PHOTOLYSIS OF DPH IN SOLUTION

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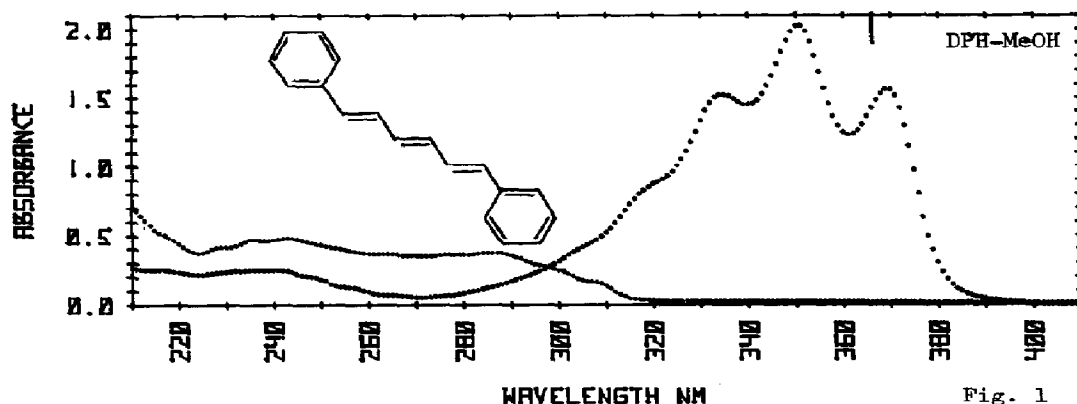Park Forest South, Illinois 60466 (U.S.A.)

Fig. 1

DPH, 1,6-diphenyl-1,3,5-hexatriene (all trans) was found to photolyze in a variety of solvents—methanol, ethanol, propanol, butanol, dioxane, 1,1,1 trifluorethanol, glacial acetic acid and even cyclohexane., Photolysis with 366 nm light, which is toward the long wavelength side of the longest wavelength absorption band, produces final distruction products which absorb at shorter wavelengths (see Fig. 1 for methanol photolysis). Multiple final products are formed (usually 3 or 4) as analyzed using gas chromatography on a concentrated bulk photolysis of 50 mg DPH/1 solvent. If nonpolar solvents are used, the products seem to be isomeric forms of the starting material. If alcohols are used the products seem to relate to a 1 DPH to 1 alcohol adjunct as anlyzed using GC/Mass Spec. Work is still going on to identify the products.
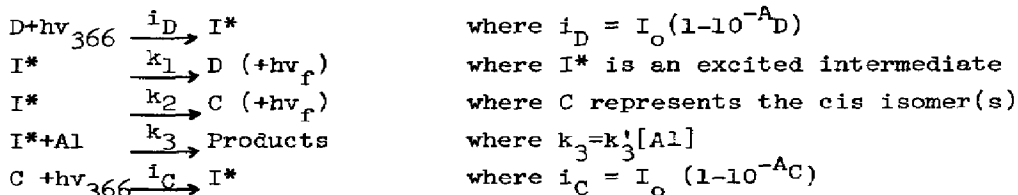
The rate of photolysis varies greatly with solvent; cyclohexane being very slow ($\sim$21 hours) and glacial acetic acid being very fast ($\sim$6 min.) for the photolysis of equal amounts of DPH. Since the starting material can be photolyzed away completely, the transmittance (T) of the 366 nm light can be monitored to give quantitative information on the rate of disappearance of DPH. Typically a 1 cm path length (b) rectangular, quartz cell filled with 3 ml of a 10^{-5}M DPH solution will produce an initial transmittance of $\sim$3% which then increases to 100% at the photolyses proceeds. Also, the blue fluorescence of the DPH solution decays away as the photolysis proceeds. Kinetic studies were usually performed using DPH-methanol solutions as these give photolysis products with absorptions shifted the furthest to the short UV. A simple mechanism which was first tried to fit the transmittance data is given below where i_a=rate of light absorption =$I_0(1-10^{-A})$, A=ϵbc=-log T= Absorbance, I_0 = incident light intensity, ϵ=molar absorptivity of DPH, [D]= molar concentration of D (DPH), k_a=first order rate constant(s) and k_b=k_b'[A1]= pseudo first order rate constant with Al refering to the alcohol solvent.

$$D + h\nu_{366} \xrightarrow{i_a} D^*$$
$$D^* \xrightarrow{k_a} D \ (+h\nu_f)$$
$$D^* + Al \xrightarrow{k_b} Products$$

$$[D^*]_{ss} = \frac{i_a}{k_a + k_b}$$

$$-\frac{dD}{dt} = i_a - k_a[D^*]_{ss}$$

The rate of decay of DPH, with D^* in steady state is then; $-\frac{dD}{dt} = \frac{k_b}{k_a + k_b} i_a$.
Converting to absorbance gives: $\frac{-dA}{dt} = I_o \epsilon b \frac{k_b}{k_a + k_b} (1-10^{-A})$. Integration
and rearrangement yields; $\log (1/T-1) = \log (1/T_o-1) - I_o \epsilon b \frac{k_b}{k_a + k_b} t$. A
plot of $\log (1/T-1)$ vs. time (t) is shown on Fig. 2 for the same solution
that gave Fig. 1. Instead of a single straight line of slope $-I_o \epsilon b \frac{k_b}{k_a + k_b}$
there are two straight line regions. The first very fast decay is
reproducible and appears with all initial DPH concentrations in all sol-
vents and is not an instrumental artifact. This indicates that the ini-
tial trans DPH is decaying to an intermediate absorber and then a photo-
stationary mixture of these are photolyzing away.

Fig. 2
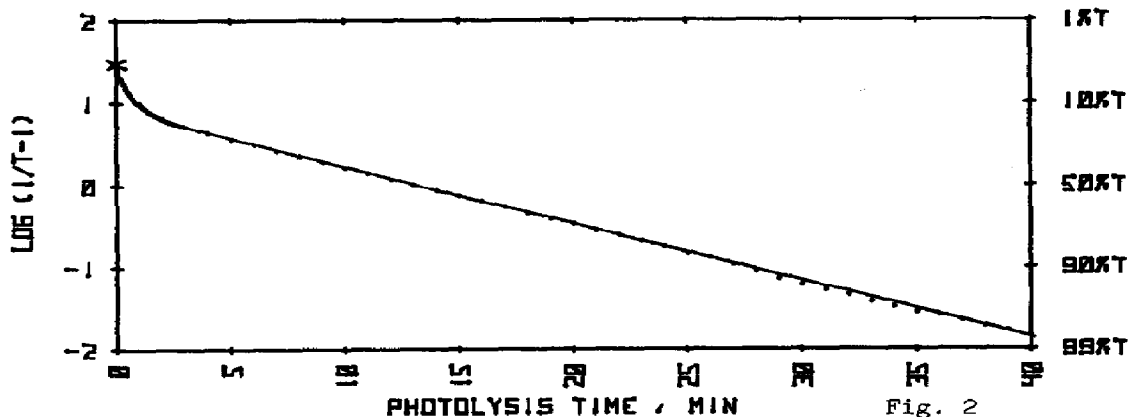
This intermediate appears to be the cis isomer(s) of DPH which have simi-
lar absorption spectra to the trans form.[1] The simplest consistent mech-
anism that can now be written is:

$$D + h\nu_{366} \xrightarrow{i_D} I^* \qquad \text{where } i_D = I_o(1-10^{-A_D})$$
$$I^* \xrightarrow{k_1} D \ (+h\nu_f) \qquad \text{where } I^* \text{ is an excited intermediate}$$
$$I^* \xrightarrow{k_2} C \ (+h\nu_f) \qquad \text{where } C \text{ represents the cis isomer(s)}$$
$$I^* + Al \xrightarrow{k_3} Products \qquad \text{where } k_3 = k_3'[Al]$$
$$C + h\nu_{366} \xrightarrow{i_C} I^* \qquad \text{where } i_C = I_o (1-10^{-A_C})$$

Here $A_D = \epsilon_D b[D]$ and $A_C = \epsilon_C b[C]$ are the absorbances of the trans (D) and
cis(C) molecules. A least squares fit of the data in Fig. 2 with the
expanded mechanism above gives three parameters which, when coupled to an
actimometry to measure I_o, results in the determination of the ratios

$$\frac{k_1}{k_{123}} = 0.736; \quad \frac{k_2}{k_{123}} = 0.250; \quad \frac{k_3}{k_{123}} = 0.0141; \text{and } R(366) = \frac{\epsilon_c(366)}{\epsilon_D(366)} = 0.605$$

where $k_{123} = k_1 + k_2 + k_3$.

To show that the cis isomer(s) is responsible for the curve in Fig. 2, the photolysis of the solution, which gave Fig. 1 & 2, was also stopped at various intervals and UV scans were made of the solution as it progressed from DPH to final products. Thus by coupling the results from the 366 nm transmittance data to a wavelength scan it was possible to extract $R(\lambda)$ values at wavelengths other than 366 nm. This resulted in the production of absorption spectra of the cis intermediate(s) as a function of time. These were normalized at 347 nm (λmax) and were found to agree with each other. The average of these spectra is given on Fig. 3 and is marked by arrows. Also shown is the normalized absorption spectrum (λmax=336nm) of 1-mono-cis DPH in hexane as determined by Zechmeister.[1]
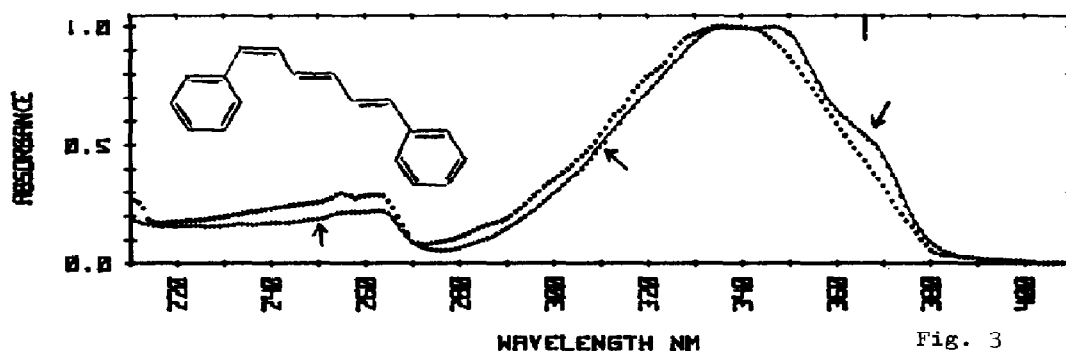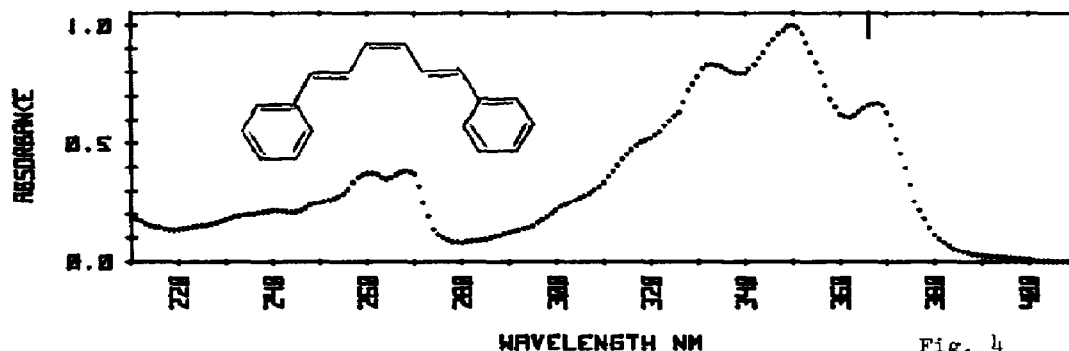

Fig. 3

Fig. 4

Although close, a better fit of our experimental curve can be obtained if we "mix" some 3-mono-cis spectrum in with the 1-mono-cis spectrum. Fig. 4 shows the normalized absorption spectrum (λmax=350nm) of 3-mono-cis DPH.[1] With 14% 3-mono-cis DPH, the best fit is obtained for the long wavelength side of our experimental curve. This, of course, assumes that the spectra do not shift in wavelength with changing solvent—hexane vs. methanol.

Our study shows that appreciable photochemistry occurs during the primary processes of excited DPH and that the anomolies in fluorescence decay time and quantum yield[2] are probably related effects. Studies to further test our mechanism are in progress.

References:
1. K. Lunde and L. Zechmeister. Journal of the American Chemical Society, 76, 2308, (1954)
2. E. D. Cehelnik, R. B. Cundall, J. R. Lockwood, and T. F. Palmer. Journal of Physical Chemistry, 79, 1369, (1975)