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PHOTOSENSITIZED OXIDATION OF 3,6-DIMETHYLOCTANE

J-F.Rontani[*] and G.Giusti

Equipe Chimie Organique Marine - Centre d'Océanologie de Marseille
U.A.41 - Faculté des Sciences de Luminy - case 901
13288 - Marseille - France

In this paper an interesting mechanism involving a Barton reaction which leads to a propagation of photooxidation processes between γ positioned tertiary carbons is described.

In the wider framework of our studies concerning the photosensitized oxidations (1) and their possible interactions with biodegradation reactions (2), we studied the photochemical degradation of anteiso branched dimethylalkanes, compounds said to be very recalcitrant to bacterial degradation (3,4) .

We worked in a Pyrex flask containing 50 ml of chloroform, 100 μl of commercial 3,6-dimethyloctane (1) and traces of anthraquinone(sensitizer) (5) . After seven days of irradiation by sunlight and evaporation of the solvent, residual substrate (degradation rate : 40 %) and photooxidation products were separated on a silica column (4) . The different photoproducts could be identified by comparison of their chromatographic retention times and mass spectra with those of standard compounds (commercial or synthetized) . The different products identified with their relative percentages were reported in table I .

Table I : Percentage of the main photoproducts of 3,6-dimethyloctane (1)

Compounds	Relative Percentage[a]
3-methylpentan-3-ol (2)	2%
5-methylheptan-2-one (3)	5%
3,6-dimethyloctan-2-one (4)	traces
3,6-dimethyloctan-3-ol (5)	18%
3,6-dimethyloctan-3,6-diol (6)	60%
unknown photoproducts	15%

[a] determined by gas chromatography (FID)

Due to the great stability of the formed radicals (1), the photochemical processes act more strongly on the tertiary carbons of 3,6-dimethyloctane (1) (formation of the compounds 2 , 3 , 5 and 6) than on the secondary ones (formation of compound 4) . The proposed mechanisms for the photosensitized oxidation of tertiary carbons 3 and 6 are described in figure 1 .

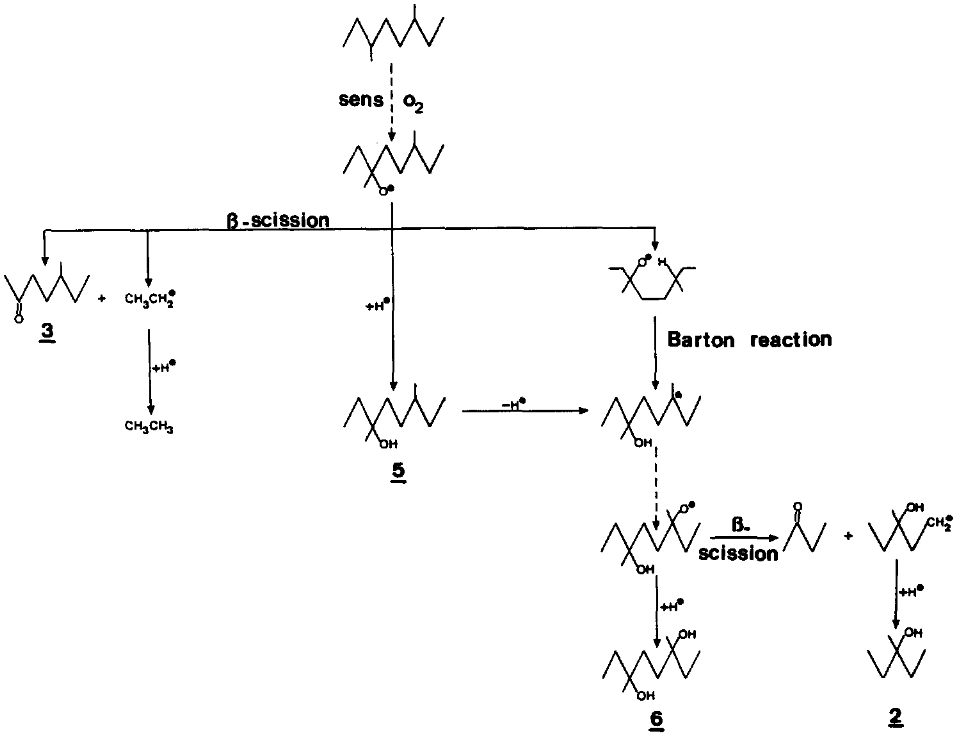

Figure 1 : Photosensitized oxidation of tertiary carbons of 3,6-dimethyloctane .

The excited photosensitizer (at the triplet state) abstracts a radical $H^\bullet$ on the carbon 3 of the substrate and generates a tertiary radical whose oxidation leads to the formation of an alkoxy radical (6,7) . The latter can then :

- either abstract a radical $H^\bullet$ on an other molecule of substrate or on a molecule of reduced photosensitizer (hemi-anthraquinone) and thus lead to compound 5 ,
- or lead after β scission reactions (8) to the formation of different ketones and notably of compound 3 ,
- or transfer the photochemical processes onto the tertiary carbon 6 which is ideally situated in γ position to allow an intramolecular abstraction of a radical $H^\bullet$ (Barton

reaction) (9,10) . The tertiary radical thus formed can lead , according to the different mechanisms previously described for carbon 3 (oxidation to an alkoxy radical followed by intermolecular abstraction of $H^{\bullet}$ or β scission processes), either to the formation of compound 6 , or to the formation of compound 2 .

These two compounds could also originate from the photosensitized oxidation of 3,6-dimethyloctan-3-ol (5) however, the very strong proportion of compound 6 formed (table I) leads us to minimize the importance of these phenomena in favour of the intramolecular abstraction of $H^{\bullet}$ previously described . This has been confirmed thanks to an attempt at photosensitized oxidation of 3,6-dimethyloctan-3-ol (5) under similar conditions;indeed, in this case the 3,6-dimethyloctan-3,6-diol (6) was produced in small quantities (approximately 0.7%) .

Moreover, during the study of photosensitized oxidation of 3,13-dimethylpentadecane (11), we have not been able to demonstrate production of 3,13-dimethylpentadecan-3,6-diol . The absence of this compound shows that, probably owing to the stability of the radical formed during the intramolecular abstraction of $H^{\bullet}$, the propagation mechanism of photooxidation processes observed in the case of 3,6-dimethyloctane (1) acts with intensity only between tertiary carbons .

What are present here are particular photosensitized oxidations affecting structures possessing tertiary carbons which are in the γ position in relation to each other . These phenomena take the form of very intensive photochemical processes propagation from one tertiary carbon to another .

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