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PHOTODIMERIZATION OF MALEIC ANHYDRIDE IN CARBON TETRACHLORIDE

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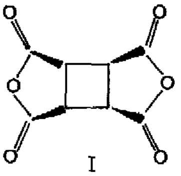
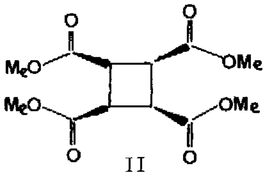
It has been known for a long time that maleic anhydride (MA) photodimerises in the solid state (1),(2) According to GRIFFIN et al the *trans*-dimer (I) is obtained


I


II

This dimerization has not been studied much in solution for there results either a reaction with the solvent (acetone, tetrahydrofuran, benzene, olefin) or a photopolymerization, induced or not, leading to oligomers (in dioxane for example (3)) To our knowledge the only dimerization observed in solution has been obtained in 1,4 dioxane (3),(4) I.NAGAHIRO et al have obtained a mixture of oligomers containing no more than about 3% of *trans*-dimer According to G O. SCHENCK (4) on the other hand, the quantum yield of benzophenone sensitised dimerization in this solvent is equal to 0 26 Among all the solvents studied by us (n heptane, cyclohexane, dodecane, benzene, dioxane, trichloro-ethylene, carbon tetrachloride) only CCl_4 enabled us to observe a quantitative dimerization

In CCl_4 the UV spectrum of the MA is fairly similar to the one observed in non complexing solvents (n heptane, cyclohexane) The $\pi\pi^*$ transition is located principally in the absorption zone of the solvent In the $n\pi^*$ band the coefficient of molar extinction ε varies approximatively from 20 to 10 l mole^{-1} cm^{-1} between 280 and 320 nm

The principal IR bands are located at 3110 cm^{-1} (ethylenic C-H), 1853, 1794, 1783

cm^{-1} (anhydride function), 885 cm^{-1} and 697 cm^{-1} The bands at 1794 and 1783 cm^{-1} have roughly the same ε value (1300 ± 50 l $mole^{-1}$ cm^{-1}) The band at 1794 cm^{-1} can be explained by a Fermi resonance (5) The latter is weaker in CCl_4 than in cyclohexane and heptane, but stronger than in complex-forming solvents (benzene, chloroform, butanol, dioxane)

Degassed solutions of MA in CCl_4 were irradiated at 296, 313 and 334 nm with a high pressure mercury vapour lamp fitted with a monochromator. A white precipitate appears which generally remains suspended The quantum yield for the disappearance of the MA is in the order of 0 2-0 3 at 296 and 313 nm, and in the order of 0 5-0 6 at 334 nm At 313 nm this quantum yield is independent upon the concentration if the latter exceeds $2x10^{-3}M$ This photolysis product can also be obtained by solar irradiation in a pyrex reactor This reaction cannot be sensitised either by benzophenone, by thioxanthone or by anthraquinone.

An elemental analysis carried out at the microanalysis laboratory of the CNRS gave the following results C 47 01%, H 2 60%, O 48 98%, Cl 1 31-1 20% This product does not therefore result from a reaction with the solvent Suspended in CCl_4 it possesses the following IR bands 3011 cm^{-1} (saturated C-H), 1860-1850, 1780 cm^{-1} (anhydride function), 962 cm^{-1}, 933 cm^{-1}, 900 cm^{-1} In solution in dimethylformamide (DMF) the bands of the anhydride function are located at 1858 and 1792 cm^{-1} As the product is slightly soluble in non polar solvents we esterified it with methanol in order to measure the molecular weight, the dipole moment and the melting point of the tetraester. We obtained M= 270 ± 40 (the molecular weight of the tetraester of the dimer is 288), μ = 3,4 ± 0,2 D and F= 144-145°C. The melting point is in excellent agreement with the value given by R.GRIEGEE (6) for the *cis-trans-cis* 1,2,3,4 tetracarbomethoxy-cyclobutane i e the tetraester of the *trans*-dimer (II). The value found for the dipole moment seems to be high for a form of this symetry, but we obtained the same value for the product of photodimerisation in the solid state which is the *trans*-dimer according to G.W. GRIFFIN and al (1). For ascertaining the *trans* structure of the photodimer we carried out dielectric measurements in tetrahydrofuran (THF) solution of the dimer ($10^{-2}M$). The dipole moment of MA is about 3,95 D (7) The *trans*-dimer is non polar. The dipole moment of the *cis*-dimer is certainly higher than 5 D We noticed that our dimer induces a very small decrease of the permittivity of THF (≃ -0 002) though the *cis*-dimer would induce an increase greater than + 0 04.

Our results show that, by direct irradiation of MA dissolved in CCl_4, we obtain quantitatively the *trans*-dimer (I)

The NMR shift of our photo-product dissolved in pyridine does not agree with the value previously reported for the *trans*-dimer obtained in 1,4 dioxane (τ = 5 36 ± 0.02 in this work, τ = 6 4 in NAGAHIRO and al. work (3)) But the photo-dimer we obtained in dioxane has two NMR signals (τ = 5 36 and 6 36 in pyridine, τ = 6 04 and 6.33 in DMSO D6). The former is identical to the shift of the photoproduct obtained in CCl_4 and the latter is attributed to dioxane adsorbed by the precipitate

The MA dissolved in CCl_4 is able to sensitise the phosphorescence of the biacetyl (max at 520 nm) but not its fluorescence It is to be noted that the ' excitation spectrum for an analysis at 520 nm does not correspond with the absorption spectrum of the MA, but reaches a maximum at about 330 nm The phosphorescence of the biacetyl cannot be sensitised either in cyclohexane or in heptane Hence the existence of a (MA CCl_4) complex is revealed, whose triplet level is likely to transfer its energy to the biacetyl (E_t= 55-57 kcal $mole^{-1}$). The structure of the IR band of the carbonyl groups of the MA tends to indicate an interaction between MA and CCl_4 This corroborates the results of D GUILLEN et al (8) who have proved the existence of a complex between tetrahydrofuran and CCl_4 The variations of the apparent quantum yield related to the wavelength can be interpreted by admitting that dimerization implies the excitation of this complex, the free excited MA not leading to the dimer

On the other hand, in CCl_4 as in the other solvents considered (cyclohexane, heptane, acetone (9), benzene (4)), the photolysis of dimethyl maleic anhydride leads to the formation of a *trans*-dimer whose quantum yield is situated between 1 and 2 The esterification of this dimer is much more difficult than for MA dimer

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