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# OXETANE FORMATION FROM EXCITED STATE OLEFIN AND GROUND STATE KETONE

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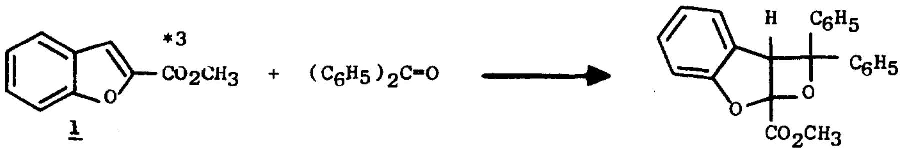
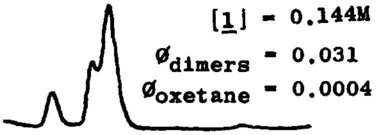
Photochemical oxetane formation is a widely reported reaction.[1,2] In all these reports there are only two examples of oxetane formation from ground state ketone and excited state olefin.[2] A report of oxetane formation from excited state dimethylbutadiene and ground state benzophenone[3a] has recently been shown to be incorrect by Barltrop and Carless.[3b] In the work of Albone[2a] there are ambiguities as to the multiplicity of the excited state involved in the reaction. The conclusions in the paper by Nozaki, et al.,[2b] while probably correct, are based on isolated product yields rather than quantum yields, and the conditions of the reaction are not clearly stated. This has prompted me to make a preliminary report of some data obtained in a general photochemical study of a series of cyclic olefins. This paper reports compelling evidence that the triplet state of methyl coumarilate (1) reacts with ground state benzophenone to form an oxetane.

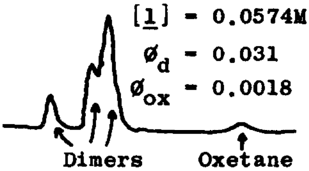


When 0.1M 1 and 0.1M benzophenone in degassed benzene is irradiated with 366nm radiation, absorbed only by benzophenone, at least 3 of the 4 possible cyclobutane dimers of 1 are formed along with an oxetane. The isolation and identification of the products is given in the experimental section. Gas chromatography traces of the products from irradiation of various mixtures of 1 and

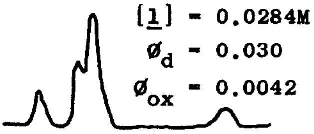
benzophenone are shown below, along with the quantum yields for the reaction. The concentration of benzophenone was held constant at 0.055M.



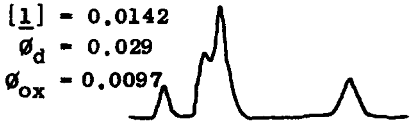
[1] = 0.144M
$\phi_{dimers}$ = 0.031
$\phi_{oxetane}$ = 0.0004



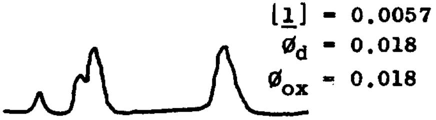
[1] = 0.0574M
$\phi_d$ = 0.031
$\phi_{ox}$ = 0.0018



[1] = 0.0284M
$\phi_d$ = 0.030
$\phi_{ox}$ = 0.0042



[1] = 0.0142
$\phi_d$ = 0.029
$\phi_{ox}$ = 0.0097



[1] = 0.0057
$\phi_d$ = 0.018
$\phi_{ox}$ = 0.018

A similar experiment was also run with the concentration of 1 held constant at 0.0071M and the concentration of benzophenone varied. In this case the results were:

| [benzophenone] | $\phi_{dimers}$ | $\phi_{oxetane}$ |
|---|---|---|
| 0.0275M | 0.026 | 0.0059 |
| 0.0550M | 0.020 | 0.0160 |
| 0.110M | 0.014 | 0.0216 |

Inspection of the above data reveals that increasing the concentration of ground state benzophenone relative to the concentration of 1 increases the quantum yield of oxetane at the expense of dimers of 1. This can only be accommodated by a reaction scheme involving oxetane formation from ground state benzophenone and excited state 1.

$$\text{Benzophenone} + h\nu \longrightarrow \text{Benzophenone}^{*3} \qquad (1)$$

$$\text{Benzophenone}^{*3} + \underline{1} \xrightarrow{k_1} \text{Benzophenone} + \underline{1}^{*3} \qquad (2)$$

$$\underline{1}^{*3} + \text{Benzophenone} \xrightarrow{k_2} \text{Oxetane} \qquad (3)$$

$$\underline{1}^{*3} + \underline{1} \begin{cases} \xrightarrow{k_3} \underline{1} + \underline{1} + \text{Heat} \\ \xrightarrow[k_4]{} \text{Dimers} \end{cases} \qquad (4)$$

$$\phi_{dimers} = \left(\frac{k_4}{k_4 + k_3}\right)\left(\frac{k_1[\underline{1}]}{k_1[\underline{1}] + k_2[\text{Benzophenone}]}\right) \qquad \phi_{oxetane} = \frac{k_2[B]}{k_2[B] + k_1[\underline{1}]}$$

The energy wasting pathway $k_3$ in equation 4 is required by a plot of $\phi^{-1}_{dimers}$ vs. $[\underline{1}]^{-1}$, which is a straight line with an intercept of 30 rather than the intercept of unity which would be required by a scheme without $k_3$. Precisely the same behavior has been reported for indene[4] and for several other dimerizations.[5]

Further compelling evidence for the formation of oxetane from excited olefin and ground state benzophenone is found in the fact that a mixture of 0.1M benzophenone ($E_t$ = 68 kcal/mole), 0.01M 1 ($E_t$ = 63 kcal/mole)[6] and 0.01M thioxanthone ($E_t$ = 65 kcal/mole) has the same quantum yield (366 nm hν) of oxetane formation as an identical solution minus the thioxanthone. In this experiment over 99% of the radiation is absorbed by the thioxanthone which then transfers its triplet energy ($\phi_{\text{intersystem crossing}}$ = 1.0 for thioxanthone) at a preferred rate to the lower energy 1.

A careful search for oxetane formation from the irradiation of 1 with acetophenone and with acetone was made. A small peak was seen on the gas chromatogram at approximately the correct retention time when acetophenone was used, but there was not enough product for analysis. The size of the peak did appear to increase with increasing acetophenone concentration. The size of the peak indicates that benzophenone is at least 100 times more effective than acetophenone in intercepting the triplet state of 1 to form an oxetane. A study is under way to determine the quantum yield of oxetane formation with substituted benzophenones and other ketones. The results will be reported at a later time.

## EXPERIMENTAL

Quantum Yields - The radiation source was a 450 watt Hanovia medium pressure mercury arc lamp filtered by Corning 0-52 and 7-39 filters. The tubes were degassed by multiple freeze-pump-thaw cycles, sealed and irradiated on a rotating tube holder. The actinometer was the 0.1M benzophenone sensitized isomerization of 0.1M trans-stilbene, for which a value of $\phi$ = 0.50 was used. The products were analyzed by gas chromatography on a 6-foot, 10% silicon oil column at 225°.

Product Identification - The first dimer on the gas chromatogram (16%) was not isolated, but combination vpc-mass spectrogram analysis showed mass peaks at 352, 320, 293, 261, 234, 176, 145 and 89 mass units (base peaks underlined).

The second dimer (30% in benzene but 70% of the total dimers in methanol-water) was isolated by irradiating a mixture of 10 g 1 in 100 ml of methanol and 20 ml water with 10 g acetophenone as sensitizer. Vacuum distillation of the starting materials in a 120° bath left a residue which was recrystallized from benzene, mp 262-265°. The mass spectrum showed peaks at 352, 293, 272, 234, 176, 145 and 89 mass units. The nmr had singlets at 204 cps (6H) and 280 cps (2H) and a multiplet at 390-430 cps (8H). The infrared spectrum and elemental analysis were in agreement with a cyclobutane dimer structure, but the stereochemistry cannot be assigned without further data.

The third dimer (54% in benzene) was isolated from irradiation of a mixture of 1 and acetophenone in benzene by distilling off the volatile materials and recrystallizing the residue from benzene, mp 229-232°. The mass spectrum showed peaks at 352, 293, 272, 234, 176, 145 and 89 mass units. The nmr showed singlets at 220 cps (6H), and 256 cps (2H) and a multiplet at 390-430 cps (8H). Again the stereochemistry cannot be assigned without further data.

The oxetane was isolated by irradiating a solution of 0.5 g 1 and 10 g benzophenone in 600 ml benzene for 2 hours under nitrogen. The solvent and benzophenone were distilled off under vacuum (120° bath) and the residue recrystallized from cyclohexane and then methanol, mp 193-194.5°. The mass spectrum showed peaks at 358, 330, 299, 271, 253, 252, 243, 194, 176, 165 and 145 mass units. The nmr had singlets at 223 cps (3H) and 316 cps (1H) and a multiplet at 400-460 cps (14H). The infrared spectrum and elemental analysis were in agreement with the oxetane structure.

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6. The point at which reversible energy transfer to the sensitizer occurs.