PHOTOSENSITIZED OXIDATION OF PRISTANE IN SEA WATER: EFFECT OF PHOTOCHEMICAL REACTIONS ON TERTIARY CARBONS

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Summary

In the presence of a photosensitizer (anthraquinone) a surface film of pristane on synthetic sea water was photo-oxidized by sunlight. The photochemical processes are affected not only by the secondary carbons (producing different 2,6,10,14-tetramethylpentadecanones), but also, and more strongly, by the tertiary carbons. This photo-oxidation leads on the one hand to the formation of tertiary alcohols and on the other hand, after α-cleavage reactions, to different fragmentations of the pristane molecule into alkanes and ketones. These very important results provide new information that must be taken into account when considering the degradation of branched alkanes in a marine environment.

1. Introduction

The degradation of branched alkanes in a marine environment has, up to now, only been considered from a biological point of view [1 - 3]. Recently Ehrhardt and Petrick [4] have shown that, resulting from the presence of numerous photosensitizers in sea water [5, 6], the *n*-alkanes are degraded abiotically under the influence of sunlight. Within the general framework of our research on the degradation of branched alkanes in a marine environment [7, 8], it seemed important to study the photo-oxidation reactions of these compounds. In this first study, we have chosen as a standard substrate pristane which is a branched alkane often detected in the marine environment. The choice of pristane is due, on the one hand, to its double biogenic [9] and anthropogenic origins, and, on the other hand, to the rarity of conditions favouring its biodegradation [1].

We have tried here to provide, for the first time, evidence of the different reactivity of the carbon atoms according to their substitution, by identifying the main photo-oxidation products formed. We also propose various mechanisms likely to explain the formation of these compounds.

2. Experimental details

2.1. Substrate

The pristane used (Sigma, purity 95%) was purified by twice-repeated column chromatography on silica gel (elution with n-hexane).

2.2. Photo-oxidation experiments

A few microlitres of an acetone solution of anthraquinone (Fluka, purum), which is a photosensitizer often detected in sea water [5], was added to a Monod flask containing 150 ml of synthetic sea water [4]. 300 μl of pristane were spread on the surface of water and the pristane was irradiated by sunlight for 15 days.

2.3. Isolation of photo-oxidation products

After the irradiation, the medium was extracted with chloroform (volume ratio of medium:chloroform of 2:1). The chloroform extracts were dried with calcium chloride, filtered, concentrated and separated by chromatography on a wet-packed (n-hexane) column (internal diameter, 1.5 cm) filled with silica gel (20 cm, Fluka 60 and 5% of water). The sample was eluted with 100 ml of n-hexane and 100 ml of chloroform; this separation gives two fractions: F_1, composed of hydrocarbons, and F_2, composed of the main photo-oxidation products.

2.4. Identification of the different compounds formed

Identification involved gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) analyses. A Girdel série 30 chromatograph with a flame ionization detector (FID) was used for retention-time data. The chromatographic operating conditions were as follows: 50 m × 0.3 mm internal diameter capillary glass column coated with OV1 (methyl silicon); temperature programmed from 110 °C to 290 °C at 3 °C min^{-1}; carrier gas pressure (helium), 0.9 bar; detector temperature, 290 °C; injector temperature, 300 °C.

Electron-impact mass spectra were obtained with a Ribermag R-10-10-C spectrometer (electron energy, 70 eV). Unknown intermediates were identified by comparison of their mass spectra and retention times with those of known standards and, in the case of reaction products for which reference substances were not available, the mass spectra were interpreted according to classical rules.

In addition to the GC–MS analyses, some characterization reactions (reduction with lithium aluminium hydride and silylation with hexamethyldisilazane) were used to identify the different compounds formed.

3. Results

Chromatographic analysis of the F_2 fraction provides evidence of the formation of numerous photo-oxidation products of pristane (Fig. 1).
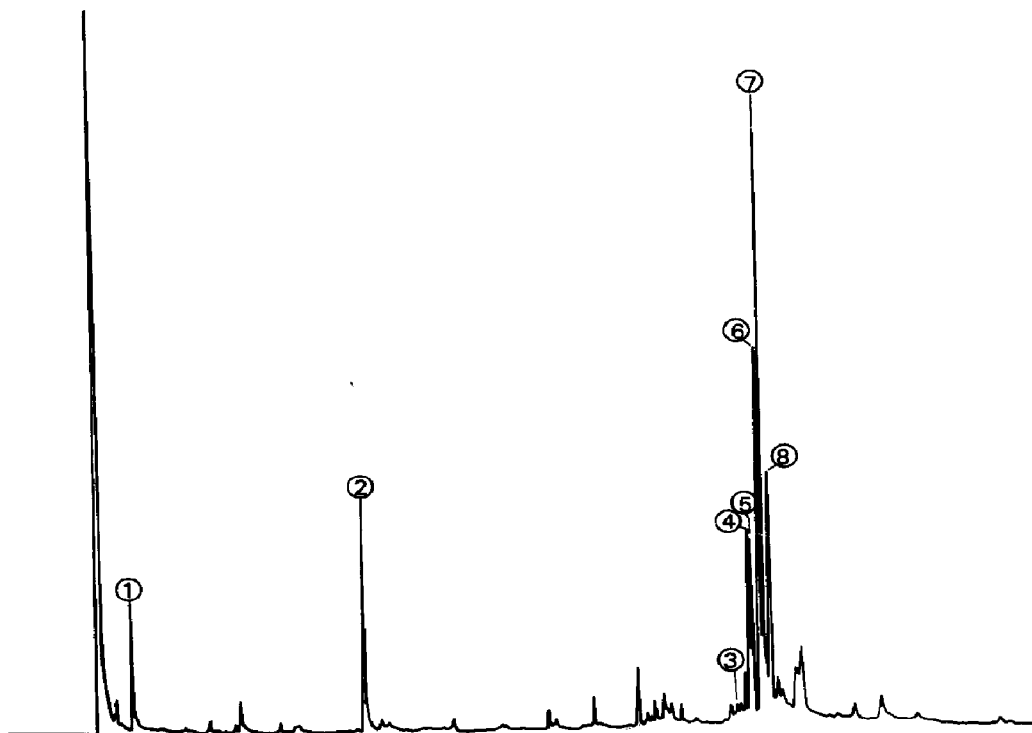
Fig. 1. Gas chromatogram of the chloroform eluate (fraction F_2).

According to the results obtained in the case of n-paraffins [4], different 2,-6,10,14-tetramethylpentadecanones were detected. These compounds can be reduced by lithium aluminium hydride (Figs. 1 and 2) and their mass spectra give molecular peaks at $m/e = 282$ together with fragmentations characteristic of aliphatic ketones (α cleavage and McLafferty rearrangement). These permitted the identification of three of the main positional isomers formed: 2,6,10,14-tetramethylpentadecanone-7 (compound 4) (Fig. 3), 2,6,10,14-tetramethylpentadecanone-5 (compound 5) (Fig. 4) and 2,6,10,14-tetramethylpentadecanone-3 (compound 8) (Fig. 5). The compounds 6 and 7 are not reduced by lithium aluminium hydride (Figs. 1 and 2) and their silylation with hexamethyldisilazane is possible only in hot dimethyl sulphoxide (DMSO) (Figs. 1 and 6); this is characteristic of tertiary alcohols [10]. The mass spectra of these compounds present no molecular peaks or peaks corresponding to dehydration, but strong α cleavages which enabled identification as 2,6,10,14-tetramethylpentadecanol-6 (compound 6) (Fig. 7) and 2,6,10,14-tetramethylpentadecanol-2 (compound 7) (Fig. 8). We also identified three methyl ketones whose mass spectra exhibit molecular peaks at m/e of 128, 198 and 268, together with a strong McLafferty peak at m/e of 58. The comparison of these mass spectra with those of known methyl ketones allowed us to identify them as 6-methyl-heptanone-2 (compound 1), 6,10-dimethylundecanone-2 (compound 2) and 6,10,14-trimethylpentadecanone-2 (compound 3).
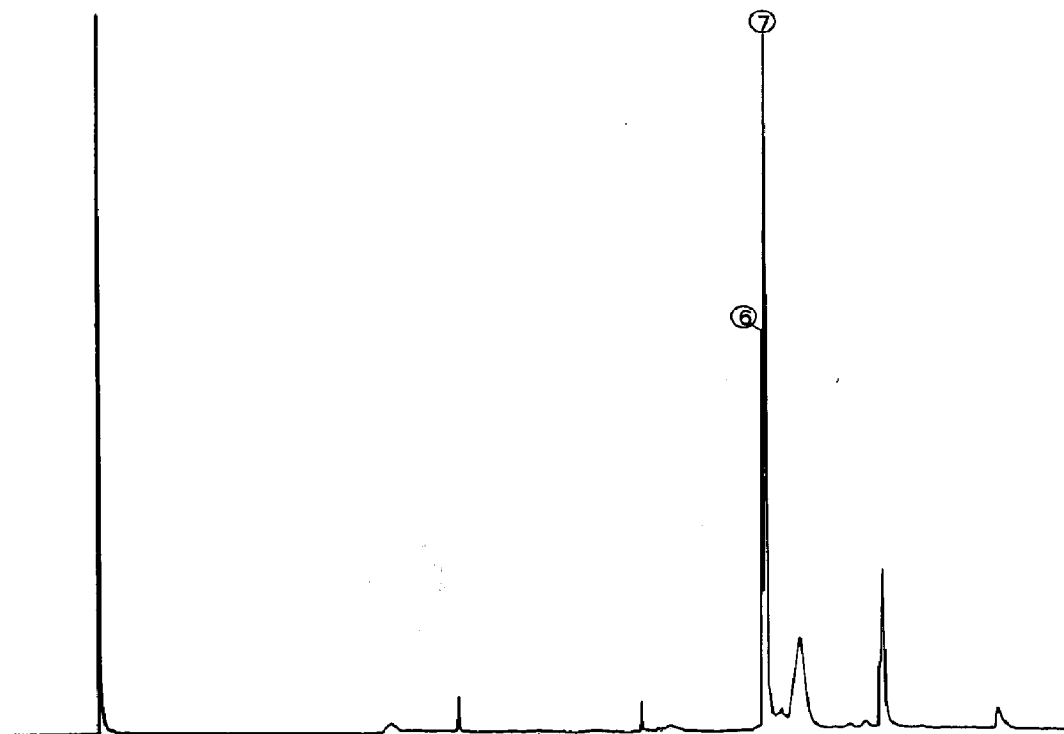
Fig. 2. Gas chromatogram of the chloroform eluate after reduction with lithium aluminium hydride.

So it seems that the photo-oxidation reactions affect the secondary carbons of pristane according to the mechanisms previously described in the case of n-alkanes [4]; these reactions lead to the formation of different 2,6,10,14-tetramethylpentadecanones. No secondary or tertiary photo-decomposition products were detected, probably because of their high volatility and low quantities.

It is interesting to note that the tertiary carbons also undergo photo-oxidation reactions. We have proposed for these reactions the mechanisms schematized in Figs. 9 and 10. These can explain the production of alcohols 6 and 7, together with the production of the methyl ketones observed (compounds 1, 2 and 3). These mechanisms were confirmed by the identification (by comparison of mass spectra and retention times with those of known standards) of 4,8-dimethylnonane and 4,8,12-trimethyltridecane in the F_1 fraction.

· If we refer to the quantity of important photo-oxidation products (especially 2,6,10,14-tetramethylpentadecanol-6 and 2,6,10,14-tetramethylpentadecanol-2), the attack of tertiary carbons of pristane seems to be favoured compared with attack of secondary carbons. This can be explained if we consider the difference in stability of the radicals formed (quaternary or tertiary) during the first step of the photo-oxidation processes (abstraction of a radical H·).
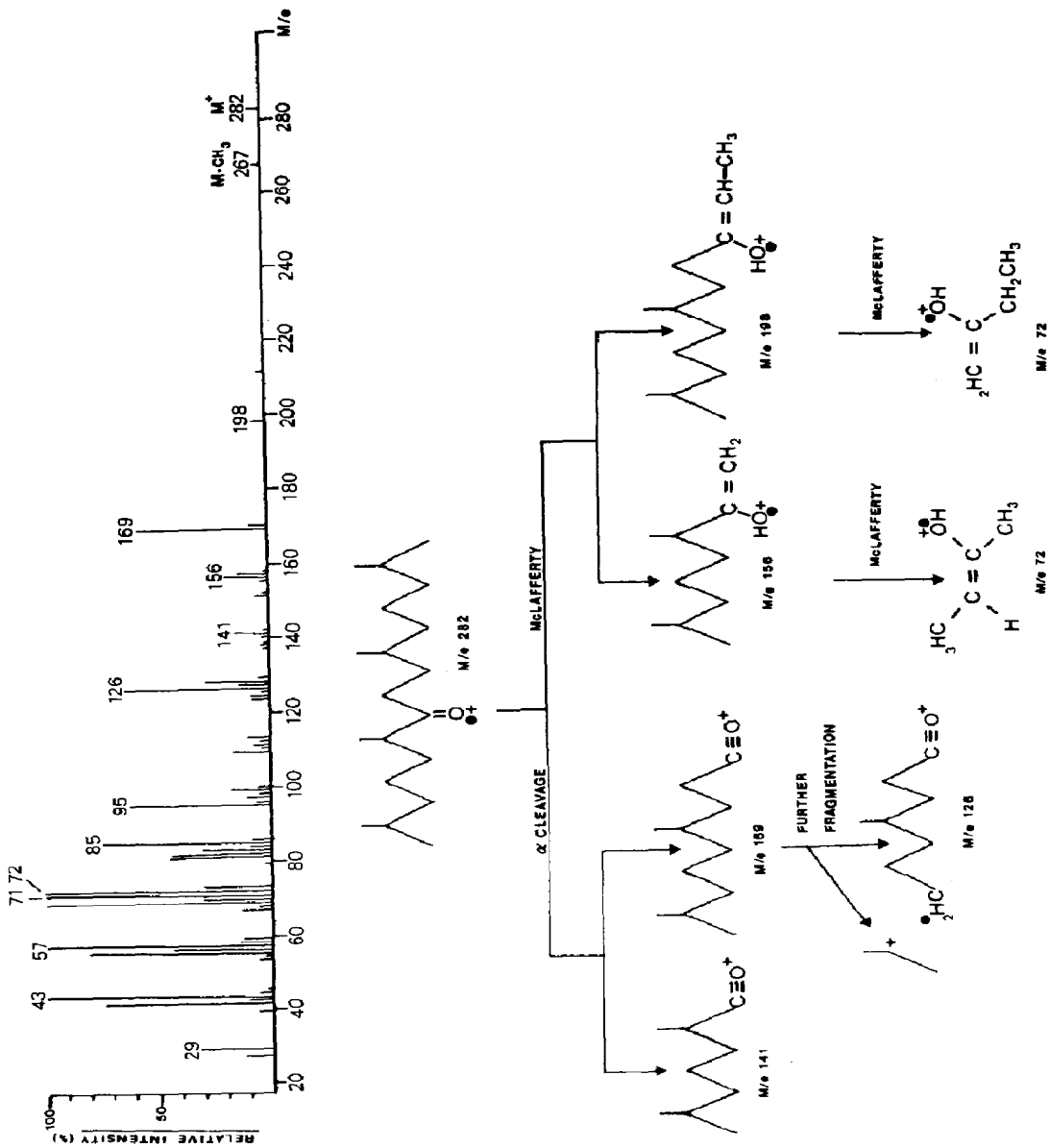
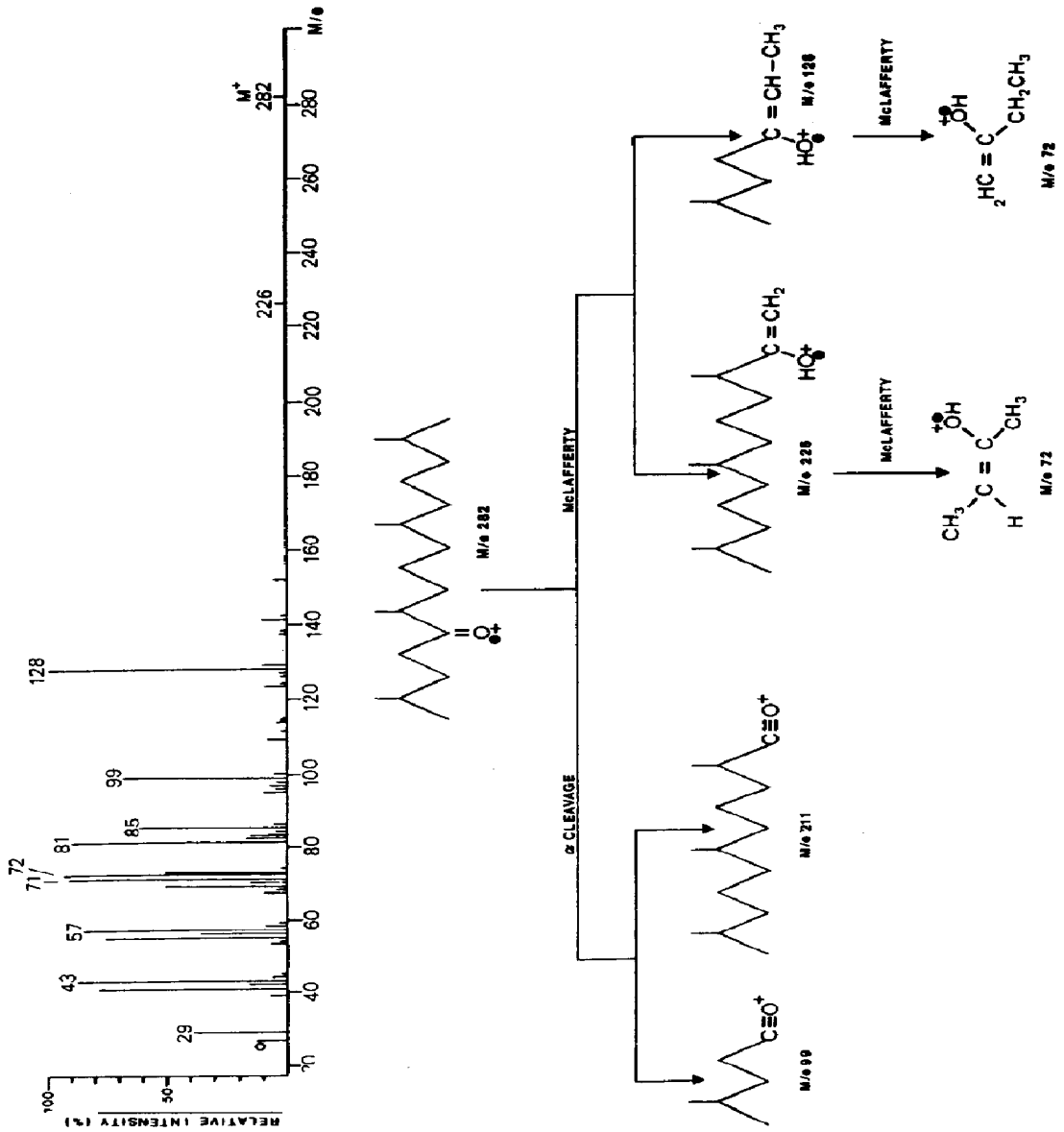Fig. 3. Mass spectrum and characteristic fragmentations of the compound 4.

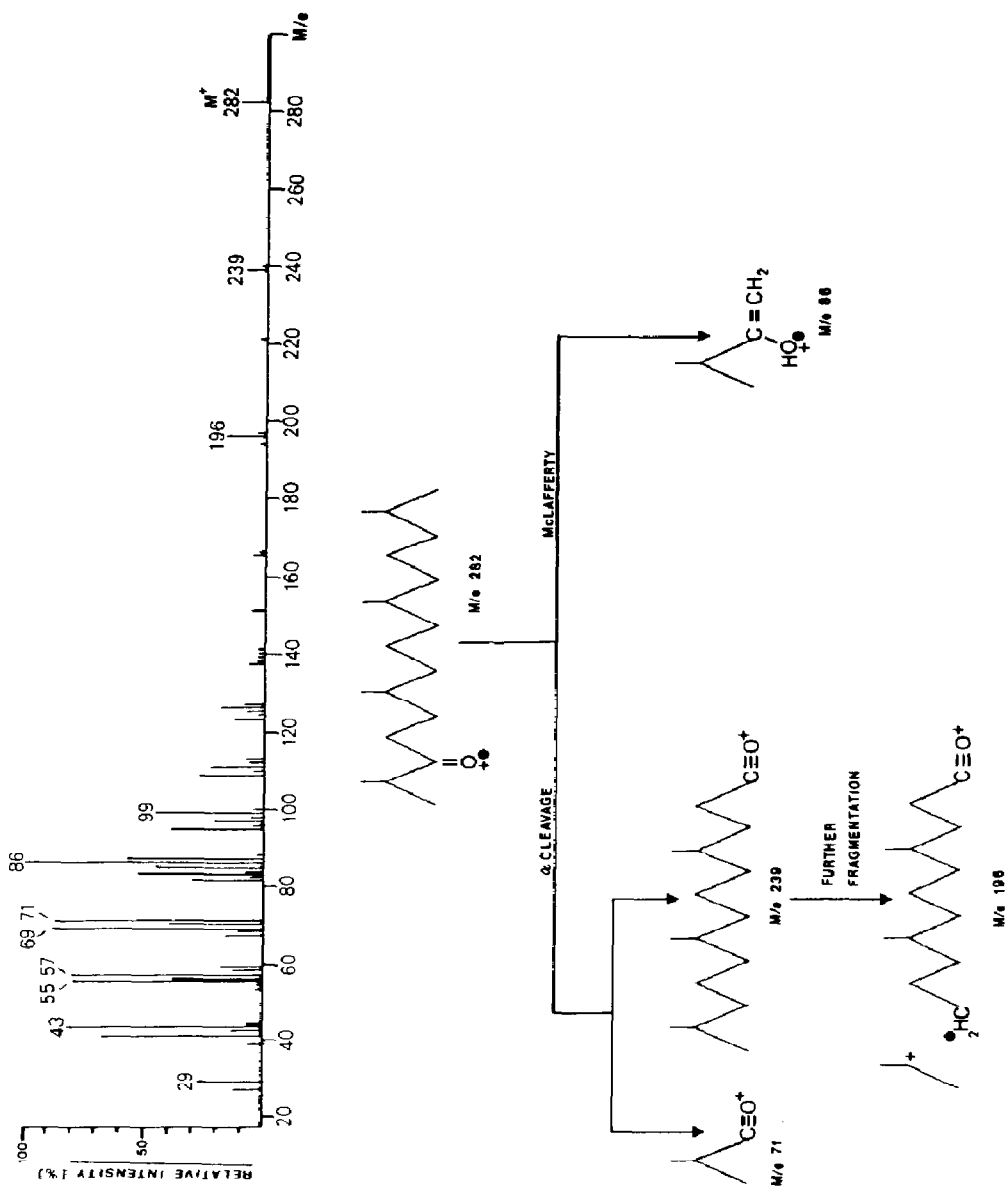Fig. 4. Mass spectrum and characteristic fragmentations of the compound 5.

Fig. 5. Mass spectrum and characteristic fragmentations of the compound **8**.
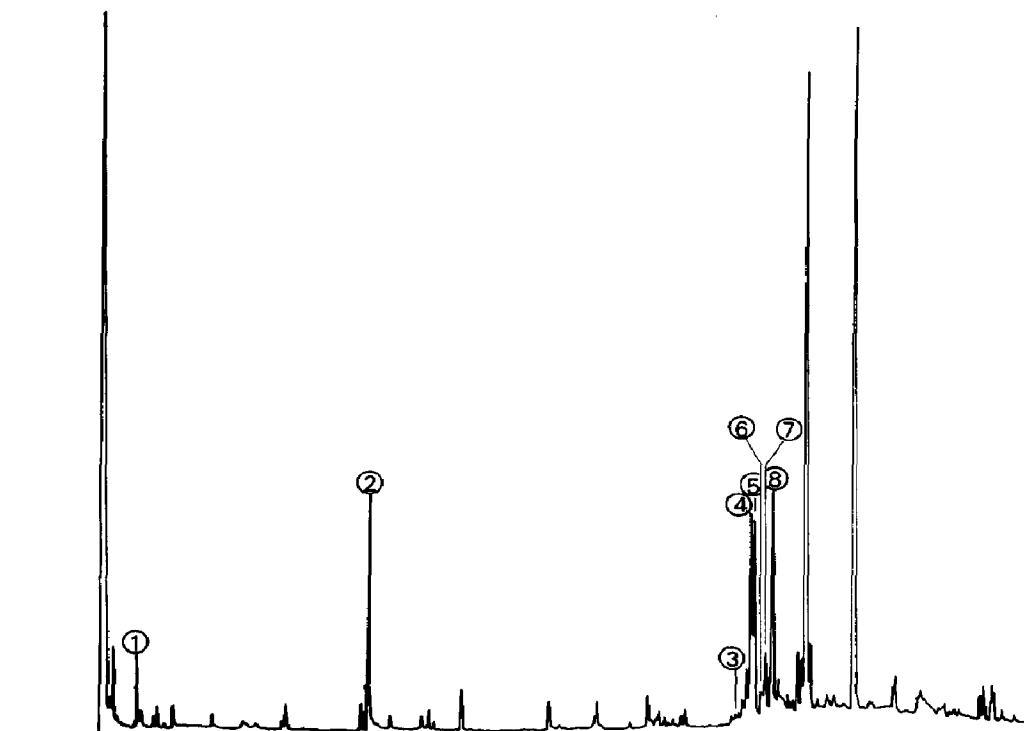
Fig. 6. Gas chromatogram of the chloroform eluate after silylation with hexamethyl-disilazane in hot DMSO.

A comparison of eicosane and pristane photo-oxidation rates indicated that the branched alkanes are effectively photo-oxidized by the sunlight more quickly than the unbranched alkanes (Table 1). These observations agree with the results obtained by Hansen [13] for the irradiation of a Libyan crude oil with a mercury lamp (wavelengths longer than 200 nm).

TABLE 1

Evolution of the ratio pristane/eicosane during sunlight irradiation

	Time (days)			
	0	8	10	15
Pristane/eicosane	0.975	0.93	0.91	0.89

4. Conclusions

In this study we have shown that, in the presence of a photosensitizer (anthraquinone), pristane is degraded abiotically under the influence of sunlight. These reactions lead to the formation of numerous compounds (ketones, tertiary alcohols and alkanes).
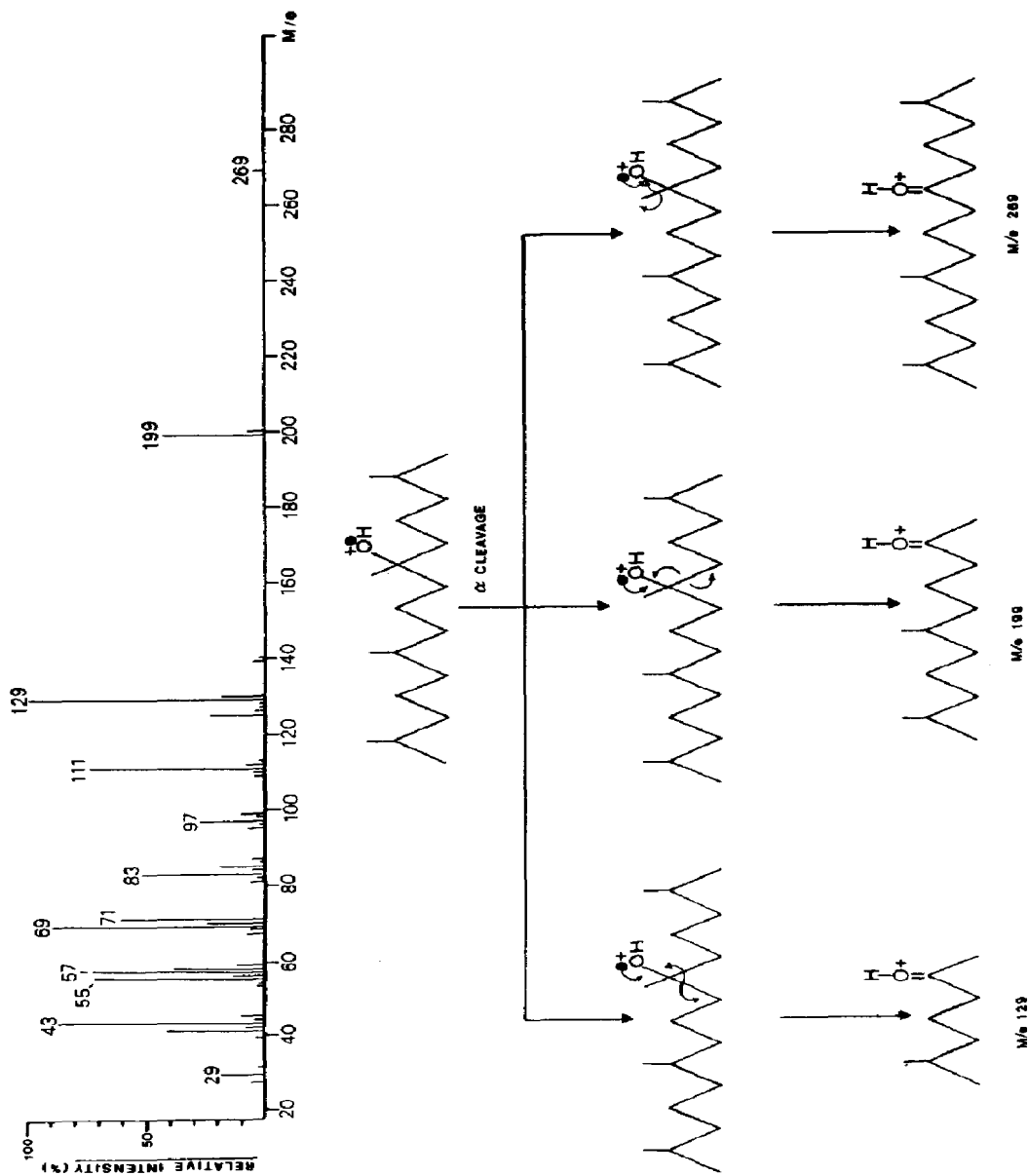
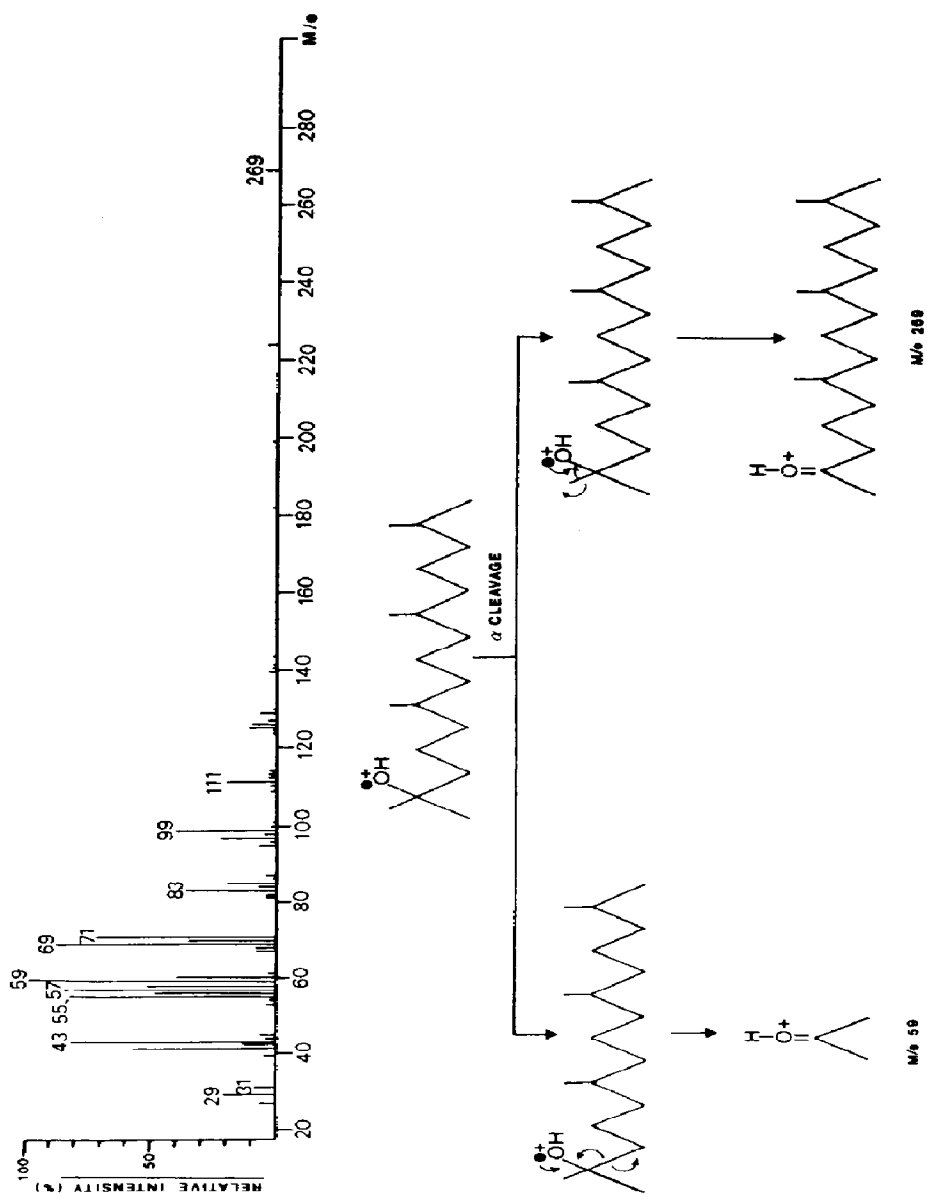Fig. 7. Mass spectrum and characteristic fragmentations of the compound 6.

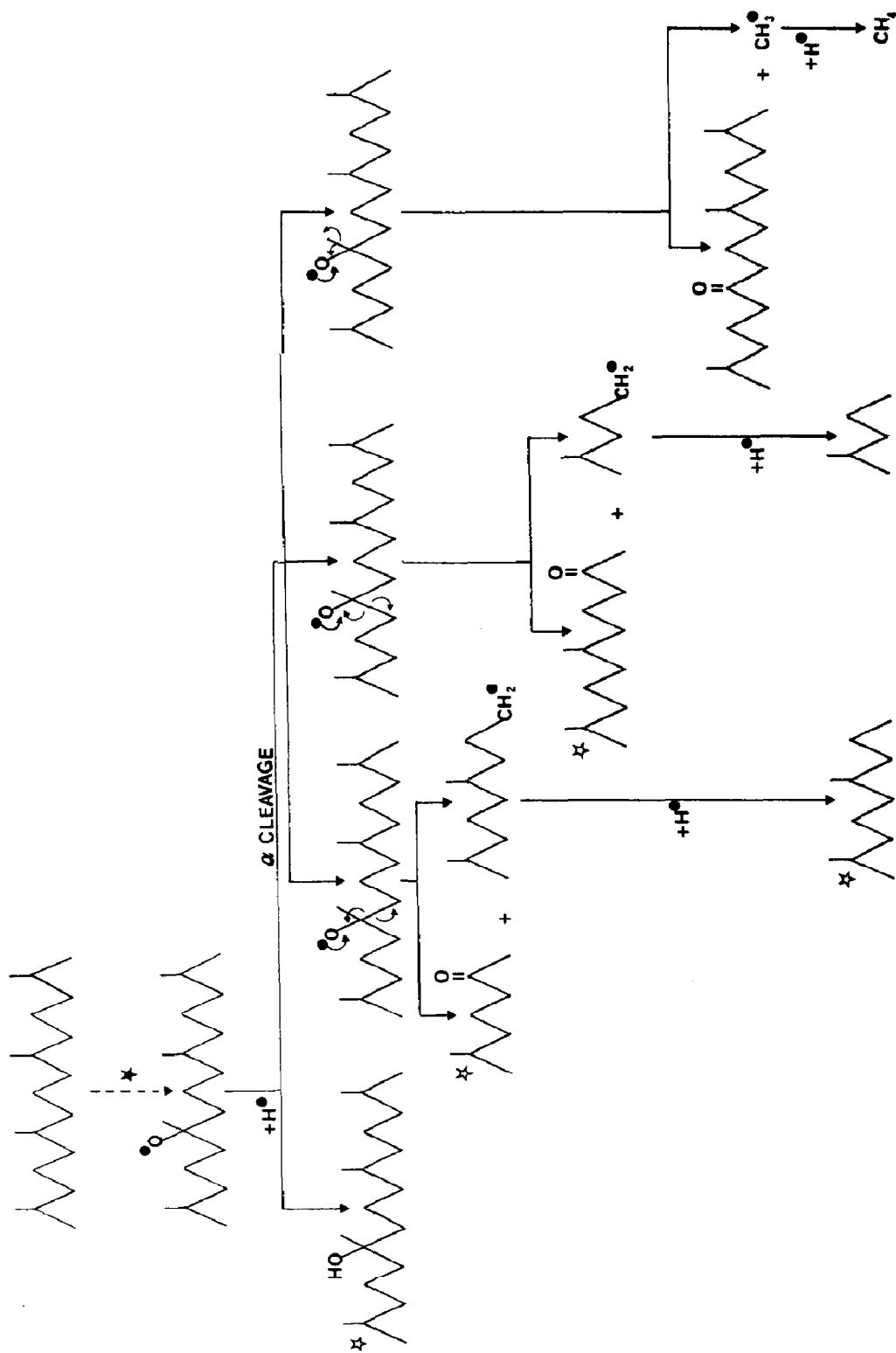Fig. 8. Mass spectrum and characteristic fragmentations of the compound 7.

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Fig. 9. Proposed pathway for the photosensitized oxidation of C(6); ☆, isolated compounds; ★, mechanisms described previously [11, 12].
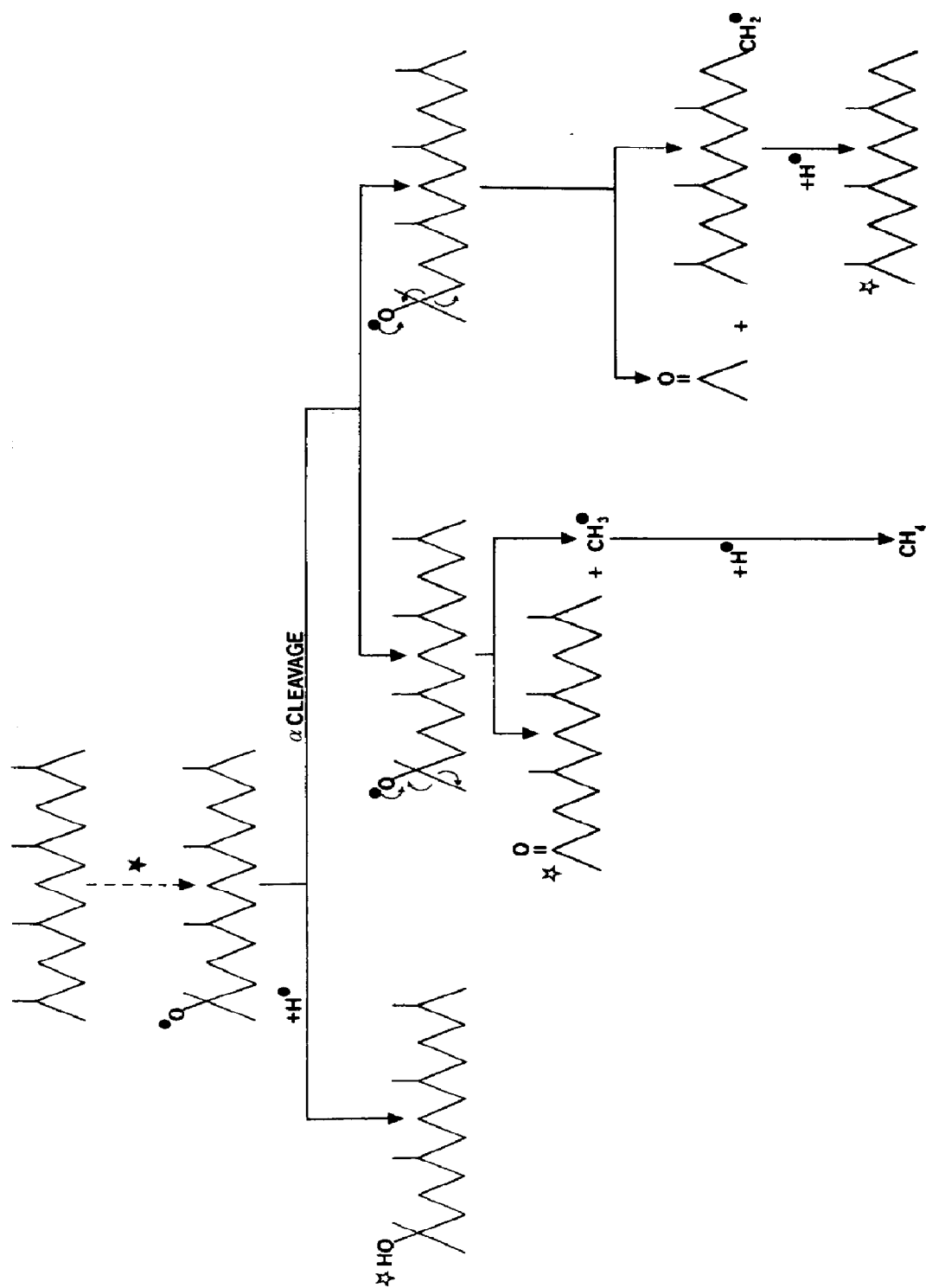
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Fig. 10. Proposed pathway for the photosensitized oxidation of C(2); ☆, isolated compounds; ★, mechanisms described previously [11, 12].
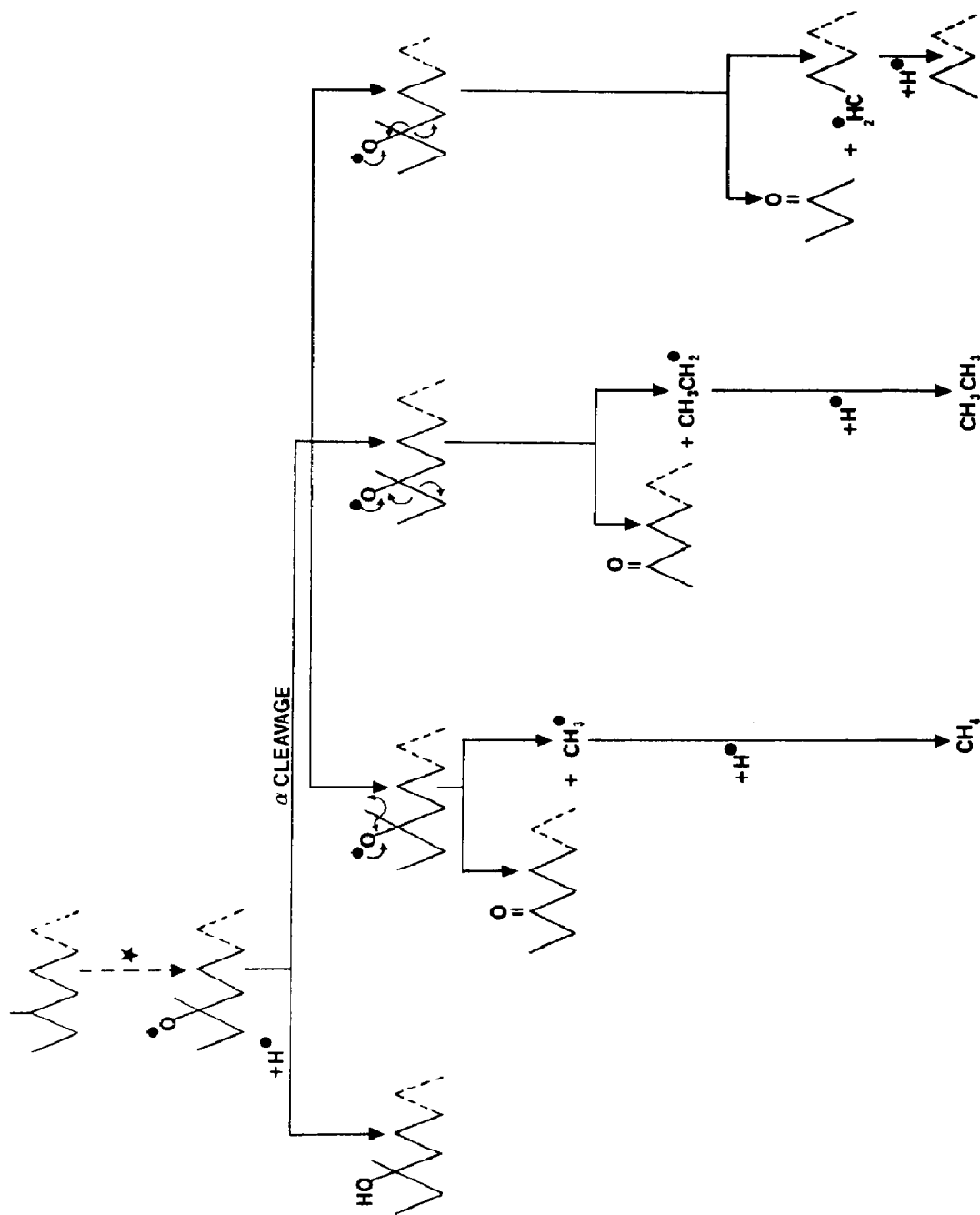
Fig. 11. Proposed pathway for the photosensitized oxidation of tertiary carbons in the case of β-methyl branched alkanes; ★, mechanisms described previously [11, 12].

The elucidation of a photochemical oxidation mechanism for tertiary carbons introduces new factors that must be taken into account by the users of biogeochemical tracers of a branched-alkane type. Indeed, the presence of branching is usually considered as an obstacle to the classical biodegradation reactions (β-oxidation) which, according to the branch position, can be inhibited or prevented (anteiso structures). Those photochemical processes which are particularly important for the tertiary carbons could lead, because of α-cleavage reactions, to an elimination of these branchings. This is particularly interesting in the case of β-branched alkanes; these structures are unanimously considered to be very recalcitrant biologically [3, 14] and could only be used with very special strains [15, 16]. The α cleavage of the alkoxy group formed in the case of these structures (Fig. 11) should lead to the formation of compounds easily assimilable by most bacteria (methyl ketones, ethyl ketones and n-alkanes).

A more precise study of these phenomena is in progress using alkanes branched at the anteiso position at both ends.

References

1   E. J. McKenna and R. E. Kallio, *Proc. Natl. Acad. Sci. U.S.A.*, *68* (1971) 1552.
2   M. P. Pirnik, R. M. Atlas and R. Bartha, *J. Bacteriol.*, *119* (1974) 868.
3   T. L. Schaeffer, S. G. Cantwell, J. L. Brown, D. S. Watt and R. R. Fall, *Appl. Environ. Microbiol.*, *38* (1979) 742.
4   M. Ehrhardt and G. Petrick, *Mar. Chem.*, *16* (1985) 227.
5   M. Ehrhardt, F. Bouchertall and H. P. Hopf, *Mar. Chem.*, *11* (1982) 449.
6   R. G. Zepp, P. F. Schlotzhauer, M. S. Simmons, G. C. Miller, G. L. Baughman and N. L. Wolfe, *Fresenius Z. Anal. Chem.*, *319* (1984) 119.
7   J.- F. Rontani, J.- C. Bertrand, F. Blanc and G. Giusti, *Mar. Chem.*, *18* (1986) 9.
8   J.- F. Rontani and G. Giusti, *Mar. Chem.*, *20* (1986) 197.
9   M. Blumer, M. M. Mullin and D. M. Thomas, *Science*, *140* (1963) 974.
10 S. Friedman and M. L. Kaufman, *Anal. Chem.*, *38* (1966) 144.
11 A. E. Klein and N. Pilpel, *J. Chem. Soc.*, *Faraday Trans. I*, *69* (1973) 1729.
12 R. G. Zika, in E. K. Duursma and R. Dawson (eds.), *Marine Organic Chemistry*, Elsevier, Amsterdam, 1981, p. 299.
13 H. P. Hansen, *Mar. Chem.*, *3* (1975) 183.
14 M. Alexander, *Biotechnol. Bioeng.*, *15* (1973) 611.
15 R. R. Fall, J. L. Brown and T. L. Schaeffer, *Appl. Environ. Microbiol.*, *38* (1979) 715.
16 W. Seuber and E. Fass, *Biochem. Z.*, *341* (1964) 35.