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PHOTOCHEMISTRY OF α-OXO-OXIMES. PART 2.[1] IRRADIATION OF 4-ETHOXYIMINO-2,6-DIMETHYLHEPTAN-3-ONE: A NOVEL TYPE II CYCLOBUTANOL FORMATION

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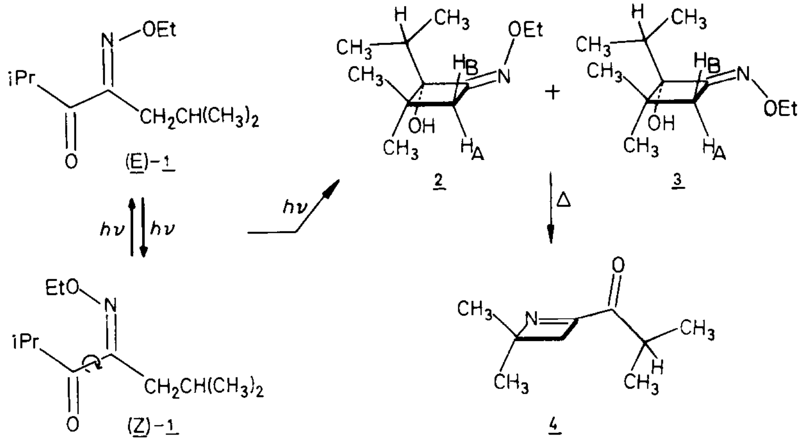
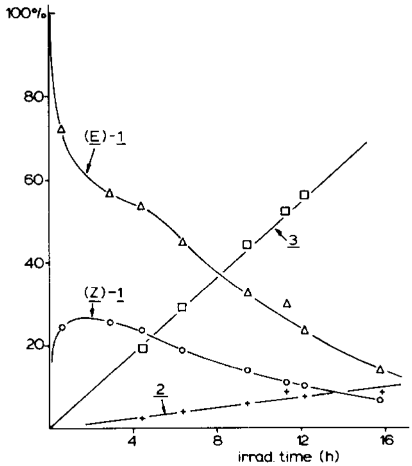
Irradiation of 4-ethoxyimino-2,6-dimethylheptan-3-one (1) with λ 313 nm in the presence of benzophenone as triplet sensitizer (E_T=69 kcal mol^{-1};[2] 91% of the incident radiation was absorbed by the sensitizer) in acetonitrile solution resulted only in the formation of a photostationary state (pss) mixture of the (E)- and (Z)-isomer.[3]

Upon direct irradiation of 1 (0.06-0.11M) with λ 313 or 366 nm in various solvents and subsequent GLC analysis of the photolysate three products (2-4) were obtained. The amounts decrease in the order 4>3>>2. Upon direct ^{1}H NMR analysis of the photolysate only the compounds 2 and 3 (and not 4) were found, with 3 being the larger component. Further, the GLC peak of 4 was rather broad and irregular in shape. Accordingly, it was concluded that 4 is not a photochemical product, but arises by thermal decomposition of 2 and 3 in the gas chromatograph.

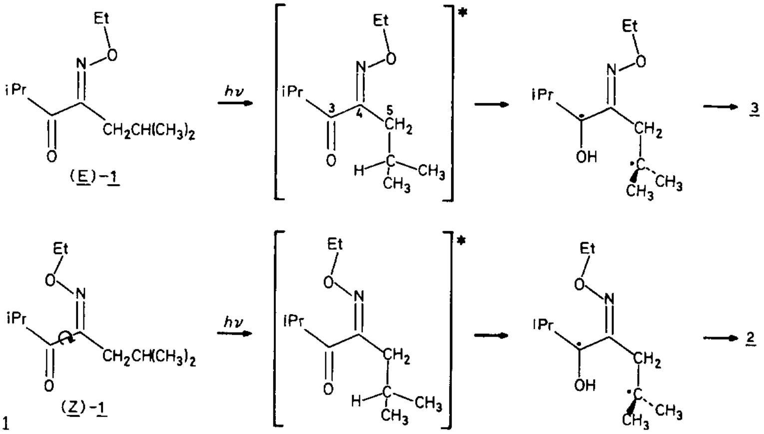


Product 2 was assigned to be (Z)-2-hydroxy-2-isopropyl-3,3-dimethylcyclobutanone oxime O-ethyl ether on the following spectral data:[4] IR (cm^{-1}, CHCl$_3$) 1705 (C=N) and 1045 (C-O); ^{1}H NMR (δ, CCl$_4$) 3.94 (q, 2H, J=7.3 Hz, $C\underline{H}_2O$), 2.19 (d, 1H, J_{AB}=14.5 Hz, $C\underline{H}_A$), 2.10 (br, 1H, $O\underline{H}$), 2.06 (d, 1H, J_{AB}=14.5 Hz, $C\underline{H}_B$), 1.98 [m, 1H, J=7.0 Hz, $C\underline{H}(CH_3)_2$], 1.16 (t, 3H, J=7.2 Hz, $C\underline{H}_3CH_2$), 1.12 (s, 3H, $C\underline{H}_3C$), 1.03 (s, 3H, $C\underline{H}_3C$), 0.91 [d, 3H, J=7.0 Hz, $CH(C\underline{H}_3)_2$], 0.87 [d, 3H, J=7.0 Hz, $CH(C\underline{H}_3)_2$]. Product 3 was assigned to be (E)-2-hydroxy-2-isopropyl-3,3-dimethylcyclobutanone oxime O-ethyl ether on the following spectral data:[4] IR (cm^{-1}, CHCl$_3$) 3610 (free OH), 3420 (br, assoc. OH), 2975, 2940, 2880, 1680 (C=N), 1465, 1385, 1145, 1090, 1040 (C-O), 945, 890, 870, 855; ^{1}H NMR (δ, CCl$_4$) 3.93 (q, 2H, J=7.0 Hz, $C\underline{H}_2O$), 2.38 (d, 1H, J_{AB}=16.0 Hz, $C\underline{H}_A$), 2.20 (br, 1H, $O\underline{H}$), 2.14 (d, 1H, J_{AB}=16.0 Hz, $C\underline{H}_B$), 1.95 [m, 1H, J=7.0 Hz, $C\underline{H}(CH_3)_2$], 1.11 (t, 3H, J=7 Hz, $C\underline{H}_3CH_2$), 1.11 (s, 3H, $C\underline{H}_3C$), 1.03 (s, 3H, $C\underline{H}_3C$), 0.94 [d, 3H, J=7.0 Hz, $CH(C\underline{H}_3)_2$], 0.85 [d, 3H, J=7.0 Hz, $CH(C\underline{H}_3)_2$]; MS (70 eV) 154 (10), 82 (36), 71 (52), 55 [15, (82-HCN): m^*_{obs} 36.91 and m^*_{calc} 36.89], 43 [100, $(71\text{-}CO)^+$: m^*_{obs} 26.08 and m^*_{calc} 26.04], 42 [26, $(43\text{-}H_2)^+$: m^*_{obs} 39.09 and m^*_{calc} 39.09]. Product 4 was assigned to be 1-(3,3-dimethyl-2-aza-1-cyclobutenyl)-2-methylpropanone on the following spectral data:[4,5] IR (cm^{-1}, CHCl$_3$) 3020, 2975, 2940, 2880, 1710 (C=O), 1470, 1026; ^{1}H NMR (δ, CCl$_4$) 2.98 (m, 1H, J=7 Hz, $C\underline{H}C{=}O$), 2.35 (s, 2H, $C\underline{H}_2$), 1.25 [s, 6H, $(C\underline{H}_3)_2$], 0.97 [d, 6H, J=7 Hz, $CH(C\underline{H}_3)_2$]; MS (70 eV) 153 (5), 83 (8), 82 [19, $(110\text{-}CO)^+$: m^*_{obs} 61.19 and m^*_{calc} 61.13], 71 [50, $(M\text{-}C_5H_8N)^+$: m^*_{obs} 33.01 and m^*_{calc} 32.95 , 56 (24), 43 [100, $(71\text{-}CO)^+$: m^*_{obs} 26.07 and m^*_{calc} 26.04].



The variation in the amounts of starting material and the products (Z)-1, 2 and 3 upon direct irradiation of 0.055M (E)-1 with λ 366 nm in acetonitrile solution with the irradiation time is shown in the Figure.[6] The amounts of 2 and 3 were calculated from the amounts of 2-4 determined by GLC on the assumption that the rate constants for the conversion of 2 and 3 into 4 are the same. The rate ratio for the formation of 3 to 2 is ca. 7. The pss of 1 was reached after two hours and has an E/Z value of 2.3.

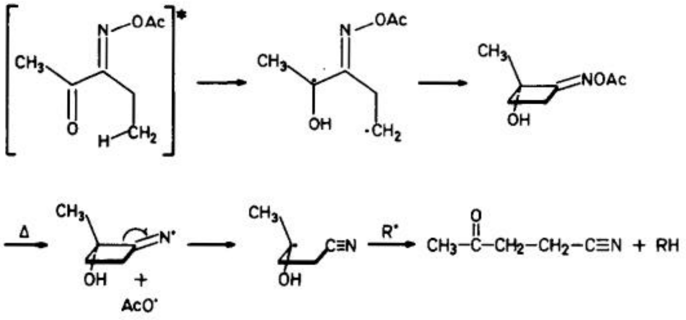
The formation of the cyclobutanol products 2 and 3 can be explained in terms of Scheme 1. The cyclobutanol formation accompanying type II photoelimination from monoketones involves an 1,4-biradical intermediate.[7] A similar type of intermediate is formed from 1-phenyl-1,2-diones containing γ-hydrogens.[8] The failure of these diketones to undergo type II photoelimination probably arises from the perpendicular orientation of the C(3) p orbital relative to the C(4)-C(5) σ bond in the biradical[7] (for the numbering see Scheme 1). In fact, with α-oxo-oxime ether 1 also no photoelimination products were observed.



Scheme 1

The formation of 4-oxopentanenitrile upon irradiation of 3-acetyloxyiminopentan-2-one (Scheme 2) is another example of intramolecular γ-H abstraction with an α-oxo-oxime derivative. The N-O bond of oxime esters is thermally labile.[3] The initially formed cyclobutanol product therefore decomposes leading eventually to the nitrile.[3] The photoreactions other than (E)-(Z) isomerization of the α-oxo-oxime ethers and esters proceed from the $S_1(n-\pi^*)$ excited state.[3]

The quantum yield for cyclobutanol formation (2+3) from 1 was estimated for acetonitrile as solvent to be *ca*. 0.02.[3] Yang reported a similar value for the triplet state cyclobutanol formation of aliphatic ketones.[9] The material balance for the 366 nm photoreaction of 1 in acetonitrile is 92%. This implies that the photodecomposition by initial N-O bond cleavage (and the type II photoelimination) is (at most) a minor process.



Scheme 2

The ratio of the rates of formation of 3 to 2 is large relative to the $(E/Z)_{pss}$ ratio (*viz.* 7 *vs.* 2.3)[10] This may be rationalized in terms of the difference in conformation of the two geometrical isomers of 1 (see the Scheme). The (E)-isomer has the planar s-*trans* conformation;[3] in this conformation the γ-hydrogen of the isobutyl group is ideally situated for the 1,5--hydrogen transfer to the excited carbonyl group. The (Z)-isomer exists in the non-planar s-*trans* conformation;[3] the isobutyl group is moved out of the position required for γ-H abstraction because of steric interaction between the oxime oxygen and the isopropyl group. This renders the rate of cyclobutanol formation lower for (Z)-1 than (E)-1 and thus explains the relatively high value for the ratio of the rates of the formation of 3 to 2.

References and notes

1. Part 1, P. Baas and H. Cerfontain, J. Chem. Soc. Perkin Trans II, 1977, 1351.
2. S.L. Murov, "Handbook of Photochemistry", Dekker, New York, 1973, p. 3.
3. P. Baas and H. Cerfontain, to be published.
4. The IR, ^{1}H NMR and mass spectra were recorded on a Perkin Elmer 125, a Varian HA-100 and an AEI MS-902 apparatus respectively.
5. The alternative structure 3,3,5-trimethyl-4-oxohexanenitrile is rejected on the following two arguments. First the absence of the C≡N stretching frequency at 2240 cm^{-1} and the presence of a very weak C=N absorption at 1603 cm^{-1} and second the occurrence of mass peak m/e 56 which is easy to explain with structure 4, but very difficult with the alternative structure.
6. The amounts were determined from the GLC peak areas and were corrected for the difference in molecular weight.
7. P.J. Wagner, Acc. Chem. Res., 4 , 168 (1971).
8. P.J. Wagner, R.G. Zepp, K.-C. Liu, M. Thomas, T.-J. Lee, and N.J. Turro, J. Amer. Chem. Soc., 98, 8125 (1976).
9. N.C. Yang and S.P. Elliott, J. Amer. Chem. Soc., 91, 7550 (1969).
10. The molar extinction coefficients at 366 nm are nearly the same for (E)- and (Z)-1.