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PHOTOCHEMICAL REACTIONS OF ENAMIDES

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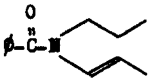
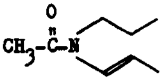
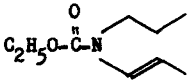
Recently we described a number of intramolecular photochemical reactions involving enamide systems and their analogs.[1] In studying the generality of these reactions, we investigated the photochemical behavior of several simple enamides, N-1-propenyl-N-1-propylbenzamide (I), N-1-propenyl-N-1-propylacetamide (II), and ethyl N-1-propenyl-N-1-propylcarbamate (III). Simple enamides (I-III) were found to undergo rapid photochemical transformation in high yields to give 3-amino-2-en-1-ones, i. e., substituted β-amino-α,β-unsaturated ketones, (IV-VI).



I



II



III

When a solution of I[2] in methanol (2.03 g in 200 ml) was irradiated with a 550-watt Hanovia mercury lamp enclosed in a quartz well, a new absorption band appears at 308 mμ. The reaction was monitored by the change in absorption spectrum and the band at 308 mμ reached a maximum after one hour. Chromatography of the reaction mixture on Florisil gave 15% (300 mg) of recovered I and 85% (1.70 g) of IV and no other detectable products. Compound IV [Found: C 76.81; H 8.68; N 6.75; mol wt 203.1315 (mass spec)] mp 87-88° (ether-hexane), gave a slowly developing but strong ferric chloride test, exhibits γ_{max} at 2.92μ (sharp, medium), 3.00-3.25μ (broad, weak) and 6.10μ (strong), and λ_{max} at 308mμ (log ε 4.4).

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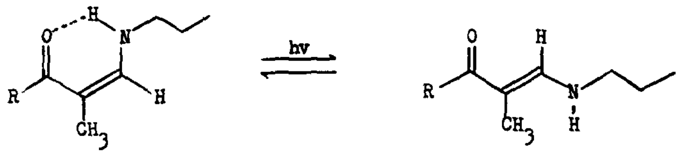
Saponification of IV yielded propiophenone and 1-propylamine, identified by comparison with authentic samples. In addition, the saponified solution gave a positive test for formate ion.[3]

On the basis of its uv spectrum,[4] the presence of both unassociated N-H and associated N-H bands in its infrared spectrum, and its chemical degradation, the product (IV) was identified to be an isomeric mixture of IVa and IVb with IVa as the major isomer. The structural assignment was verified by its nmr. The nmr spectrum exhibits aromatic protons at 2.66τ (5H), N-H at 4.15-4.90τ (1H), $C=C-CH_3$ at 8.19τ (3H), $CH_3CH_2CH_2-N$ at 9.20τ (triplet, 3H), 8.2-8.9τ (unresolved multiplet, 2H) and 6.99τ (multiplet, 2H), in addition two sets of doublets at 3.05τ (J = 14 cps, 0.85H) and 3.15τ (J = 12 cps, 0.15H) which were assigned to be the olefinic proton in IVa and IVb.[5] It is interesting to note that the trans isomer (IVa) which has no intramolecular hydrogen bond is the major product. Since the products are formed in a photochemical reaction, the trans:cis ratio of 85:15 may represent a photochemical equilibrium rather than the thermodynamic equilibrium.



IVb R = ϕ IVa R = ϕ

Vb R = CH_3 Va R = CH_3

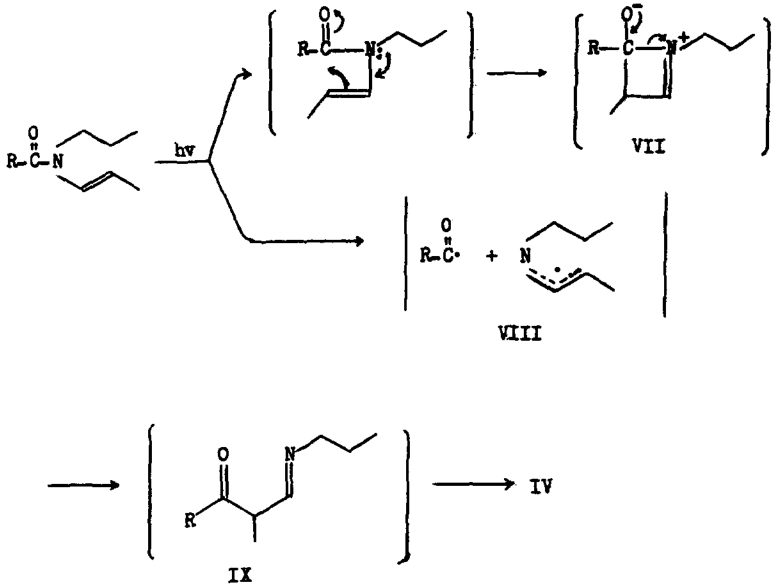
VIb R = OC_2H_5 VIa R = OC_2H_5

$$\text{IVa} + \text{IVb} \xrightarrow{OH^-} \phi COC_2H_5 + CH_3CH_2CH_2NH_2 + HCO_2^-$$

When N-1-propenyl-N-1-propylacetamide (II)[2] was irradiated in methanol under similar conditions, a new band appeared at 299 mμ which reached a maximum after two hours. Again, only one product was formed as indicated by TLC. As the product was found to be unstable on a variety of absorbents the reaction mixture was distilled. Compound V was isolated in 60% yield, bp 74-6° (1.0 mm), with extensive decomposition in the pot. The compound [Found: C 67.97; H 10.81; N 9.59; mol wt 141.1151 (mass spec)] gives a slow-developing but strong ferric chloride test, and exhibits γ_{max} at 3.0μ, 6.05μ and 6.20-6.50μ (broad), and λ_{max} at 299 mμ (logε 4.33) in methanol which shifts to 280 mμ (logε 4.08) and 312 mμ (logε 3.63) in methylcyclohexane.[4] Again the photoproduct is a mixture of cis and trans isomers as indicated by the presence of two doublets of equal area in the nmr, at 2.68τ (Va J = 13.5 cps) and 3.42τ (Vb J = 12 cps). Also present in the nmr are separate signals for olefinic methyl groups at 8.21τ and 8.33τ for Vb and Va indicating the single olefinic methyl signal observed for IV is a case of accidental degeneracy.

Ethyl N-1-propenyl-N-1-propylcarbamate (III) was synthesized from the corresponding aldimine and ethyl chloroformate and irradiated to determine whether the unsaturated carbamate would rearrange analogus to the enamides. When III was irradiated as in the previous cases, a new band appeared at 285 mμ which reached a maximum after 1-3/4 hours. The ir spectrum and the nmr spectrum indicated that only a small amount of III was left in the reaction mixture and VI was formed in 80% yield. As in the previous two cases, VI was formed as a mixture of trans VIa and cis VIb isomers in a ratio of 2:3 as indicated by two olefinic proton doublets at 2.73τ (J = 14 cps) and 3.50τ (J = 12.5 cps). However, thus far we were unable to purify VI by either chromatography or distillation without extensive decomposition. In order to demonstrate that the photorearrangement of III to VI had taken place, the crude irradiation mixture was saponified. Acetaldehyde and 1-propylamine were isolated in the saponification products. Acetaldehyde was identified as its 2,4-DNP derivative and by comparison with an authentic sample. Acetaldehyde was formed during the saponification from the decarboxyaltion of initially formed pyruvic acid.[6] In a separate experiment, it was shown that pyruvic acid was converted into acetaldehyde under our saponification conditions.

The photochemical rearrangement of enamides is analogus to the photochemical rearrangement of enol esters,[7] except it proceeds more efficiently and in much higher yield. The reaction may be formulated through a four-member ring intermediate (VII) or an acyl radical and an enamino radical (VIII) in a cage as the intermediate. The β-imino carbonyl compound (IX) formed will then undergo prototropic shift to give the 3-amino-2-en-1-one as the product. The possible synthetic application and the generality of these reactions are being investigated.



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