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PHOTOSENSITIZED CONJUGATION OF METHYL 9,12-OCTADECADIENOATE

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Summary

The conjugation of methyl 9,12-octadecadienoate (DH) is a reaction of industrial interest. It has been photochemically performed with iodine as photosensitizer ($\lambda = 520$ nm). The reaction is a radical chain process which is inhibited by galvinoxyl, the overall quantum yield decreasing from 1.9 to 1.3 with the irradiation time. The rate is given by the empirical expression k $[i]^{0.56}[DH]^{1.22}[I_2]^{0.40}$ where i is the light intensity. The reaction leads to a mixture of methyl 9,11-octadecadienoate and methyl 10,12-octadecadienoate with $E,E:Z,E:Z,Z$ in the molar ratio of 0.72:0.26:0.02 in 80% yield.

This study illustrates the possibility of applying solar radiation to an industrial process.

1. Introduction

Photosensitized reactions are those where radiation is not directly absorbed by the substrate which reacts, but is absorbed by an external compound.

In many cases, photosensitization has a synthetic potential as reviewed by Albini and Bettinetti [1], Gollnick [2] and Kavarnos and Turro [3], but the best system is obtained when light transforms the photosensitizer into a paramagnetic species able to induce a thermal chain reaction. This transient intermediate then does its work without further need of photons to carry on the reaction. In the situation where termination reactions are not efficient, the overall quantum yield is greater than unity.

Several examples of such chain reactions induced by electron transfer have been recognized in electrochemistry [3 - 7] and photochemistry [8]. Also, it has been known for many years that chain reactions can be induced by the homolysis of an external substance under irradiation, but usually this photoinitiator is consumed.

This paper reports the photoconjugation of methyl 9,12-octadeca-dienoate (methyl linoleate) (DH) catalysed by iodine since the added iodine is homolytically cleaved by visible light but regenerated afterwards. Thus, it is an example of a reaction where the photoinitiator is not consumed and where one absorbed photon leads to more than one converted molecule.

The conjugation of DH is a reaction of industrial interest since cyclo-addition reactions can occur from the conjugated dienes, leading either to cyclic dimers [9] or to adducts bearing a reactive function in the hydro-phobic chain.

2. Results

The fatty acid portion extracted from grape-seed oil contains 72% of Z,Z-9,12-octadecadienoic acid. Its methyl ester, irradiated (λ = 400 - 800 nm) in carbon disulphide at 20 °C with about 0.75 wt.% iodine as photo-initiator, leads to a mixture of methyl 9,11-octadecadienoate and methyl 10,12-octadecadienoate in about 80% overall yield, as summarized in Scheme 1. The same molar ratio of stereoisomers is found whatever the con-ditions E,E:Z,E:Z,Z in the ratio 0.72:0.26:0.02 [10].
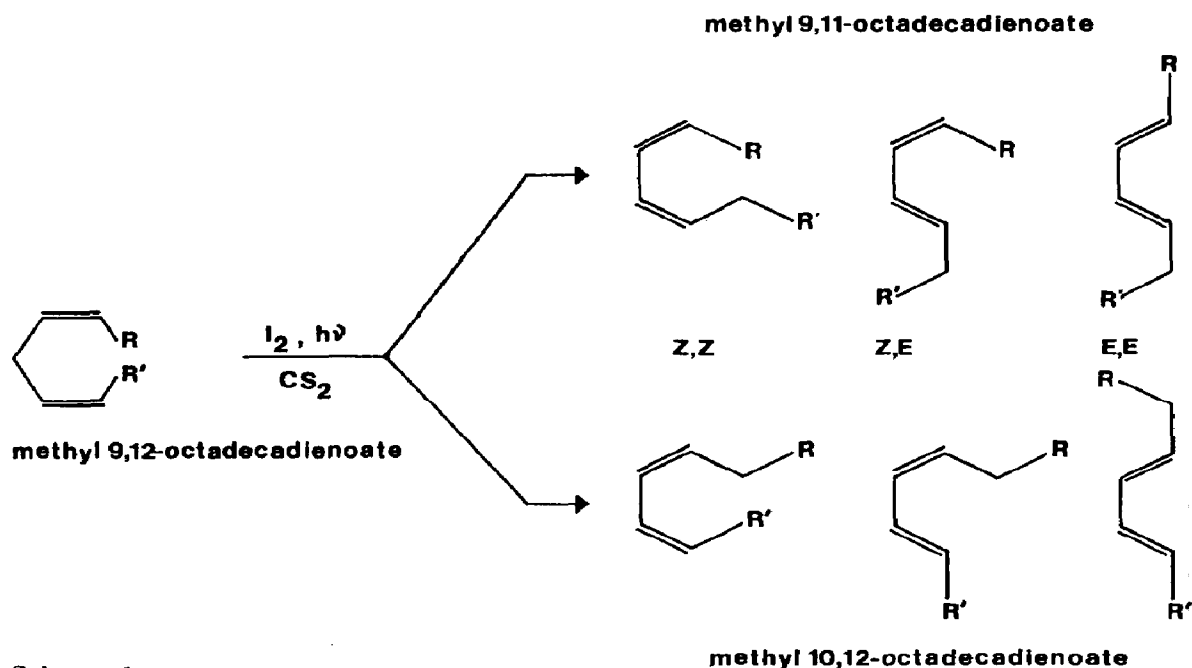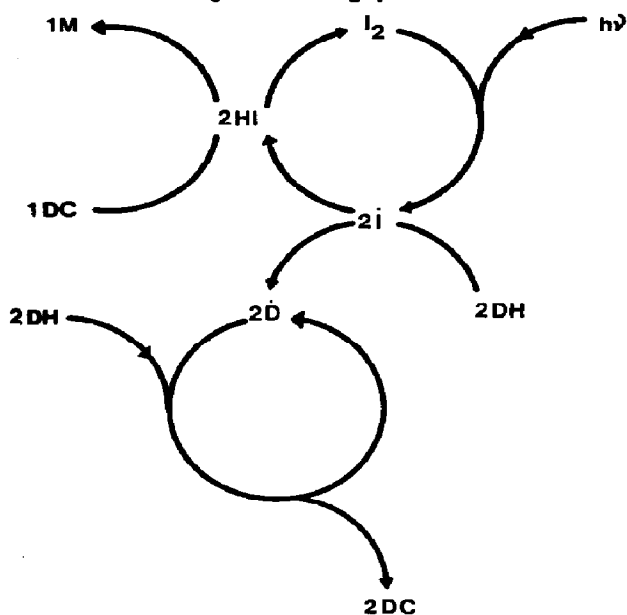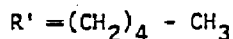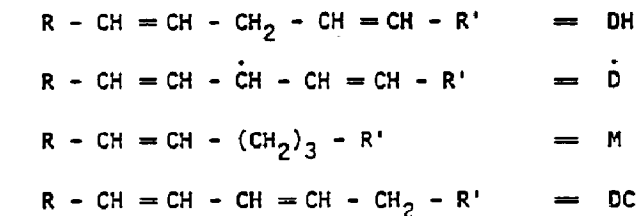

Scheme 1.

These results agree with those of Chipault and Hawkins [11] who showed that conjugated Z,E-methyl octadecadienoate photoisomerized into the E,E form when iodine was added under visible irradiation.

Some minor products are formed, *i.e.* 0.5% methyl octadecenoate, 0.5% methyl octadecatrienoate and 0.5% dimers.

The overall quantum yield for the disappearance of DH is greater than unity.

2.1. Mechanism

The reaction is a chain process whose initiation step is the homolysis of iodine by light and the abstraction by an iodine radical of the H-11 of the DH, followed by HI and D· formation (Scheme 2). The chain vector is the C-11 radical D· whose electron is delocalized on the next two π orbitals. The following step is the abstraction of an H-11 atom (S_H 2) on a second DH molecule with the formation of a conjugated π system, *i.e.* methyl 9,11-octadecadienoate or methyl 10,12-octadecadienoate.

R – CH = CH – CH$_2$ – CH = CH – R'   ═ DH

R – CH = CH – ĊH – CH = CH – R'   ═ Ḋ

R – CH = CH – (CH$_2$)$_3$ – R'   ═ M

R – CH = CH – CH = CH – CH$_2$ – R'   ═ DC

R' = (CH$_2$)$_4$ – CH$_3$

R = CH$_3$OOC – (CH$_2$)$_7$

Scheme 2.

The propagating step is the recycling of iodine by reaction of HI with a conjugated ester. The reaction is then photocatalytic with respect to the photons consumed.

2.2. Overall quantum yield

An overall quantum yield Φ_0 value of greater than unity (Table 1) is proof of the chain mechanism.

Moreover, Φ_0 decreases with irradiation time. By extrapolating to zero irradiation time, $\Phi_0 = 1.9$. For a reaction on a preparative scale, our results suggest that $\Phi_0 = 1.3$ for a high conversion process. To minimize quantitative problems connected with self-inhibition, the reactions carried out to determine the quantum yield variation with reaction parameters and the inhibitory effect of galvinoxyl were performed at a low conversion ratio (about 12%).

TABLE 1

Variation in the substrate consumption and overall quantum yield with irradiation time

Irradiation time[a] (min)	Consumption of the substrate[b] (%)	Φ_0 (overall)
8	12.15	1.71
15	35.00	1.86
30	42.50	1.57
50	48.40	1.58
70	53.00	1.34

[a]XBO 1600 W xenon lamp, water filter.
[b]Substrate, DH (0.25 mol l^{-1}); photosensitizer, iodine (4 × 10^{-3} mol l^{-1}); solvent, carbon disulphide.

2.3. Reaction rate variations as a function of light intensity and concentration of the reactants

The dependence of the reaction rate on light intensity and reactant concentration has been treated by several researchers [12, 13]. The variation in the rate with these parameters provides further information on the nature of the termination step [14 - 16].

In the case of a unimolecularly photoinduced chain reaction, it is assumed by Huyser [13] that the reaction rate is determined by the concentration of the initiator and by the rate of its decomposition which depends on the intensity of the incident light.

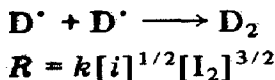In our case the following type of termination reactions (with the corresponding rate laws) may occur.
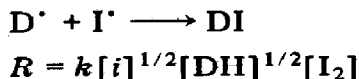
(i) The coupling of two iodine radicals

$$I^{\cdot} + I^{\cdot} \longrightarrow I_2$$
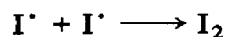
$$R = k[i]^{1/2}[DH][I_2]^{1/2}$$

where i is the intensity of the incident light, [DH] the substrate concentration and [I_2] the iodine concentration.

(ii) The coupling of two $D\cdot$ radicals

$$D\cdot + D\cdot \longrightarrow D_2$$

$$R = k[i]^{1/2}[I_2]^{3/2}$$

(iii) The cross-coupling between $D\cdot$ and $I\cdot$

$$D\cdot + I\cdot \longrightarrow DI$$

$$R = k[i]^{1/2}[DH]^{1/2}[I_2]$$

We were able to describe the rate of reaction by the following empirical equation [17]:

$$-\frac{dc}{dt} = k[i]^{0.56}[DH]^{1.22}[I_2]^{0.40}$$

Therefore the experimental values we obtained suggest that the main termination step is the coupling of two iodine radicals. This agrees with the very low yield of dimer formed (about 0.5%) and with the absence of iodo-octadecadienoate in the reaction products.

2.4. Inhibition of the reaction by galvinoxyl

The use of galvinoxyl to diagnose a radical mechanism has been described previously [18]. In our experiment it decreases the reaction rate (and Φ) when the molar ratio of galvinoxyl to DH is greater than 4/250 (Fig. 1).

Moreover, if under the same experimental conditions the galvinoxyl is added (galvinoxyl:DH in the ratio 4:250) to the medium 30 min after the beginning of the reaction, it stops the reaction completely.

The inhibition of the reaction is complete when the molar ratio of galvinoxyl to iodine is unity. Thus, we propose that the initiation of the reaction is due to iodine radical formation under irradiation. When half of these atoms are trapped by galvinoxyl the chain is no longer propagated.

2.5. Iodine recycling from HI

This transformation is the propagation step of the chain reaction (see Scheme 2). We propose that the HI which is generated into the chain leads to I_2 and to isomeric methyl octadecenoates (M) corresponding to the transformation of methyl 9,11-octadecadienoate and methyl 10,12-octadecadienoate.

$$R-CH=CH-CH=CH-R' + 2HI \longrightarrow I_2 + R-(CH_2)_2-CH=CH-R'$$
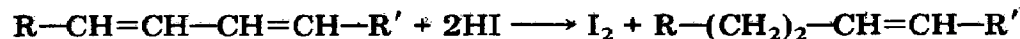
Indeed, we found isomeric methyl octadecenoates as byproducts of the photoconjugation reaction (see Section 2).

We checked separately that, also in a non-degassed solution, the reaction between HI and the methyl octadecadienoates (conjugated or unconjugated) was responsible for I_2 regeneration.

A solution of HI in carbon disulphide (0.06 mol l^{-1}) slowly produced I_2 in the dark. In 1 h there was found to be a 12% transformation. The addition
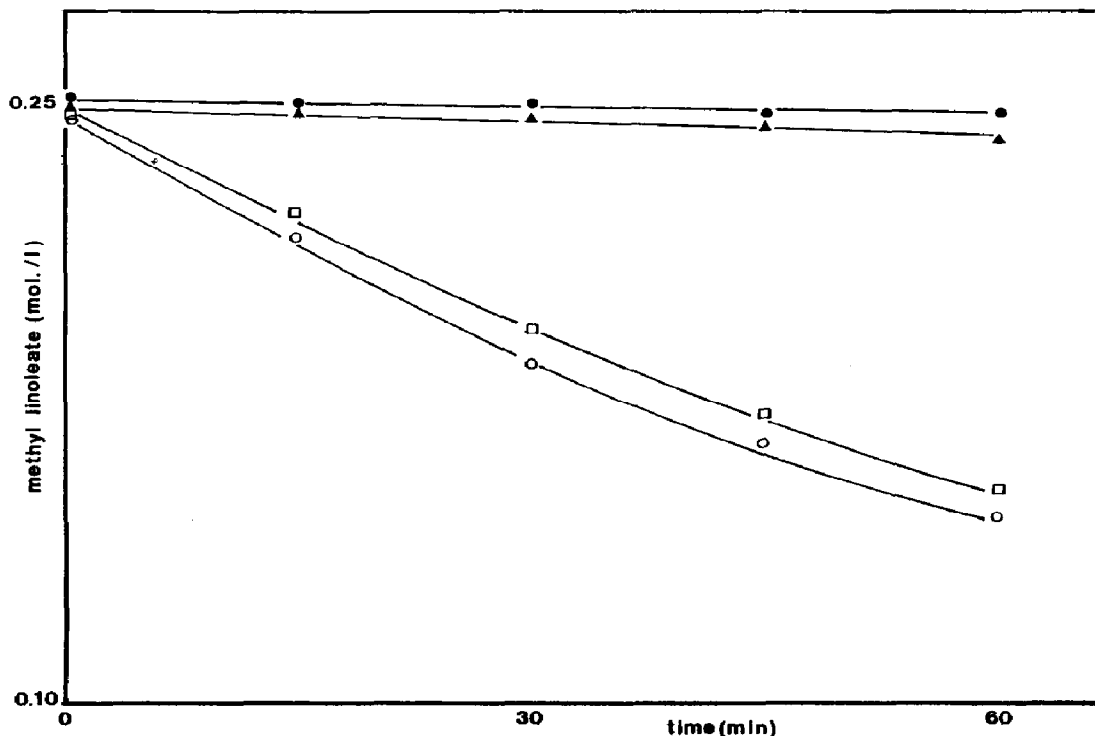
Fig. 1. Decrease in the reaction rate with increasing concentration of the galvinoxyl{
O, zero; □, 1×10^{-3} mol l^{-1}; ▲, 4×10^{-3} mol l^{-1}; ●, 8×10^{-3} mol l^{-1}.

of a mixture of conjugated esters (0.03 mol l^{-1}) increased the rate of I_2 formation (Fig. 2): there was an HI transformation of 91% in 1 h. The same result was obtained with the addition of the starting unconjugated ester (0.03 mol l^{-1}): there was an HI transformation of 71% in 1 h. In both cases isomeric methyl octadecenoates were identified as byproducts in 3% yield.

Moreover, the I_2 formation from the thermal reaction of HI with the conjugated or unconjugated dienes was proposed earlier by Kubota and Hashimoto [19].

3. Conclusion

This study of the iodine-photoinduced conjugation of methyl 9,12-octadecadienoate illustrates the possibility of applying a photochemical process using solar radiation. Three facts favour such a possibility.

(i) The efficient radiation is in the visible range (520 nm).

(ii) The photoinitiator is added in a non-stoichiometric amount (1/250) and is not consumed at all after 250 cycles.

(iii) The reaction is a radical chain. It does not consume one photon per transformed molecule. It would be interesting to determine this energy balance.
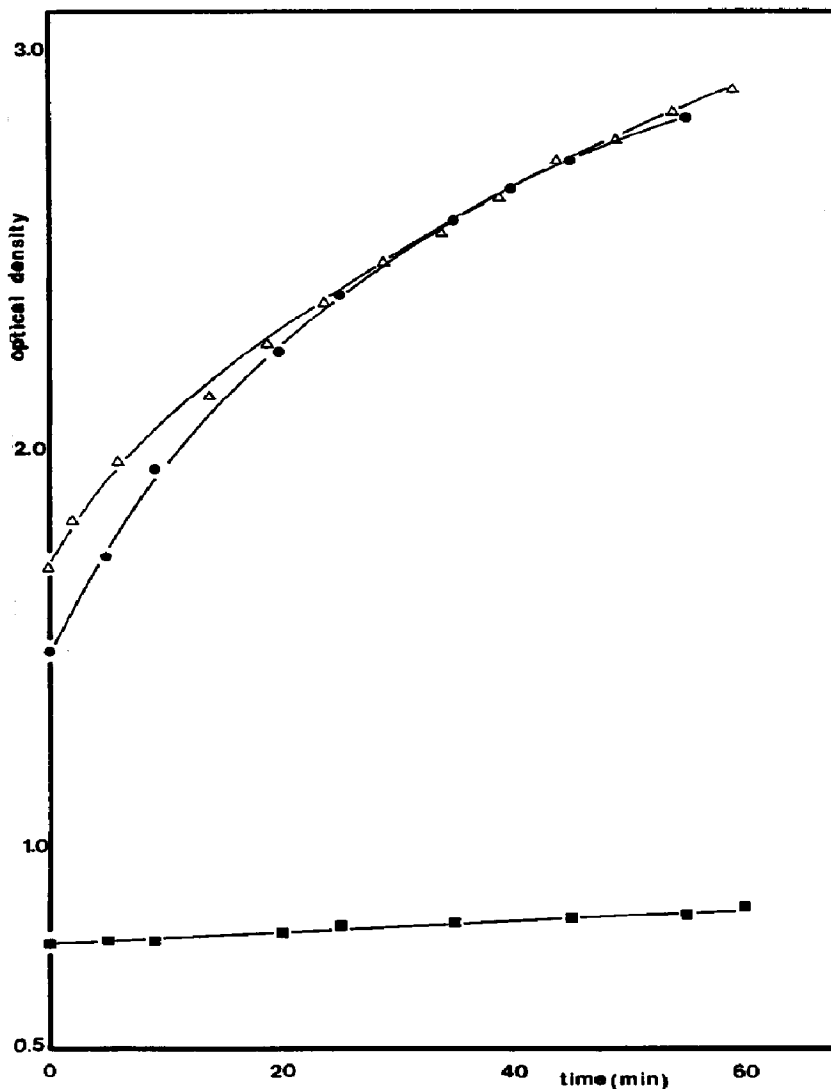
Fig. 2. Iodine formation from HI and dienic fatty acid esters shown by the optical density at 520 nm in CS_2 as solvent: ■, HI (0.06 mol l^{-1}); ●, HI (0.06 mol l^{-1}) + conjugated esters (0.03 mol l^{-1}); △, HI (0.06 mol l^{-1}) + unconjugated ester (0.03 mol l^{-1}).

Furthermore, few secondary products are formed.

Experiments already performed under solar irradiation in a specially designed reactor confirmed these assumptions.

4. Experimental details

4.1. General methods

Analyses using gas chromatography (GC) were performed on a Girdel G 300 chromatograph fitted with an integrator (Spectra Physics SP 4100). A

capillary W COT column (25 m × 0.28 mm) coated with Carbowax 20M was used at 180 °C with helium as vector gas. The samples were prepared in methyl-*t*-butyl ether as solvent (2 - 5 wt.%).

The UV spectra were recorded on a Uvikron 810 (Kontron Analytical) spectrometer with hexane (Merck, spectrosol) or carbon disulphide as solvent.

The IR spectra were recorded on a Beckman Acculab IV spectrometer. Samples were dissolved in carbon tetrachloride or in carbon disulphide (1 wt.% solution).

4.2. Materials

Carbon disulphide (Carlo Erba), hexane (SDS), methanol (SDS), iodine (Merck) and hydrogen iodide (Merck) were commercial samples and were used without further purification.

The 9,12-octadecadienoic acid (linoleic acid) [20] was prepared according to the following procedure. NaOH (258 g) in distilled water (516 ml) was added slowly with stirring to a mixture of refined grape-seed oil (1200 g) and 96% ethanol (1200 ml). The mixture became homogeneous on heating. After refluxing for 1 h it was allowed to stand for 1 h with occasional stirring to avoid solidification. Then distilled water (1200 ml) and 6 N sulphuric acid (2000 ml) were added keeping the solution below 50 °C.

The solution was extracted with ethyl ether (2000 ml), and the organic layer was washed with water until the water remained at pH 7 and dried over sodium sulphate.

After removing the ethyl ether, the fatty acid residue was mixed in a 6 l flask with urea (1019 g) dissolved in anhydrous methanol (3150 ml). The mixture was refluxed until homogeneous and was allowed to stand at room temperature overnight. The solution was filtered and the filtrate was diluted with acidic water. Pure 9,12-octadecadienoic acid was recovered by extraction with hexane, washing and drying: its purity found by GC was about 98%.

The following procedure was used for the preparation of DH. 9,12-Octadecadienoic acid (500 g) was introduced into a 2 l flask with anhydrous HCl–methanol (500 ml) (prepared by adding acetyl chloride to cold methanol). The mixture was refluxed for 1.5 h. After cooling, the two phases were separated, and the methanolic layer was diluted with water and extracted with hexane. The hexane portion was combined with the ester portion, and both were washed first with sodium carbonate and then with water, the emulsion having been broken by adding ethanol. After drying (over sodium sulphate) and removing hexane by vacuum distillation, DH was recovered pure (98% by GC).

4.3. A typical photochemical experiment

The lamp was switched on 20 min before the beginning of the reaction to attain a constant intensity. Figure 3 shows the experimental set-up.
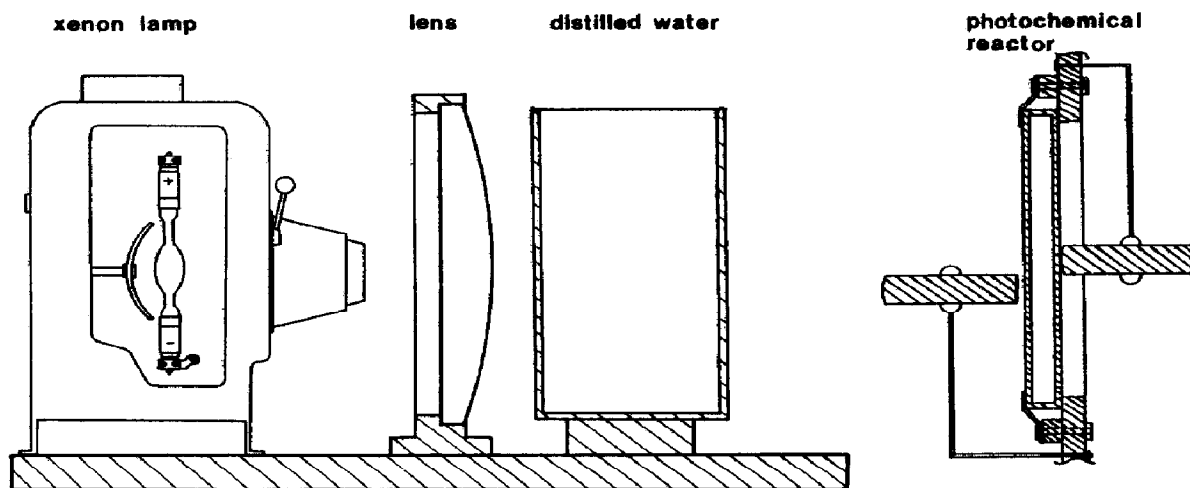
xenon lamp   lens   distilled water   photochemical reactor

Fig. 3. The experimental set-up for the photochemical reaction.

The reactor was degassed with nitrogen for 15 min. The iodine ((1×10^{-3}) - (4×10^{-3}) mol l^{-1}) was dissolved in carbon disulphide (500 ml) in the dark, and DH (0.25 - 0.5 mol l^{-1}) was added. The mixture was introduced into the reactor, degassed with nitrogen, closed with a rubber septum and irradiated for 1.5 h. Samples (2 ml) were withdrawn through the septum with a syringe every 15 min. They were treated in a flask as follows. Iodine was removed by adding zinc powder (300 mg). The flask was shaken for 1 min and the organic layer was collected. This treatment was repeated if necessary. The carbon disulphide was removed by a stream of nitrogen. The residue was dissolved in methyl-t-butyl ether and analysed by GC.

4.4. Identification of the reaction products

Identification was performed either by GC using standards or by gas chromatography—mass spectrometry (GC–MS) after converting the products into the trimethylsilyl ether derivatives [21].

4.5. Photochemical process

For the photochemical process [22] a lamp (Osram XBO 1600 W xenon lamp) whose IR radiation was removed by a 0.18 m water filter was used. The system was set up with a convergent lens at 0.32 m and a plane reactor at 2.7 m from the lamp.

The results with variable intensities were obtained by adding a rheostat acting on the lamp source (600 - 1200 W m^{-2}). Quantitative experiments were performed in two plane reactors of diameter 200 mm and thickness 15.5 or 25 mm whose faces were perpendicular to the light beam.

4.5.1. Light intensity measurements

The optical system was fitted with two cells (LCP Solarmeter) placed before and behind the reactor. The incident and transferred energies were recorded for the whole reaction time on a J. J. Instruments CR 600 recorder.

4.5.2. Quantum yield measurements

The quantum yield measurements were performed by adding a Jobin Yvon diffracting grating (1200 lines mm^{-1}) to the previously described optical system. The selected spectral wavelength was 520 ± 10 nm. The reaction was carried out in a spectrophotometer cell (10 mm path) and the absorbed light was measured with the LCP Solarmeters.

The conditions were as follows: light intensity, 91 W m^{-2}; carbon disulphide 5 ml; iodine concentration, 4×10^{-3} mol l^{-1}; DH concentration, 0.25 mol l^{-1}; irradiation time, 8 min; maximum substrate consumption, 12.5%.

Acknowledgment

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