Tetrahedron Letters No. 25,pp. 1-3, 1960. Pergamon Press Ltd. Printed in Great Britain

PHOTODIMERIZATION OF SOME α,β-UNSATURATED LACTAMS[1]

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(Received 28 October 1960)

THE dimerization of activated olefins by irradiation with ultraviolet light is one of the oldest and most widely-studied reactions in photochemistry.[2,3] There are, however, no reports of the action of ultraviolet light on α,β-unsaturated lactams. We wish to report that N-methyl-2-pyridone (b.p. 121°/10 mm, λ_{max}^{EtOH} 302 mμ, $\varepsilon = 5700$) is rapidly converted by ultraviolet light to a solid dimer (m.p. 222.0-222.5°; Found: C, 66.25; H, 6.4; N. 12.95. mol. wt. 226. λ_{max}^{EtOH} 312 mμ, $\varepsilon = 100$. Calc. for $C_{12}H_{14}N_2O_2$: C, 66.0; H, 6.5; N, 12.8. mol. wt. 218), which reverts to N-methyl-2-pyridone upon heating above its melting point. It is evident from inspection of the ultraviolet spectra that the α,β-unsaturated system present in the monomer is no longer present in the dimer, which thus may be represented as I or Ia. The presence

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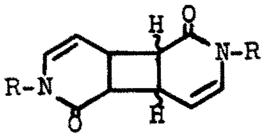
[1] This work was supported by a research grant (CY-2551) to Princeton University from the National Cancer Institute of the National Institutes of Health, Public Health Service.

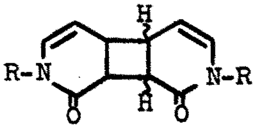
[2] A. Schönberg, Präparative organische Photochemie p. 30. Springer Verlag, Berlin (1958).

[3] P. de Mayo in Advances in Organic Chemistry: Methods and Results (Edited by R. Raphael, E.C. Taylor and H. Wynberg) p. 367. Interscience, New York (1960).

of the isolated double bonds in I (or Ia) was readily confirmed by hydrogenation to a tetrahydro derivative (m.p. 285-286°. Found: C, 64.85; H, 8.2; N, 12.4. λ_{max}^{EtOH} only end absorption about 220 mμ. Calc. for $C_{12}H_{18}N_2O_2$: C, 64.8; H, 8.2; N, 12.6.) and by conversion to a diepoxide (m.p. 324-326°. Found: C, 57.7; H, 5.8; N, 11.3. Calc. for $C_{12}H_{14}N_2O_4$: C, 57.6; H, 5.6; N, 11.2). Determination of the dipole moment of the dimer as 0.07 D (in $HCCl_3$) clearly establishes I as the correct structure.



I, R = CH_3
II, R = H

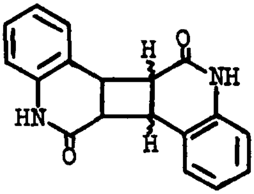


Ia, R = CH_3

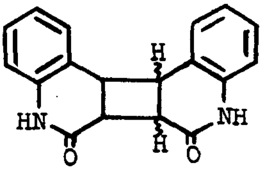
Irradiation of 2-pyridone (m.p. 106-107°) in aqueous solution yields a dimer (II) (m.p. 225.5-227.5°. Found: C, 62.8; H, 5.3; N, 15.0. Calc. for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.3; N, 14.7) which upon methylation with dimethylsulfate and alkali gives I, identical in every respect with the product obtained directly from N-methyl-2-pyridone.

The use of this photodimer as a synthetic intermediate for the preparation of both pyridine and cyclobutane derivatives is under active investigation; results will be reported independently.

Irradiation of a suspension of N-methyl-2-quinolone (m.p. 74°) in cyclohexane or in water yields a dimer (m.p. 211.5-212°. Found: C, 75.6; H, 5.8; N, 9.0; mol. wt. 272. Calc. for $C_{20}H_{18}N_2O_2$: C, 75.4; H, 5.7; N, 8.8; mol. wt. 318) which, because of its dipole moment of 4.62 D (in $HCCl_3$) must be assigned structure IIIa rather than III. Heating reconverts it rapidly and quantitatively to N-methyl-2-quinolone.



III



IIIa

The different orientations of the dimers I and IIIa is undoubtedly due to the fact that N-methyl-2-pyridone was irradiated either as the neat liquid or in homogeneous solution in ethanol, while N-methyl-2-quinolone was irradiated in suspension. Similar cases of dependence of the course of dimerization on the physical state of the compound being irradiated are well-known.[2,3]