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PHOTOISOMERIZATION OF A α-ARYL-γ-OXO-α,β-UNSATURATED CARBOXAMIDE. RING ENLARGEMENT TO A CYCLOHEPTATRIENE DERIVATIVE.

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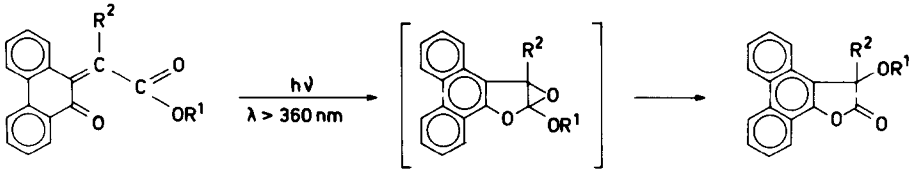
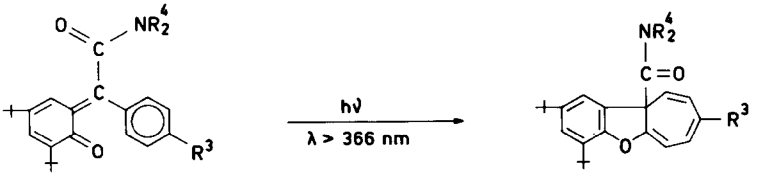
As a part of our investigations of photochemical cycloadditions with acetylenes we reported the formation of γ-lactones 2 by irradiation of α-phenyl- or α-methyl-γ-oxo-α,β-unsaturated esters 1, R^1=Alkyl, R^2=Ph of Me.[1]



1 postulated 2

The corresponding α-alkyl-γ-oxo-α,β-unsaturated amides underwent a photochemical intramolecular hydrogen abstraction reaction.[2] When the γ-oxo-α,β-unsaturated amides 3 [4] were irradiated however, a different rearrangement was observed.



a) R^3=H,R^4=Et
b) R^3=H,R^4= *i*-Pr
c) R^3=Me,R^4=Et

3 4

Starting from 3a (m.p. 168-170°C, red crystals)[4], an isomer was obtained in 85% yield after chromatography on SiO_2/CH_2Cl_2. The IR spectrum showed in CCl_4 $\tilde{\nu}$ (C=O) at 1640 cm^{-1} and $\tilde{\nu}$ (C=C) at 1610 cm^{-1}. In the ^1H NMR spectrum (CCl_4) four vinylic hydrogen atoms were found at δ=6.1-6.4 and one at δ=5.23 (d, J=9.6 Hz, 1H) instead of five aromatic hydrogen atoms. The two vinylic hydrogens in 3 had become aromatic (δ=7.20 and δ=7.25, doublets, J=2.5 Hz). Further peaks were found at δ=1.33 and δ=1.43 [s, $C(CH_3)_3$], at δ=0.71 (t, J=7 Hz, $2xCH_3$) and at δ=3.00 (m, $2xCH_2$-N) indicating an $(CH_3CH_2)_2N$-CO group. These data as well as ^{13}C NMR data pointed to the cycloheptatriene derivative 4a.

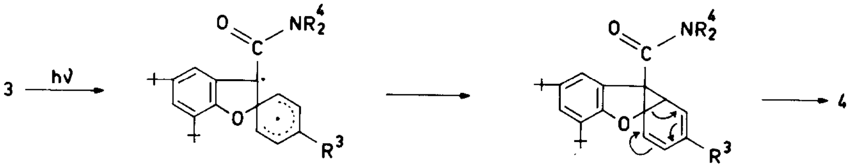
The formation of 4a is somewhat related to the formation of a cycloheptatriene derivative in the photochemical reaction of 1-methoxy-1-propyne with benzophenone, which we reported some years ago.[5]

The amide 3b, gave an analogous irradiation product in 55% yield (m.p. 90-92°C).

In order to unravel the complicated vinylic pattern of the cycloheptatrienic amide, and to obtain information about the reactionpath of its formation, the 4-methyl-substituted compound 3c was irradiated yielding 75% of 4c as white crystals, m.p. 113-115°C. Its ^1H NMR spectrum (CCl_4) showed peaks at δ=1.33 and 1.41 [s, $C(CH_3)_3$], at δ=0.71 (t, J=7 Hz) and δ=2.99 [m, $(CH_3CH_2)_2N$-CO-], at δ=2.07 (s, CH_3), at δ=7.19 and 7.23 (doublets, J=2.5 Hz, two aromatic hydrogen atoms in *meta* position), at δ=5.22 and δ=6.12 (doublets, J=9.6 Hz, -CH=CH-) and at δ=6.00 and δ=6.15 (doublets, J=6.9 Hz, =CH-CH=). The coupling constant of 6.9 Hz is in accordance with a dihedral angle of about 30-40° as measured in a Dreiding model.

Its UV spectrum[6] and ^{13}C NMR spectrum[7] were in accordance with structure 4c. In addition the structures 4a-4c were confirmed by their mass spectra exhibiting $[M\text{-}CONR^4_2]^{+\cdot}$ as base peak (formation of a stable tropylium ion).

The formation of the cycloheptatrienic amides 4 can be visualized analogous to the scheme of reference 5, assuming consecutively attack of the oxygen atom of the ketone on C(1) of the aromatic ring, ring closure to a norcaradiene and ring opening to a cycloheptatriene; *cf*. ref.8.



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References

1. A. Mosterd, L.J. de Noten and H.J.T. Bos, Recl. Trav. Chim. Pays-Bas 96, 16 (1977).
2. A. Mosterd and H.J.T. Bos, ibid 94, 220 (1975).
3. Irradiation of ≈1 gram 3 in 450 ml of benzene with Philips H.P.4-N-125W without bulb, through GWV glass with λ>366 nm during ≈25 h at ≈15°C.
4. Prepared from R^3-C_6H_4-C≡C-NR^4_2 and 3,5-di-*tert*-butyl-*o*-benzoquinone in chloroform at room temperature in an instantaneous reaction; yields >80%.
5. H. Polman, J.S.M. Boleij and H.J.T. Bos, Recl. Trav. Chim. Pays-Bas 91, 1088 (1972).
6. UV (hexane, λ_{max}/nm (ε/l $mol^{-1}cm^{-1}$): 213 (29000, sh), 233 (14000, sh), 266 (4000), 297 (4400).
7. ^{13}C NMR ($CDCl_3$) showed peaks at δ=12.2 ppm (2xCH_3); δ=23.7 ppm (CH_3); δ=29.3 and 31.6 ppm [2x$(\underline{C}H_3)_3C$]; δ=34.3 and 34.7 ppm [2x$(CH_3)_3\underline{C}$]; δ=40.9 ppm [2xCH_2N]; δ=57.7 ppm ($\underline{C}$-C=O); δ=99.4 ppm ($\overline{CH}$=C-O); δ=117.7, 119.8, 122.4, 122.8, 128.2, 130.5, 132.7, 134.4, 146.0, 149.6 and 152.3 ppm (sp^2-carbons) and δ=167.1 ppm (C=O).
8. J. Druey, E.F. Jenny, K. Schenker und R.B. Woodward, Helv. Chim. Acta 45, 600 (1962).