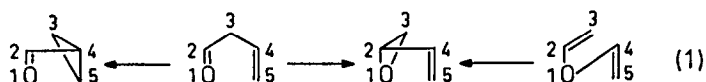


PHOTOCHEMISTRY OF BIS(2-METHYL-1-PROPENYL)ETHER AND
 2,2,4,4-TETRAMETHYL-6-OXABICYCLO[3.1.0]HEXAN-3-ONE:
 ON THE SEARCH FOR THE OXYDI- π -METHANE REARRANGEMENT

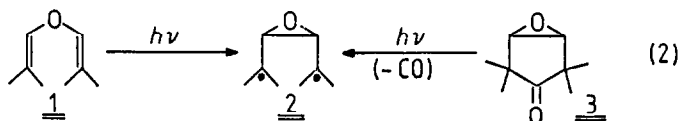
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SUMMARY: π, π^* -Excitation of bis(2-methyl-1-propenyl)ether leads to products derived from a vinyl-vinyloxy radical pair; photochemical decarbonylation (n, π^*) of the title ketone provides an entry into the diradical manifold of the oxydi- π -methane rearrangement.

While the oxadi- π -methane rearrangement of β, γ -enones leading to cyclopropyl ketones (Eq.1) is abundantly documented¹, formation of vinyl epoxides is not competitive on energy grounds.

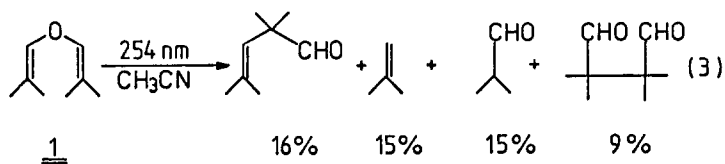


However, divinyl ethers could in principle serve as precursors to vinyl epoxides (Eq.1) via the novel oxydi- π -methane rearrangement. No examples of the latter process appear to have been reported. Consequently, the photolysis of the divinyl ether 1 was undertaken in search of this unprecedented rearrangement. Analogous to the di- π -methane process, the oxiranyldicarbonyl diradical 2 could intervene as intermediate (Eq.2), so that the photodecarbonylation of the



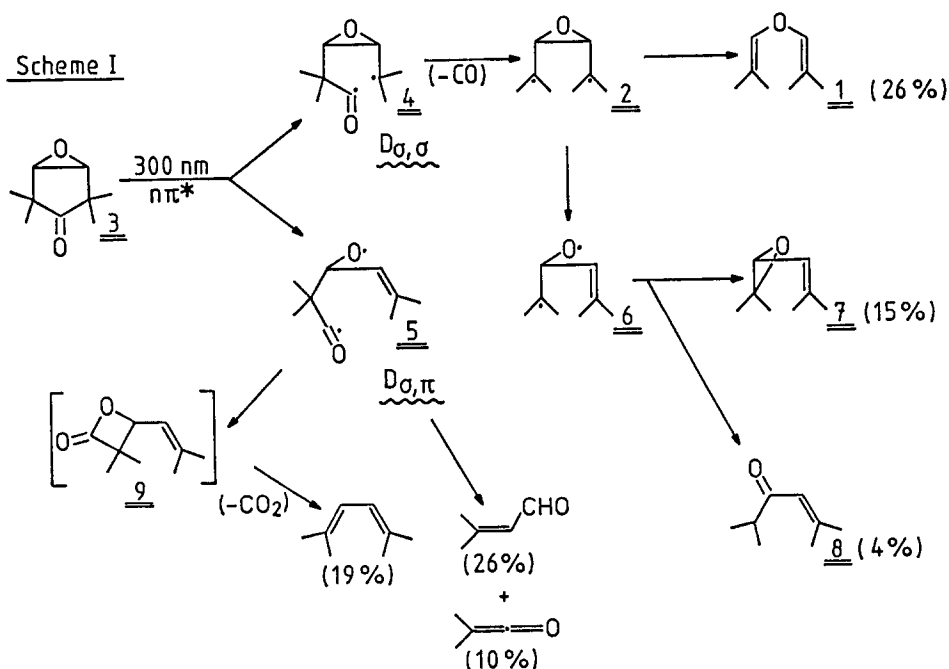
epoxycyclopentanone 3 was examined as independent entry into the oxydi- π -methane rearrangement.

Photolysis of the divinyl ether 1² in acetonitrile at 254 nm afforded the products shown in Eq.3. The corresponding vinyl epoxide, expected product of the oxydi- π -methane rearrangement, was not formed. Control experiments on an authentic sample confirmed that the vinyl epoxide was stable under the photolysis conditions and should have accumulated. By means of



trapping, cross-over and CIDNP experiments³ it was shown that these products were derived from a vinyl-vinyloxy radical pair, formed by cleavage of the carbon-oxygen bond. Photoelectron spectroscopy⁴ on divinyl ether 1 suggested that the lowest excitation is of the π, π^* -type. In this respect, the photochemistry of divinyl ethers resembles that of furans, for which it has been shown⁵ that π, π^* -excitation leads to carbon-oxygen bond cleavage to afford as initial intermediate a vinyl-vinyloxy diradical. Consequently, divinyl ethers appear to be inappropriate substrates for observing the oxydi- π -methane rearrangement.

The photochemistry of the epoxycyclopentanone 3⁶ was more encouraging. At 300 nm in pentane the quantum yield of substrate consumption was $\phi_S = 0.29$, affording the photoproducts shown in Scheme I. The relative yields are given in parentheses, total product balance was



ca. 90%, and identification was achieved by comparison of GC retention times and mass spectra (GCMS) with the authentic substances.

On irradiation at 300 nm an n, π^* -excited epoxy-cyclopentanone n, π^* -3 is formed, which affords initially the acyl-carbinyl diradical 4. Concerted chelotropic decarbonylation of cyclopenten-3-ones has been proposed in n, π^* -excitation⁷, but still lacks unambiguous experimental proof. Furthermore, such decarbonylation is questionable because n, π^* -excited carbon monoxide should result. For the specific case of the n, π^* -3 \rightarrow 4 transformation, a tritopic process⁸, the diradical 4 can assume the $D_{\sigma, \pi}$ and the $D_{\sigma, \sigma}$ configurations, of which the latter is energetically favored. Direct correlation leads to the $D_{\sigma, \pi}$ -4 diradical, while avoided surface crossing affords the $D_{\sigma, \sigma}$ -4 diradical. For the latter facile decarbonylation (formation of ground state carbon monoxide) produces the dicarbonyl diradical 2, which either fragments into divinyl ether 1 or into the 1,3-diradical 6. Cyclization of the latter leads to the vinyl epoxide 7, the searched for oxydi- π -methane product, while a 1,2-hydrogen shift gives enone 8. Transformations 6 \rightarrow 7 + 8 are well documented for oxatrimethylenes.⁹

For energy reasons the $D_{\sigma, \pi}$ -4 diradical is not directly accessible on n, π^* -excitation in the case of unstrained cycloalkanones.¹⁰ However, for the n, π^* -excited epoxy-cyclopentanone 3 α -cleavage with concurrent oxirane opening to the oxyl-acyl diradical $D_{\sigma, \pi}$ -5 appears energetically feasible. The $D_{\sigma, \pi}$ -5 diradical should be reluctant to decarbonylate because again an n, π^* -excited carbon monoxide would result. Instead, it is well lined up for fragmentation into dimethylketene and 3-methyl-2-butenal. Alternatively, cyclization of the diradical 5 generates the labile β -lactone 9¹¹, which decarboxylates to the 2,5-dimethyl-2,4-hexadiene.

These preliminary results suggest that photoextrusion reactions of suitable substrates can provide interesting opportunities to enter into novel heterodi- π -methane rearrangements. In this way the postulated 1,3- and 1,4-diradicals, which are not directly accessible, can be independently generated and their mechanistic behavior explored.

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 11. 3,3-Dimethyl-4-(2-methyl-1-propenyl)oxetan-2-one (9), detected by low temperature spectroscopy; $^1\text{H NMR}$ (C_6D_6): $\delta = 4.57$ (d, $\underline{J} = 8.8 \text{ Hz}$; 1H, oxetane-H), 5.10 (dmc, $\underline{J} = 8.8 \text{ Hz}$, 1H, vinyl-H). - $^{13}\text{C NMR}$ (C_6D_6): $\delta = 55.70$ (s; oxetane-C), 79.17 (d; oxetane-CH), 120.19 (d; vinyl-CH), 141.30 (s; vinyl-C), 175.42 (s; CO). - IR (CCl_4): $\nu_{\text{CO}} = 1832 \text{ cm}^{-1}$. - The methyl resonances could not be assigned with certainty in this reaction mixture.

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