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UV-LASER PHOTOCHEMISTRY: RETRO-CLEAVAGE IN THE BENZOPHENONE-SENSITIZED PHOTOLYSIS OF Δ^3-1,3,4-OXADIAZOLINES INTO DIAZOALKANES.

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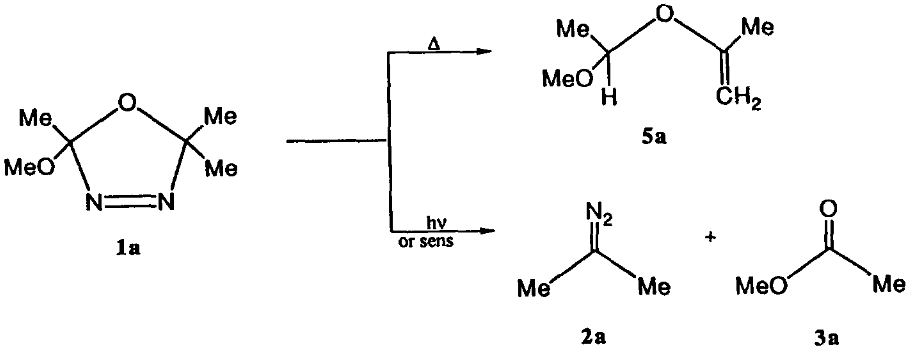
Abstract: Triplet-sensitized photolysis of 2-methoxy-2,5,5-trimethyl-Δ^3-1,3,4-oxadiazoline (**1a**) led to the retro-cleavage products diazoalkane **2a** and the ester **3a**, for which the triplet diazenyl diradical **6a** is postulated as precursor.

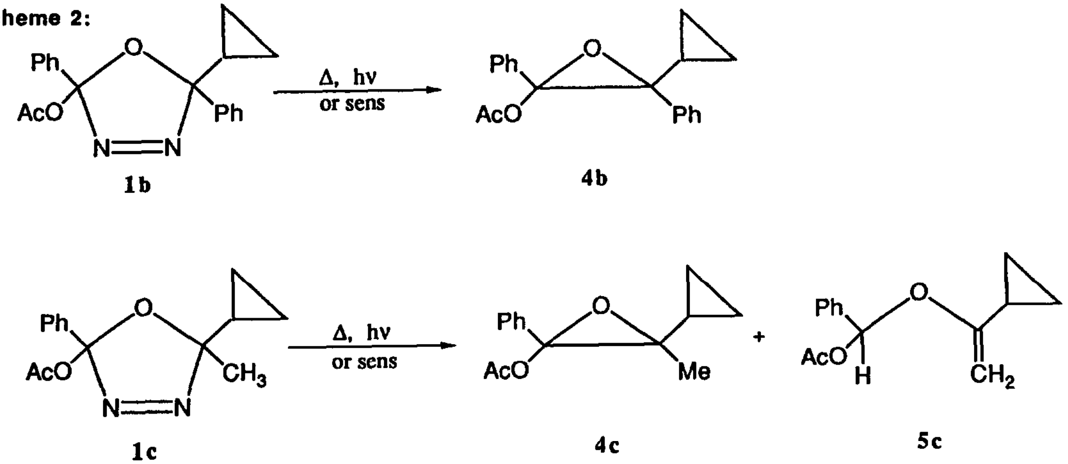
Warkentin et al.[1] recently reported that the photolysis of 2-alkoxy-Δ^3-1,3,4-oxadiazolines produces diazoalkanes and esters. He pointed out that benzophenone sensitization had no noticeable effect on the efficiency of the photolysis of **1a** nor on the product composition. Although the intervention of diazenyl diradicals [2,3] was convincingly established in the direct photolysis (singlet state process) of azoalkanes through the fact that such intermediates cleave into diazoalkanes [2], for the triplet-sensitized photolysis denitrogenation into cyclopropane products is preferred. In view of the photomechanistic implications, these results prompt us to present our preliminary work on the triplet-sensitized photolysis of oxadiazoline **1a**, showing for the first time that indeed retro-cleavage to the diazoalkane **2a** and the ester **3a** takes also place in the triplet state manifold (Scheme 1).

Scheme 1:



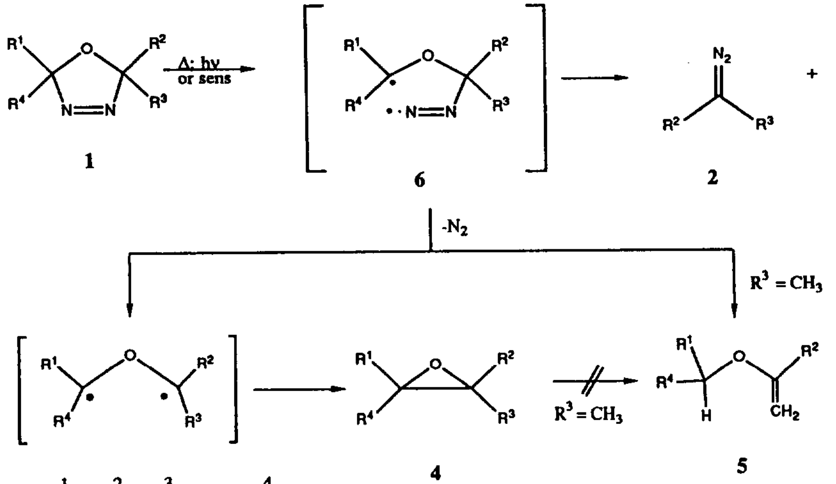
While the thermolysis of 2-methoxy-2,5,5-trimethyl-Δ^3-1,3,4-oxadiazoline (**1a**) afforded the enol acetal **5a**, the direct and benzophenone-sensitized photolyses led to 2-diazopropane (**2a**) and methyl acetate (**3a**), analogous to photochemical cleavages which have already been reported for the direct photolysis of azoalkanes[3] (Scheme 1). In contrast, the acetoxy-Δ^3-1,3,4-oxadiazolines **1b,c** produced the corresponding epoxides **4b,c** and the enol acetal **5c** (Scheme 2)[4]. To avoid direct photolysis (singlet state process) the argon ion laser was used as irradiation source. At $\lambda = 363.8$ nm the extinction coefficients of 2-methoxy-2,5,5-trimethyl-Δ-1,3,4-oxadiazoline ($\varepsilon = 0.1$) and benzophenone ($\varepsilon = 104$) differ sufficiently to permit exclusive excitation of the benzophenone, an efficient triplet sensitizer. By means of control experiments, it was shown that cleavage of Δ^3-1,3,4-oxadiazoline **1a** affording diazoalkanes **2a** and ketone **3a** doubtlessly proceeds via a triplet-excited species. Thus, no cleavage was observed in the direct irradiation ($\lambda = 363.8$ nm) of **1a**; however, as recently reported[1a], irradiation of the same reaction mixture at $\lambda = 333.6$ nm led immediately to the characteristic red color of the 2-diazopropane (**2a**), the latter additionally confirmed by its 2120-cm^{-1} band in the IR spectrum.

Scheme 2:



These results are rationalized in terms of the mechanism shown in Scheme 3. Thus, analogous to the thermolysis[1] and direct photolysis of the Δ^3-1,3,4-oxadiazolines **1**, also for the benzophenone-sensitized process the diazenyl diradical **6** is proposed as key intermediate. Triplet energy transfer between triplet benzophenone and Δ^3-1,3,4-oxadiazoline **1a** (Scheme 4) affords the latter in its triplet excited state; subsequent C-N bond cleavage leads to the triplet diazenyl diradical **6a** ^{3}, which suffers C-O bond cleavage to produce 2-diazopropane (**2a**) and methyl acetate (**3a**). Alternatively, efficient ISC via oxygen atom-enhanced spin orbit coupling[5] in the triplet diazenyl diradical **6a** ^{3} generates first the singlet diradical **6a** ^{1}, which then serves as precursor to the observed cleavage products in the triplet-sensitized photolysis of the Δ^3-1,3,4-oxadiazoline **1a**.

Scheme 3:



a: $R^1 = R^2 = R^3 = Me, R^4 = MeO$
b: $R^1 = R^3 = Ph, R^2 =$ cyclopropyl, $R^4 = AcO$
c: $R^1 = Ph, R^2 =$ cyclopropyl, $R^3 = Me, R^4 = AcO$

Scheme 4:

$$Ph_2C = O^{*3} + 1a \longrightarrow Ph_2C = O + 1a\ ^{*3}$$

$$\begin{tikzcd} 1a^{*3} \arrow[r] & 6a^3 \arrow[rr, "ISC"] \arrow[dr] & & 6a^1 \arrow[dl] \\ & & 2a + 3a & \end{tikzcd}$$

The fact that for the cyclopropyl-substituted oxadiazolines **1b,c** no cyclopropylcarbinyl rearrangement[6] products were observed, as also reported for analogous derivatives by Warkentin [1a], suggests that this free radical clock is too slow (ca. 10^8 s^{-1}) for cyclopropylcarbinyl ring-opening to compete with the rate at which products are formed. For this purpose the much faster cis-1,2-diphenylcyclopropylcarbinyl radical probe (> 10^{10} s^{-1}) [7] might be useful in establishing the intervention of the diazenyl diradical **6a**.

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4) In the synthesis of 2-acetoxy-5-cyclopropyl-2,5-diphenyl-Δ^3-1,3,4-oxadiazoline (**1b**) one stereoisomer was formed whereas for 2-acetoxy-5-cyclopropyl-5-methyl-2-phenyl-Δ^3-1,3,4-oxadiazoline (**1c**) an 80:20 mixture of the two possible stereoisomers was formed.

1b: ^{1}H-NMR (CD_2Cl_2, 200 MHz): δ = 0.34 - 0.68 (m, 4H, cyclopropyl-H), 0.95 - 1.17 (m, 1H, cyclopropyl-H), 1.70 (s, 3H, -CH_3), 7.15 - 8.02 (m, 10H, aromatic-H).- ^{13}C-NMR (CD_2Cl_2, 50 MHz): δ = 2.01 (t), 2.34 (t), 12.7 (d), 21.9 (q), 127.6 (d), 127.9 (d), 128.0 (d), 128.9 (d), 130.8 (s), 134.4 (s), 135.2 (s), 136.6 (s), 168.2 (s).- UV (CH_3CN): λ (lg ε) = 320 nm (2.570).

1c: ^{1}H-NMR ($CDCl_3$, 200 MHz): **major isomer**: δ = 0.37 - 0.67 (m, 4H, cyclopropyl-H), 1.32-1.54 (m, 1H, cyclopropyl-H), 1.64 (s, 3H, -CH_3), 2.05 (s, 3H, -$OCCH_3$), 7.26 - 8.17 (m, 5H, aromatic-H); **minor isomer**: δ = 0.37 - 067 (m, 4H, cyclopropyl-H) 1.32 - 154 (m, 1H, cyclopropyl-H), 1.68 (s, 3H, - CH_3), 2.01 (s, 3H, - $OCCH_3$), 7.26 - 8.17 (m, 5H, aromatic-H).-

^{13}C-NMR ($CDCl_3$, 50 MHz) : **major isomer**: δ = 1.88 (t), 2.30 (t), 17.6 (d), 22.0 (q), 22.7 (q), 126.5 (d), 127.7 (s), 128.7 (d), 130.0 (d), 131.1 (s), 134.7 (s), 167.4 (s); **minor isomer**: δ = 1.97 (t), 2.11 (t), 17.7 (d), 21.9 (q), 23.2 (q), 126.8 (d), 128.0 (s), 128.7 (d), 130.4 (d), 129.7 (s) 145.6 (s), 167.4 (s).- UV (CH_3CN): λ (lg ε) = 314 nm (2.540).

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