PHOTOCHEMICAL BEHAVIOUR OF THE 16-METHYL(3, 5)[11]ISOXAZOLOPHANE AND OF THE RELATED 14-METHYL-15-AZABIC YCLO[12.1.0]PENTADEC-15(1)-EN-13-ONE.

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Studies of the photochemical behaviour of heterocyclic five-membered ring compounds have received considerable attention in recent years.⁽¹⁾

The isoxazoles-oxazoles photorearrangement is now well known to proceed through an intermediate ketoazirine. ⁽²⁾Recently a different mechanism has been reported in one case. ⁽³⁾

We wish to report herein the preliminary results of the photochemical behaviour of the 16-methyl(3, 5)[11]isoxazolophane (II) and of the related ketoazirine (III).

The 16-methyl(3, 5)[11]1soxazolophane (II)⁽⁴⁾was prepared [82% yield] by reaction of the readly accessible methyl-2-cyclotetradecan-1, 3-dione (I)⁽⁵⁾ with hydroxylamine and acidic cyclisation of the intermediate monooxime. [(II), mp 53° from n-pentane; ir (nujol):1630, 1160, 1070, 1020, 890, 740, 705 and 670 cm⁻¹; nmr (60 MHz, CDCl₃, $\boldsymbol{\delta}$):2.65 (4H, m) 1.95 (3H, s); uv (EtOH): 225 (ε 5800); m/e: 235 (M⁺)(5), 41(100)].



Irradiation of (II) (0.0127 mol) in acetone (300 ml) through pyrex with a high pressure Hg lamp (125 W), gave, after 23 h, a photoproduct (III) and unchanged starting material (II). Pure (III) was obtained [40% yield] by SiO_2 column chromatography. The structure of 14-methyl-15-azabicyclo[12.1.0]pentadec-15(1)-en-13-one (III) was assigned on the basis of its analytical and spectroscopic data. [(III), mp 58° from $\text{Et}_2\text{O/n-hexane}$; ir (nujol):1790(w) and 1700(s) cm⁻¹; nmr (60 MHz, CDCl₃, **6**):2.9(2H, m) 2.05(2H, m);uv (EtOH):238 (ϵ 1500) 293 (ϵ 73), m/e: 235 (M⁺)(3), 41(100)].

As expected, ⁽⁶⁾ irradiation of (III), in anhydrous Et_2O with a low pressure Hg lamp, gave, in nearly quantitative yield, the 13-methyl(2, 5)[11]oxazolophane (IV). [(IV), bp 92°/O.O1 ir (film): 164O, 158O, 1275 and 1195 cm⁻¹; nmr(1OO MHz, CDCl₃, b):2.71(2H, m)2.55(2H, m) 2.O2(3H, s)1.65(4h, m);uv (EtOH):224 (ϵ 6000); m/e: 235 (M⁺)(23), 41 (100)].

Moreover, upon heating in methanol solution in the presence of a catalytic amount of Na_2CO_3 , ^(2b) (III) afforded (IV).



The oxazolophane (IV), treated with methyl tosylate $[5 \text{ min}, 125-130^{\circ}]$ and subsequent ring opening with NH₄OH solution [pH 8.5-9], ⁽⁷⁾afforded the 3,5-dioxo-1,2-dimethylazacy-clopentadecane (V). [(V), mp 53° from n-hexane; ir(nujol):1720 and 1640 cm⁻¹;nmr (100 MHz, CDCl₂, δ): 5.21 (1H, q, J=7 Hz) 2.87 (3H, s); m/e: 267 (M⁺)(5), 58 (100)].



During the above irradiation conditions and in all solvents considered $[CH_3CN, Et_2O, C_6H_6, CH_3COCH_3]$ there was not observable conversion of the azirine (III) into the isoxazole (II). This fact is in contrast with the photorearrangements of 2-aroyl-3-aryl-2H-azirines ^(2b, c) but is analogous to the photorearrangement of 2-benzoyl-2, 3-diphenyl-2H-azirine ^{2a)} and of 3-phenyl-2H-azirine-2-carbaldehyde. ⁽⁸⁾

Surprisingly, irradiation of the ketoazirine (III) [pyrex filter, high pressure Hg lamp] in an anhydrous Et_2O or CH_3CN solution, afforded a single new photoproduct (VI). Even at high irradiation time, complete conversion of (III) into (VI) was not achieved. We have been unable so far to isolate (VI) in a pure state, although (VI) proved to be thermally stable. Vacuum distillation [115-120°/O.1] of the crude photolysate afforded, in 88% yield, a mixture of (III) and (VI) [1:1 ratio by nmr]. Spectroscopic data of this mixture strongly suggests the presence of a ketoketenimine. In the ir spectrum absorption bands are at 2040 (-N=C=C-) and 1660

 $(-CO-C=C-) \text{ cm}^{-1}$. In the nmr spectrum (90 MHz, $CDCl_3$, **b**) signals are at 3.73 (t, J=7 Hz, $-CH_2-N=$) and 1.7 (s, $CH_3-C=C-$). In the uv spectrum a strong absorption band at 266 nm (CH_3CN) and at 260 nm (Et_2O) was present. Attempted separation of the (III)-(VI) mixture by SiO_2 column chromatography induced the transformation of (VI) into a new compound (VII), which could also be obtained by treating the (III)-(VI) mixture in THF-H₂O with a catalytic amount of H_2SO_4 .

The structure of 2, 4-dioxo-3-methylazabicyclopentadecane was assigned to (VII) on the basis of its analytical and spectroscopic data. [(VII), mp 132° from CH_2Cl_2/Et_2O , ir (nujol):33OO, 1715 and 1630 cm⁻¹; nmr(1OO MHz, CDCl₃, **b**):6.35(1H, bs, exch. with D₂O) 3.5(1H, q, J=7Hz) 3.3(2H, m) 2.56(2H, m); m/e: 253(M⁺)(19), 41(1OO)].



In conclusion, we wish to point out that the photobehaviour of this azirine is controlled by the wavelength of the irradiation but at λ 300 nm an unprecedented rearrangement to the ketoketenimine (VI) occurs. This is a unique case since, to the authors knowledge, ketenimines and their derivatives are reported to be formed directly from the isoxazoles. ^(2a, e, f)

The dependence of the photochemical behaviour of the azirine (III) on the substitution pattern and/or on the conformational control of the carbocyclic ring, is at present under study. The exploitation of the photobehaviour of bicyclic azirines as synthetic entry to novel heterophanes is also in progress.

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