

THE PHOTOCHEMICAL *CIS-TRANS* ISOMERIZATION OF 2-CARBOMETHOXY-2-BUTENE

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SUMMARY

The direct and sensitized photoisomerization of the two isomers of 2-carbomethoxy-but-2-ene, methyl tiglate and methyl angelate, has been studied in solutions in cyclohexane and ethanol. The isomerization quantum yields at 254 nm are, tiglate \rightarrow angelate, 0.090; angelate \rightarrow tiglate, 0.030; they are independent of solvent and concentration. There is a side reaction ($\Phi = 0.005$) of the singlet state with the angelate which forms 3-carbomethoxy-but-1-ene.

Isomerization and some compound formation occurs on photosensitization and this has been studied at 313 nm and 366 nm using acetone, benzophenone, acetophenone and anthraquinone as sensitizers. For the results with benzophenone the excitation and decay ratios have been determined and the results suggest that acetone acts by simple energy transfer while the other compounds either transfer or form intermediate complexes which lower the quantum yields for isomerization.

Comparison of the singlet and triplet results and correlation with the probable potential energy diagram indicates that isomerization is only important when the $\pi-\pi^*$ and $n-\pi^*$ states differ appreciably in energy. In the singlet states which are close in energy, internal conversion is the most probable means of energy dissipation.

INTRODUCTION

Although there have been extensive studies of photochemical isomerization in ethylenic molecules¹ and in other hydrocarbons² there has been little quantitative interest in conjugated systems which involve $n \rightarrow \pi^*$ transitions as well as $\pi \rightarrow \pi^*$ transitions. Computer calculations^{3,4} with π -electron approximations have provided plausible models to correlate with the experimental data and now that theoretical approaches are available⁵ to include other electrons as well it will be necessary to test the predictions against quantitative experimental results. Experi-

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mental studies on $n-\pi^*$ systems have largely been confined to nitrogen-substituted stilbenes^{6,7} such as the styryl pyridines or azobenzenes but Barltrop and Wills⁸ have studied the photoisomerization of ethyl crotonate. Our own work started from a report by Tolberg and Pitts⁹ that ethylidene acetone, methyl propenyl ketone, photoisomerized readily. In a preliminary study¹⁰ we found that the compound was difficult to handle because of its slow non-photochemical isomerization at room temperature. We then turned to the 2-carbomethoxy-2-butene for which we have measured the quantum yields for both direct and photosensitized isomerization. The yields for the direct process were small showing that the state excited is stable to isomerization and crossover to the unstable $\pi-\pi^*$ states is unlikely.

EXPERIMENTAL

Methyl tiglate and methyl angelate (*trans*- and *cis*-2-carbomethoxy-2-butene respectively) were photolyzed in solution and the products were analyzed by vapour phase chromatography.

Two techniques were used, both described in detail elsewhere. Some photolyses were made in quartz capillaries¹¹ but the majority were made with our semi-micro technique¹² in which the reagents are contained in a 1 cm³ water-jacketed Spectrosil cell stirred with a stream of pure nitrogen.

The radiation at 254, 313 and 366 nm was obtained from a mercury arc lamp, Osram HBO 500 W, fitted with interference filters (Barr and Stroud Ltd.) or solution filters.

The products were analyzed on a 2.7 m column of 10% polyethylene glycol adipate (w/w) on 80–100 mesh Chromosorb P run at 380 K in a Pye 104 Chromatograph.

Methyl tiglate was prepared by esterifying tiglic acid (Koch-Light Ltd.) with methanol and H₂SO₄. After ether extraction it was purified by preparative gas chromatography using a 4.6 m column of 15% polypropylene glycol on Chromosorb W at 418 K (boiling point 412.5 K at 766 Torr; $D_4^{20} = 0.947$ at 20°C).

Methyl angelate was prepared by irradiating the tiglate, dissolved in cyclohexane, for 12 hours in an immersion reactor fitted with a medium pressure mercury arc. After solvent removal the compound was purified by preparative chromatography (boiling point 400.7 K; $D_4^{20} = 0.941$).

Two actinometers were used: potassium ferrioxalate¹³ for measurements in the semi-micro apparatus and 2-pentanone in the capillary technique¹¹.

RESULTS

The ultra-violet spectra each show a clear maximum in the far ultra-violet (Table 1) which is attributable to a mixture of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The absorptivity falls to a low value at 254 nm but it is still sufficient for photolysis. An

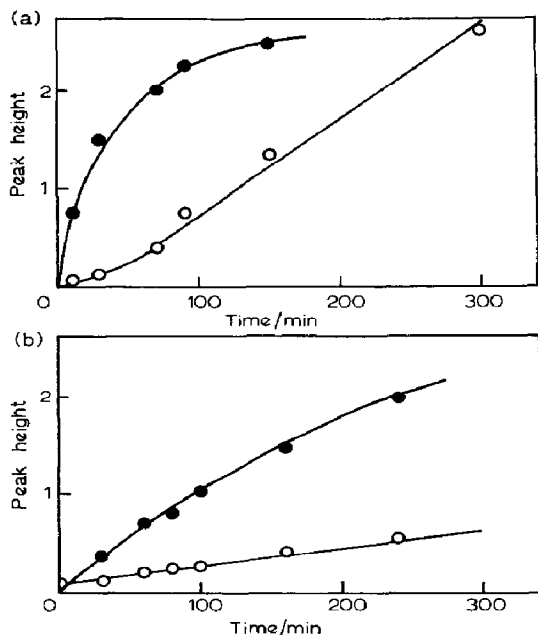


Fig. 1. (a) Photolysis of methyl tiglate in capillaries to high conversion; yield of methyl angelate (II), ●, and 3-carbomethoxy-but-1-ene III, ○. (b) Photolysis of methyl angelate in the semi-micro apparatus to small conversion; yield of methyl tiglate (I), ● and 3-carbomethoxy-but-1-ene III, ○.

The effect of quenchers on the direct photolysis was studied. Addition of heptene or cyclohexene had no effect; dienes could not be used since their absorption spectrum falls in the same region as the esters. Oxygen, bubbled through the solution, or addition of MnCl_2 or NiCl_2 inhibited part of the photolysis. For example, for photolysis in ethanolic solution the rate of photolysis was reduced from 1.60 to $1.16 \times 10^{-11} \text{ mol min}^{-1} \mu\text{l}^{-1}$ with 0.205 M MnCl_2 . A maximum of $\sim 30\%$ of the reaction in either direction could be inhibited in this way.

An attempt was made to study the thermal isomerization; samples of methyl tiglate were heated in sealed capillaries for 92 hours at 576 K . There was only a small amount of conversion and no further measurements were made.

The isomerization in either direction could be photosensitized at 313 nm or 366 nm with several added ketones; Fig. 2 shows the results for various concentrations of ester in a solution of benzophenone in cyclohexane. Some consolidated results for four sensitizers are shown in Table 2. With anthraquinone several other, unidentified, products were observed and the photoisomerization was seen to be only a minor reaction. Additional products were also observed with benzophenone which mass spectrometry indicated to be oxetanes. In none of the photosensitized runs was compound III observed. Biphenyl, naphthalene, benzil and pyrene, all of which have triplet energies less than 275 kJ mol^{-1} , would not photosensitize the reaction on irradiation at either 313 or 366 nm .

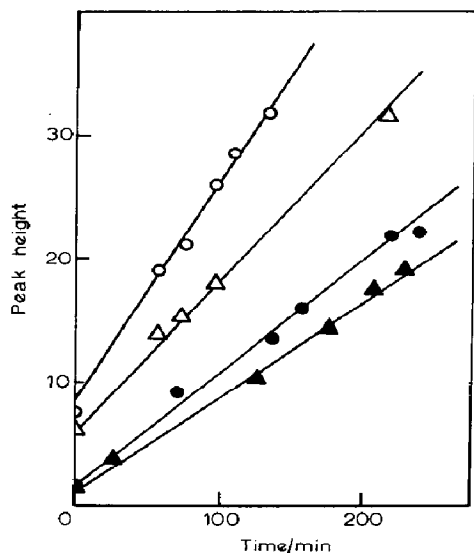


Fig. 2. Photosensitized isomerization of methyl tiglate; yield of angelate at various concentrations of tiglate: ▲, 1.3 M; ●, 2 M; △, 4 M; ○, 6 M. Concentration of benzophenone in cyclohexane = 0.005 M, $\lambda = 313$ nm.

TABLE 2

PHOTOSENSITIZERS

	E_T	Φ (λ/nm)	Photostationary state
Acetone ^a	330	0.26 (313, 366)	51%
Benzophenone ^b	278	0.14 (366)	53%
Acetophenone ^c	308	0.26 (313, 366)	49%
9, 10-Anthraquinone ^d	263	0.019 (313)	—

^a In cyclohexane; acetone, 1.4 M; ester, 0.07 M.

^b In cyclohexane; benzophenone, 0.4 M, ester, 0.03 M.

^c Ester, 0.06 M; acetophenone, 1 M.

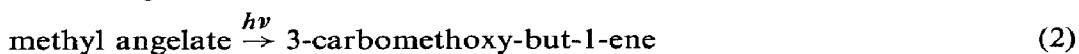
^d Ester, 0.07 M; anthraquinone, 0.009 M.

DISCUSSION

It is evident from the quantum yields that neither the photoisomerization:



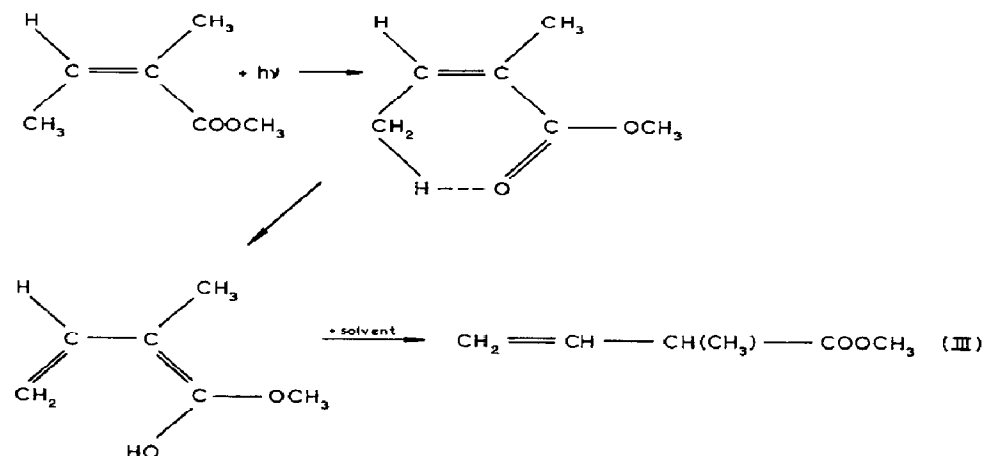
nor the rearrangement:



are the main processes by which the tiglate or angelate divests itself of the photon energy at 254 nm. There are no alternative decomposition paths as there are for the butenes¹⁴ at 185 nm and the results are quite similar to those of Tolberg and

Pitts⁹, with the analogous enone, ethylidene acetone, who found that decomposition was a minor process at room temperature although some isomerization did occur.

The pattern of reactions (1) and (2) is similar to that found by Barltrop and Wills⁸ for ethyl crotonate. The results in Fig. 1 and the incorporation of a deuterium atom from methyl deuterioalcohol indicates that probably there is the same mechanism for rearrangement from the *cis*-isomer (methyl angelate):



As photosensitization does not produce any of the rearrangement product (III) the photorearrangement must be a reaction peculiar to the singlet state of the angelate.

A possible potential energy diagram for the system is shown in Fig. 3; the energies are derived from the spectra and from the photosensitized results (see below). The energy barrier in the ground state is taken from the activation energy for the thermal isomerization of methyl crotonate¹⁵. Several groups^{16,17} of workers have calculated potential curves for enone systems in which the $\pi \rightarrow \pi^*$ states exhibit a potential minimum at the 90° position while the $n \rightarrow \pi^*$ states have a barrier to rotation. The relative positions of the levels are not known; there is experimental evidence¹⁸ to suggest that $n \rightarrow \pi^*$ triplets relax rapidly to the less reactive $\pi \rightarrow \pi^*$ triplet but this is not helpful here since, from the quenching behaviour, so little of the photoreaction goes through the triplet state. The photosensitized results which show that the triplet state isomerizes readily indicates that the $\pi \rightarrow \pi^*$ state is lower than the $n \rightarrow \pi^*$ state.

In terms of this diagram: after excitation, the majority of molecules find their way from the $n \rightarrow \pi^*$ state to the ground state by internal conversion. Less than 10% cross to the $\pi \rightarrow \pi^*$ state and isomerize. Of these $\sim 3\%$ isomerize *via* the triplet state. It is possible to interfere with the last process¹⁹ by adding Mn^{2+} , Ni^{2+} or O_2 . With the Mn^{2+} salts a linear Stern-Volmer plot was obtained which gave an apparent lifetime for the triplet state of 1.4×10^{-8} s, if quenching is diffu-

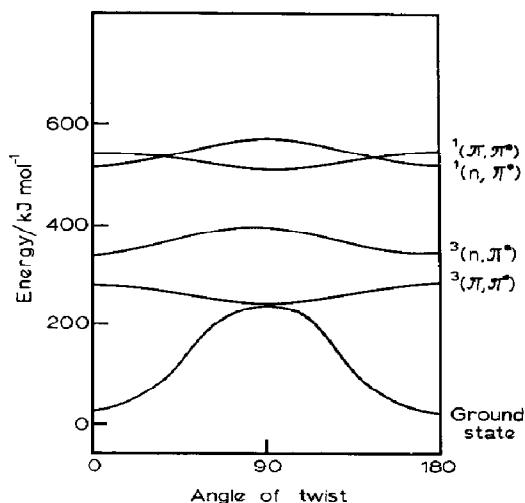


Fig. 3. A possible potential energy diagram for the tigate-angelate system. The energies of the states are plotted against the angle of twist, ϕ , about the central double bond. The actual energies, crossover points etc. are all rather uncertain.

sion controlled. The mechanism of this highly efficient internal conversion is not clear; similarly high efficiencies have been found in other systems involving $n-\pi^*$ excited states. For example, the quantum yield for *trans* \rightarrow *cis* isomerization in 4,4'-bis-pyridylethylene is 0.003 while in stilbene it is 0.48²⁰; the low value was attributed to enhanced rates of radiationless decay when $n-\pi^*$ and $\pi-\pi^*$ states mix²¹.

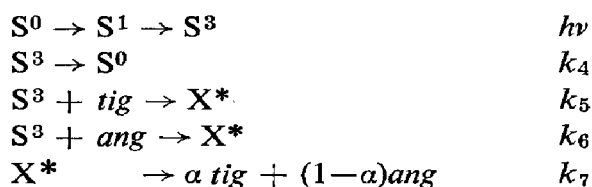
The results of the photosensitized experiments fit into a pattern similar to that suggested by other workers^{22,23}, particularly by Saltiel and his collaborators²⁴ for several systems including the acetone photosensitization of pent-2-ene.

Acetone and acetophenone are high energy sensitizers, transferring energy to the ester which may then isomerize. Naphthalene, benzil and pyrene have triplet energies lower than that of the ester and do not photosensitize the isomerization. However, although anthraquinone has $\sim 12 \text{ kJ mol}^{-1}$ less energy in its triplet state than biphenyl, it does photosensitize the reaction but not so efficiently as the high energy compounds. With anthraquinone and also to some extent with benzophenone some oxetane formation is observed. An explanation of these effects is that when the olefin acceptor and ketone donor have similar energies, a Schenk²⁵ biradical intermediate can be formed:



This may decompose to form either isomer or undergo ring closure to form an oxetane. The intermediate is more likely to be part of the mechanism with ketone sensitizers of lower energy, so that with anthraquinone, oxetane formation is an important process, while with benzophenone, the triplet energy is such that the oxetane formation is less likely than isomerization.

If the reaction with benzophenone is considered as a transfer the results can be fitted with a simple mechanism:



A steady state treatment give the photostationary state, $[\text{tig}]/[\text{ang}]$, and the initial quantum yields to be:

$$[\text{tig}]/[\text{ang}] = k_6/k_5 [\alpha/(1-\alpha)] \quad (\text{i})$$

$$1/\Phi(\text{tig} \rightarrow \text{ang}) = (1 + k_4/k_5 [\text{tig}]/(1-\alpha)) \quad (\text{ii})$$

$$1/\Phi(\text{ang} \rightarrow \text{tig}) = (1 + k_4/k_6 [\text{ang}]/\alpha) \quad (\text{iii})$$

When the results in Fig. 2 are treated with the last two equations Fig. 4 is obtained, with straight lines similar to those of Saltiel. From the ratio of the intercepts the decay ratio $\alpha/(1-\alpha)$ is $1.20 (\pm 0.2)$; the ratio of the slopes is $1.38 (\pm 0.1)$ and from eqn. (i), this should equal the photostationary state ratio which is measured separately to be $1.13 (\pm 0.15)$. The difference probably reflects the general inaccuracy of slope/intercept techniques. The excitation ratio, k_6/k_5 , is obtained from

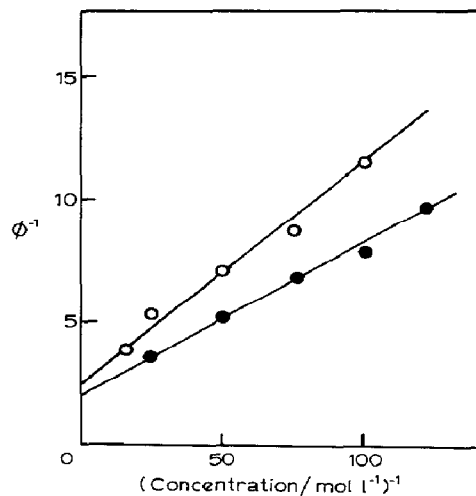


Fig. 4. The isomerization of methyl tiglate and methyl angelate, photosensitized by benzophenone. Plots of reciprocal quantum yield *versus* reciprocal ester concentration. O, angelate to tiglate; ●, tiglate to angelate.

both the ratio of the slope/intercept for both plots and also from the limiting quantum yields at high ester concentration; it is 1.20 (\pm 0.2). The limiting yields are: angelate \rightarrow tiglate, 0.50 (\pm 0.1); tiglate \rightarrow angelate, 0.42 (\pm 0.1).

These figures are similar to those obtained by Saltiel²⁴ for the acetone photosensitized isomerization of pent-2-ene. The deviation of $\alpha/(1-\alpha)$ from unity may reflect asymmetry in the potential surface or it may indicate, as Saltiel suggested, the involvement of the Schenk intermediate in the reaction.

Comparison of the conclusions from the direct photolysis and the photosensitized reaction indicates that for the singlet states efficient internal conversion inhibits the isomerization; the efficiency being due to mixing of the $n-\pi^*$ and $\pi-\pi^*$ singlet states. Isomerization is observed in the triplet states which are separated in energy, and internal conversion is not a favoured process, presumably due to the small mixing.

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