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PHOTOCHEMISTRY OF NON-CONJUGATED DIENONES II[1]: ELECTROCYCLIC REACTIONS OF SOME 1,2-DIMETHYLENECYCLOHEXANES

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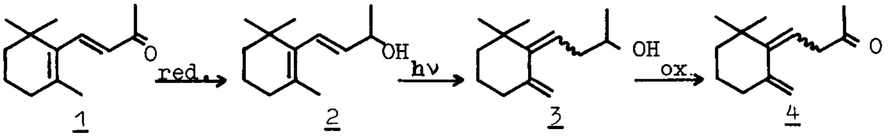
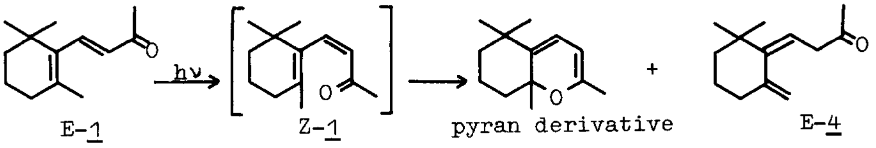
As part of our studies on non-conjugated dienones[1] we recently succeeded in synthesizing both the isomers of <u>retro</u>-γ-ionone(4)[2] following the principles of the synthesis by Mousseron-Canet et al.[3] (chart I).



<u>trans</u>-β-ionone β-ionol <u>retro</u>-γ-ionol <u>retro</u>-γ-ionone

chart I

DeMayo[4] also succeeded in isolating a product to which he ascribed the structure of <u>retro</u>-γ-ionone on the basis of its NMR-spectrum. This latter work was carried out as a completion of the work by Büchi and Yang[5] on the photolysis of β-ionone(1) (chart II).



<u>trans</u>-β-ionone <u>cis</u>-β-ionone <u>trans</u>-<u>retro</u>-γ-ionone

chart II

Neither Mousseron-Canet[3] nor DeMayo[4] specify the configuration [(Z)- or (E)-]

of the isolated *retro*-γ-ionol(3) and *retro*-γ-ionone(4), although their written structures suggest the E-configurations (chart II). Comparison of our spectra with the spectrum of DeMayo[4] now enables us to ascribe the E-configuration to the isomer isolated by him.

Upon photolysis[6] of β-ionol(2) (chart III) we observed a rapid disappearance of 2. At the same time a product was formed of which the spectral data[7] were in accordance with (E)-*retro*-γ-ionol(E-3). Further irradiation of the solution led to the slow formation of a compound with spectroscopic properties fairly similar to those of the primary photoproduct. By means of spin-spin decoupling and NOE NMR experiments[8] on both the primary and the secondary photoproduct, the primary product was identified as (E)-*retro*-γ-ionol(E-3) and the secondary product as the corresponding (Z)-isomer(Z-3) (chart III).[8] Finally, prolonged irradiation of the original reaction mixture, as well as photolysis of a solution of pure Z-3, produced a compound to which the bicyclooctene structure 5 [9] was ascribed (chart III). Compound 5 was also formed, but at a very low rate, when Z-3 was left at -20°C for several days without irradiation. Heating of 5 for 15 min. at 150°C produced Z-3. Oxidation[10] of the alcohols E-3, Z-3 and 5 yielded the corresponding ketones E-4, Z-4 and 6 [11] respectively (chart III). Under the chosen conditions of oxidation, the formation of Z-4 was always accompanied by the formation of large quantities of 6. Heating of 6 at 150°C for 15 min. gave Z-4, which upon standing slowly converted back to 6 again.

In the present study we did not once observe an electrocyclic reaction of E-3 or E-4 with formation of the corresponding cyclobutene derivative. This deviating behaviour of both E-3 and E-4 towards ring closure may be explained in terms of steric interference by the side chain which inhibits bond formation between C_1 and C_4 of the butadiene system[12]. On the other hand the ring closure in Z-3 and Z-4 might be enhanced because of release of steric interference between the α-methylene of the side chain and the two geminal methyl groups.

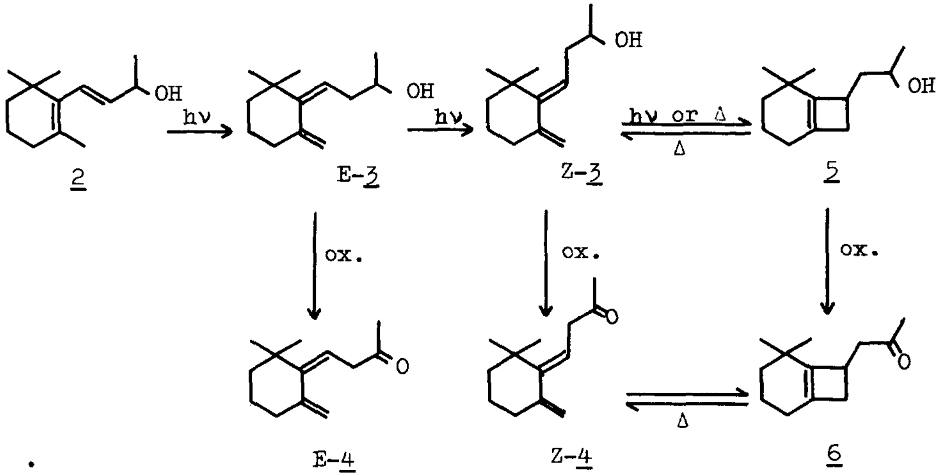


chart III

The bicyclooctene derivative 5 consists of a 1:1 mixture of the two pairs of diastereoisomers, as became evident from the NMR-spectra obtained using Eu^{III}-2,2,6,6-tetramethyl heptadionate as a shift reagent. The original doublet of the methyl group adjacent to the carbinol was shifted towards lower field and split into two distinct doublets of equal intensity. To our knowledge this different behaviour of diastereoisomers towards Eu^{III}-2,2,6,6-tetramethyl heptadionate has no precedent in the literature. The photolyses of the (E)- and (Z)-retro-γ-ionones will be reported shortly.

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4. P. DeMayo, J.B. Stothers and R.W. Yip, Can. J. Chem. **39**, 2135 (1961).
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6. Photolyses were carried out using 2% ethanolic solutions in a Rayonet photochemical reactor equipped with 254 nm lamps. The photolyses were monitored by means of GLC analyses of the reaction mixture (5 m 5% Carbowax 20M on Chromosorb-W 45-60 mesh at 140°C).
7. The compounds were identified by their IR-spectra (Unicam SP-200), UV-spectra (Shimadzu UV-200), NMR-spectra (Varian HA-100) and Mass-spectra (AEI MS-9).
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9. 2,2-Dimethyl-8-(2-hydroxypropyl)bicyclo[4.2.0]oct-1(6)-ene.
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11. 2,2-Dimethyl-8-(2-oxopropyl)bicyclo[4.2.0]oct-1(6)-ene.
12. At room temperature ring closure with formation of 3-methylcyclobutene is approximately 10 times slower for (Z)- than for (E)-1,3-pentadiene.[13]
13. R. Srinivasan, private communication.