photochemistry of N-acetyl butyramide (8a) in alcohol and alcohol dioxane solutions. In addition to the expected products 10, 11 and 9a, the esters 14a-c (R=CH_3, C_2H_5 and $(CH_3)_2CH$ respectively) from the trapping of the corresponding ketene were obtained in yields ranging from 16-42% of the amount of 10 formed. If we assume that alcohol trapping of the ketene intermediate occurs efficiently, then 10 must arise from both the α cleavage and the type II processes.



The alternative type II process across the imide moiety has no precedent in carbonyl photochemistry. In the normal case,[10] abstraction of a γ hydrogen from a carbon α to an sp^2 hybridized center leads to cyclobutane formation rather than type II cleavage. The absence of efficient cleavage in those cases has been explained by suggesting that stabilization of the allylic radical precludes effective overlap of the newly formed radical center with the C-C σ bonding orbital of the α-β bond, i.e., the orbitals become orthogonal. In the case of the imide moiety however, the incipient radical is cross conjugated. Since there is less potential radical stabilization, there is less driving force for the odd electron containing orbital to become orthogonal to the C(O)-N σ bonding orbital. The required overlap remains and efficient cleavage occurs.





We are presently examining the competitive type I and type II cleavages in N substituted alkyl imides to study the effect of changing the stability of the incipient α cleavage radical pair on the photochemistry of these materials.

Acknowledgment

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References

1. Y. Kanaoka and Y. Hatanaka, J. Org. Chem., 41, 400 (1976).
2. Y. Kanaoka, H. Okajima and Y. Hatanaka, J. Org. Chem., 44, 1749 (1979).
3. K. Maruyama, T. Ishitoku and Y. Kubo, J. Am. Chem. Soc., 101, 3670 (1979).
4. P. H. Mazzocchi, S. Minamikawa and P. Wilson, J. Org. Chem., 44, 1186 (1979); Tetrahedron Letters, 4361 (1978); P. H. Mazzocchi, S. Minamikawa and M. Bowen, J. Org. Chem., 43, 3079 (1978); Heterocycles, 9, 1713 (1978); P. H. Mazzocchi, M. Bowen and N. Narain, J. Am. Chem. Soc., 99, 7063 (1977).
5. C. H. Nicholls and P. A. Leermakers, J. Org. Chem., 35, 2754 (1970); P. H. Mazzocchi and M. W. Bowen, J. Org. Chem., 41, 1279 (1975); P. H. Mazzocchi, J. Thomas and F. Danisi, J. Org. Chem., 44, 50 (1979).
6. Quenching studies on **8a-c** (piperylene) show curved Stern-Volmer plots indicating that the reaction takes place from two excited states, presumably the first excited singlet and triplet. This reaction was run in the presence of 0.1 M piperylene, conditions under which we have shown that the triplet component of the **8** photochemistry is completely quenched.
7. Solly and Benson have shown that the bond dissociation energy of the R-C(=O)-H bond in a series of aldehydes is independent of the nature of the R group. R. K. Solly and S. W. Benson, J. Am. Chem. Soc., 93, 1592 (1971).
8. Under conditions in which the triplet is quenched, the yield of products (glpc) from 8a was **9a** (36%), **10** (45%) and **11** (20%) in t-butanol solvent, 15% conversion. Irradiation of **8a** in 10% ethanol dioxane to 55% conversion gave **9a** (41%), **10** (48%), **11** (12%) and **14b** (10%, 21% of the **10** formed).
9. E. A. Noe and M. Raban, J. Am. Chem. Soc., 97, 5811 (1975).
10. P. Wagner, Acc. Chem. Res., 4, 168 (1971).

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