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PHOTOCHEMISTRY OF NON-CONJUGATED DIENONES III[1] : PHOTOLYSIS OF *RETRO*-γ-IONONES.

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In a recent paper[1] we described the formation of both the ionone isomers (Z)-*retro*-γ-ionone (I) and (E)-*retro*-γ-ionone (VI) (charts 1 and 2) *via* the corresponding alcohols. In this paper we describe the behaviour of (Z)- and (E)-*retro*-γ-ionone on direct photolysis[2].

Irradiation of I in ethanol gives rise to the formation of only one product, which is identical with the bicyclic ionone II obtained previously[1] by oxidation of the corresponding alcohol (chart 1). This electrocyclic reaction also proceeds thermally at room temperature, but the thermal reaction is very slow as compared with the photochemical reaction.

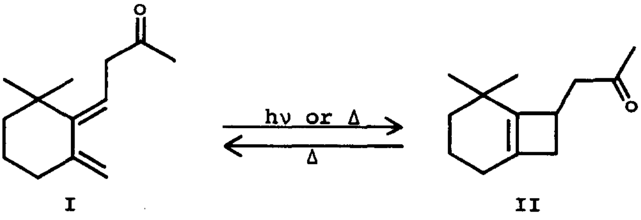
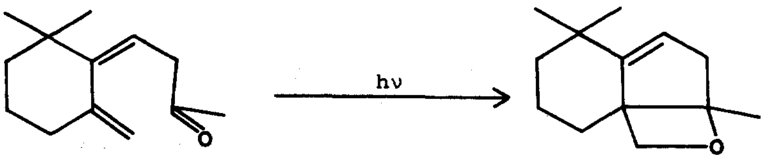


chart 1

Irradiation of (E)-*retro*-γ-ionone (VI) in ethanol gives rise to the formation of one major product, which we identified as the tricyclic oxetane VII[3] (chart 2) on the basis of spectral evidence[4]. The IR spectrum of VII exhibits the typical oxetane band[5] at 995 cm^{-1} and the out-of-plane olefinic C-H deformation band at 870 cm^{-1}. The presence of the olefinic bond is confirmed by the Raman spectrum, which exhibits the C=C stretch vibration band at 1638 cm^{-1}.



VI VII

chart 2

The PMR spectrum (fig. 1) consists of: 1. three methyl singlets (three protons each) at 1.03 and 1.14 ppm $\left(Me_{2(a)}\right)$ and at 1.31 ppm $\left(Me_{(b)}\right)$; 2. a complex pattern of the methylene groups in between 2.2 and 1.2 ppm (six protons total); 3. a two proton singlet at 4.38 ppm assigned to the oxetane methylene group $\left(CH_{2(e)}\right)$ and 4. an ABX-system of the cyclopentene methylene group $\left(H_c\right.$ and H_d at 2.21 and 2.52 ppm, J_{cd}= 17 Hz and J_{cf}= J_{df}= 2 Hz$\left.\right)$ with the olefinic proton $\left(H_f\right.$ at 5.39 ppm, triplet with J= 2 Hz$\left.\right)$, which could be resolved by means of double resonance.

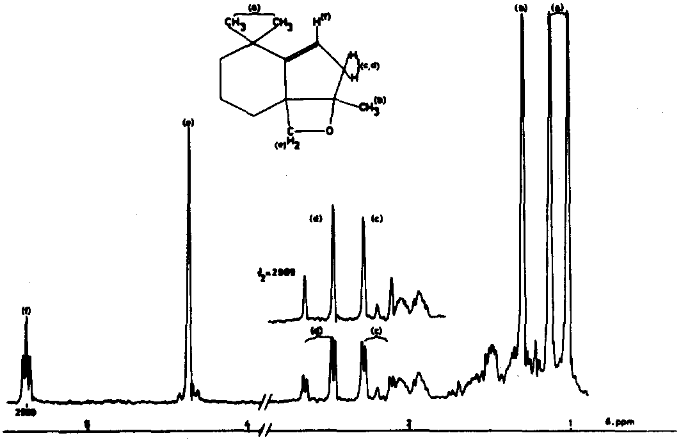


fig. 1: 100 MHz PMR spectrum of the oxetane VII in CCl_4; TMS as int. standard.

The mass spectrum of VII shows the molecular ion peak at m/e 192 ($C_{13}H_{20}O$; 1.15 % TIC), the base peak at m/e 147 (13.64 % TIC) and a significant peak at m/e 162 (4.91 % TIC) resulting from loss of fragment $H_2C{=}O$ from the molecular ion.

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From other work[6] it is known that (E)-*retro*-γ-ionone (VI) is formed as a byproduct in the photolysis of (E)-β-ionone (III), the main product being the pyran derivative V. We now observed (chart 3) that the amount of VI relative to V in the reaction mixture increases gradually with increasing reaction time. Also, irradiation[2] of V in ethanol gives rise initially to the formation of VI, but subsequently to the formation of the oxetane VII. These observations indicate that both VI and V may arise from III *via* the same intermediate, which has been proposed[6,7] to be (Z)-β-ionone (IV)(chart 3). The intermediacy of IV is of course of crucial importance in accounting for the thermal electrocyclic reaction to V.

The same authors[7] further suggested that VI would arise from IV *via* the enol of VI; this process formally represents a 1,7-hydrogen shift. However, we consider it more likely that VI is formed directly from excited β-ionone *via* a 1,5-hydrogen shift[8] as the diene moiety in β-ionone exists in the required cisoid (*viz. s-cis*) conformation[9]. Thus (Z)-β-ionone (IV) does not necessarily have to be an intermediate in the formation of VI from III. Preliminary experiments on the photolysis of III at low temperatures[10] furnish some evidence that VI can be formed directly from III. For at -50°C thermal ringclosure of IV to V can be expected to be suppressed, whereas it is to be expected that the photochemical 1,5-hydrogen shift to VI will relatively less be suppressed. In fact the relative rate of formation of VI over V is greater at -50°C than at room temperature.

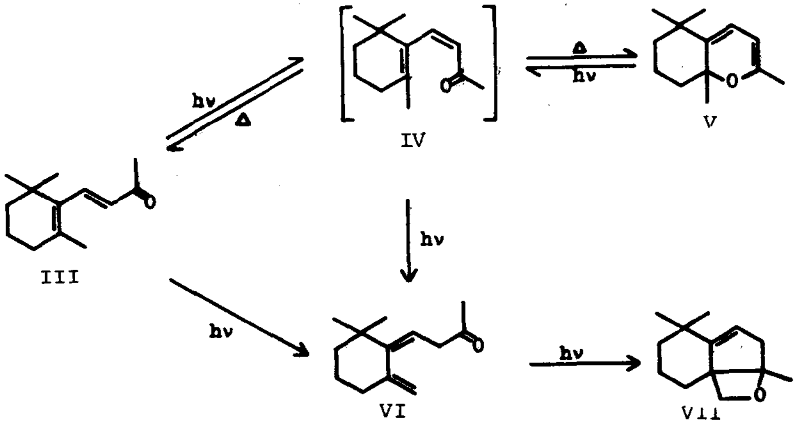

chart 3

Conclusions

The final product of the direct photolysis of (E)-β-ionone is the oxetane VII.

Direct photolysis of the three known *retro*-ionones gives rise to three different types of reactions as a result of the different steric constraints of the molecules. In the case of (E)-*retro*-γ-ionone (VI) the carbonyl group and the exocyclic methylene group are sterically in a favoured position (chart 2) for undergoing an intramolecular $[2\pi + 2\pi]$cycloaddition[11] with oxetane formation, whereas (Z)-*retro*-γ-ionone (I) undergoes an electrocyclic reaction with formation of a cyclobutene ring. In the absence of these sterically imposed processes, (E)-*retro*-α-ionone undergoes a sigmatropic 1,3- or 1,5-acyl shift[12].

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4. The various spectra were recorded on the following instruments: Unicam SP-200 (IR spectra), Coderg PH1 with CRL52MG laser (Raman spectra), Varian HA-100 (PMR spectra), Varian Mat 711 (mass spectra) and Shimadzu UV-200 (UV spectra).
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