Photocycloaddition in Liquid Ethyl Cinnamate and in Ethyl Cinnamate Glasses. The Photoreaction as a Probe into the Micromorphology of the Solid

P. L. Egerton, E. M. Hyde, J. Trigg, A. Payne, P. Beynon, M. V. Mijovic, and A. Reiser*

Contribution from the Research Division, Kodak Limited, Headstone Drive, Harrow, Middlesex, HA1 4TY, United Kingdom. Received August 19, 1980

Abstract: Irradiation of neat liquid ethyl cinnamate at room temperature and of ethyl cinnamate glasses at −80 and −196 °C produces cyclodimers in high yield. Six of the possible eleven isomers have been identified in the products. Their contributions to the overall dimer fraction differ widely; in the photolysis of liquid ethyl cinnamate, a head-to-head dimer, δ-truxinate, is the principal component, while photolysis of low-temperature ethyl cinnamate glasses produces α-truxillate, β-truxinate, and δ-truxinate in about equal proportions. This change in product distribution is attributed to the immobilization of the reactants in the solid glass, which causes the photoproducts to be determined by the configuration of reactant pairs in the matrix. Thus, the product distribution after irradiation carries information on the distribution of site geometries in the unirradiated solid.

The cyclodimerization of cinnamic acid in its crystalline forms is one of the oldest and best known reactions of solid-state photochemistry.[1,2] In the crystalline phase the efficiency of the process is determined entirely by the dimensions of the crystal lattice[3,4] and may be altered drastically by small changes in geometry. Because of this, the steric requirements of the reaction were thought to be so critical as to rule out cycloaddition between cinnamoyl groups in the disordered arrays of an amorphous matrix.[5] This view appeared to be supported by an observation of Krönert,[6] who had irradiated neat liquid ethyl cinnamate and had found only traces of cyclobutanes in the photolysis products. Krönert's results cast doubt on the accepted mode of action of poly(vinyl cinnamate)[7,8] and of a whole class of related industrial photopolymers[9-11] where photocycloaddition was assumed to provide the mechanism for the formation of intermolecular cross-links. It was therefore decided to reexamine the photolysis of liquid ethyl cinnamate in some detail, and to extend the investigation to ethyl cinnamate glasses which represent a more realistic model of a photoreactive polymer matrix.

Accordingly, thin films of ethyl cinnamate were exposed, through Pyrex filters, to a mercury arc, and the reaction products were analyzed by gas chromatography, NMR spectroscopy, and combined gas chromatography–mass spectrometry, calibrated with authentic samples of the products. In both liquid and solid ethyl cinnamate, high yields of cyclodimers were obtained, but the distribution of isomers in the solid-state reaction was different from that found in liquid-phase photolysis. The effect is attributed to the immobilization of the reactants. Because of it, the product distribution in the matrix is thought to be determined not by the relative reactivities of the various encounter configurations, but by the frequency of occurrence in the solid of those pair geometries which resemble the final products. This view is an extension to matrix photochemistry of the topochemical approach developed by Schmidt and Cohen.[3,12] If it applies, the products of photo-cycloaddition reflect the distribution of site geometries in the original matrix, and to the extent that the matrix is represented by the ensemble of sites, the photoreaction may be said to act as a probe into the micromorphology of the solid.

Experimental Section

General Procedures. For larger scale experiments ca. 500 mg of ethyl cinnamate were spread as a thin film between two Pyrex plates (20 cm × 20 cm) and exposed to a 500-W Hanovia mercury lamp. For small-scale experiments 2 to 10 mg were deposited on the inner wall of a round-bottom Pyrex flask by evaporating a solution. Very stable liquid films were prepared in this way. Irradiation was carried out at room temperature or in a cooling bath of dry ice (CO_2) in carbon tetrachloride (−20 °C), acetonitrile (−45 °C) and methanol (−80 °C), or liquid nitrogen (−196 °C).

After irradiation, the samples were washed out from the flask with trichlorethylene and chromatographed on preparative silica plates (Merk, 2 mm SiO_2 with F-254 indicator). Elution was with a 4:1 mixture of petroleum ether 60–80 °C and ethyl acetate.

Materials. *trans*-Ethyl cinnamate (bp 271 °C) was supplied by Aldrich Chemical Co.

Diethyl β-Truxinate. *trans*-Cinnamic acid (Aldrich Gold Label) freshly recrystallized from 1,2-dichloroethane, when it is obtained almost exclusively in the β form,[13] was exposed to a medium-pressure mercury arc through a Pyrex filter. The photoproduct is predominantly β-truxinic acid, with a small quantity of α-truxillic acid present. The acids were converted to the esters via the acid chlorides.[14]

Diethyl α-Truxillate. *trans*-Cinnamic acid was annealed for 48 h at 70 °C. By this treatment virtually all β-cinnamic acid is changed to the more stable α form. Irradiation of the annealed crystals produces quantitatively α-truxillic acid.[15] This was esterified as before.

Diethyl δ-Truxinate. Dilute solutions (1%) of propylene 1,3-dicinnamate (PDC) and of *n*-butylene 1,4-dicinnamate (BDC) in cyclohexane were irradiated for 72 h in Pyrex flasks with a mercury lamp. Intramolecular cyclization occurred according to the scheme
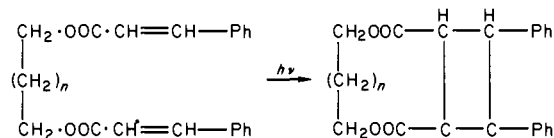
After solvent removal by evaporation, the photolysate was hydrolyzed with dilute NaOH and the acids precipitated, washed, and re-esterified via the acid chlorides (thionyl chloride method). The main product of the irradiation of PDC is β-truxinate with a smaller amount of δ-truxi-

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Table I. Retention Times of the Cyclodimers of Ethyl Cinnamate in a Fused Silica Capillary Column[a]

structure		retention time, min standard	retention time, min photo-lysate
neotruxinate		18.4	18.3
δ-truxinate		19.8	19.5
μ-truxinate		19.9	19.8
ε-truxillate		20.5	(20.5)
β-truxinate		20.7	20.5
α-truxillate		21.0	21.0
γ-truxillate		21.3	(21.0)
ζ-truxinate		22.7	22.3

[a] 25 m, SP2100, 50 °C for 1 min, then to 180 °C at 30 °C/min.

nate.[16] The photolysis of BDC produces predominantly δ-truxinate with a smaller contribution from β-truxinate.[17] The NMR spectra of the major products were in both cases consistent with the above assignments.

Diethyl μ-Truxinate. This isomer was prepared following the procedure given by Green and Rejto[18] by irradiating a solution of 600 mg of *trans*-stilbene and 4 g of diethyl fumarate in 100 mL of cyclohexane (mercury lamp + Pyrex filter). After evaporation of the solvent the unreacted components were removed by thick-layer chromatography. The majority product is μ-truxinate, with smaller contributions from δ-truxinate and some neotruxinate.

Diethyl ζ-Truxinate. By analogy with the preceding experiment, irradiation of 750 mg of *trans*-stilbene with 6 g of diethyl maleate in 150 mL of cyclohexane gave μ-truxinate and ζ-truxinate as the main products, together with some neotruxinate and some β-truxinate.

Diethyl ε-truxillate and diethyl γ-truxillate were prepared following the procedure given by Stoermer and Emmel.[19]

Gas Chromatography. Samples for gas chromatography were evaporated to dryness and dissolved in chloroform to give a concentration of approximately 1 mg/mL. For quantitative work, an internal standard (*n*-nonadecane) was also added and 0.1 μL of each sample was injected into a Hewlett-Packard 5840 gas chromatograph fitted with an all-glass capillary inlet system. Separation was achieved on a 14-m WCOT glass capillary column coated with OV-1. The sample was injected in the splitless mode with the column temperature at 50 °C. After 30 s the column temperature was raised to 180 °C at a rate of 30 °C/min and held at that temperature for 20 min. Under these conditions the retention times shown in Table I were found.

Mass Spectrometry. Mass spectra of the cyclodimers were taken on a VG MICROMASS ZAB 2F mass spectrometer in the electron impact

Table II. Distribution of Cyclic Isomers in the Photolysis Products of Ethyl Cinnamate

	liquid 25 °C	glass −20 °C	glass −45 °C	glass −80 °C	glass −196 °C
neo	7.1	5.5	5.0	5.6	3.0
–	2.5	6.0	5.0	1.2	2.3
δ	55.2	31.8	27.5	24.0	22.1
μ	0.5				
β	24.0	35.3	36.0	34.6	36.0
α	6.3	15.2	22.7	32.0	36.6
ζ	4.4	6.2	4.2	2.6	

mode. They provide a means of distinguishing between truxinic (head-to-head) and truxillic (head-to-tail) dimers.[20,21] While truxillates can undergo only symmetrical cleavage, truxinates reveal products of both symmetrical and assymmetrical cleavage. In the last mode, the ion
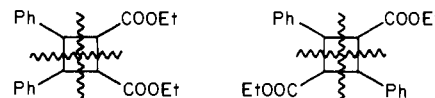
EtOOC·CH=CH·CO⁺ is produced, with a mass peak at m/e 127, in a region uncluttered by other fragments. This mass peak in the fragmentation pattern of the cyclodimer is therefore diagnostic for a head-to-head configuration of the substituents.

Nuclear Magnetic Resonance. ^{1}H NMR spectra were recorded in deuteriochloroform on a JEOL/FX-100 Fourier Transform NMR Spectrometer, using tetramethylsilane as the internal standard. The spectra were identified by comparison with literature data,[22-24] and by consideration of chemical shifts and of the coupling constants of the protons on the cyclobutane ring.

The chemical shifts of the ester methylene groups show an upfield shift in the α isomer where they are shielded by the adjacent aromatic ring in the cis position and similar shifts are seen in all the cyclobutane ring protons in this isomer. In all three compounds the lower field ring signals show broadening due to long-range (4-bond) coupling from the phenyl ring.

A full report on the NMR spectra of the cyclodimers of ethyl cinnamate is in preparation.

Results and Discussion

Photolysis of Liquid Ethyl Cinnamate. The most important result of our experiments is the finding that, in the photolysis of liquid ethyl cinnamate, cyclodimers account for over 90% of the photoproducts. This removes a serious objection[5] against the possibility of photocycloaddition in amorphous systems.

The remaining 5 to 10% of the products are oligomers, the analysis and IR spectra of which are consistent with the general formula
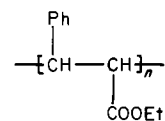
This structure is also supported by the ^{13}C NMR spectrum of the fraction and by its mass spectrum, in which the peaks of the trimer and of the tetramer ions were observed.

In liquid ethyl cinnamate cycloaddition has to compete with cis–trans inversion about the reactive CH=CH double bond. The extent of this competition is illustrated in Figure 1, where the concentrations of *trans*- and *cis*-cinnamate and the overall concentration of cyclic products are plotted as a function of irradiation time. It can be seen that in the liquid environment isomerization is faster than cyclization; on irradiation, a quasistationary state

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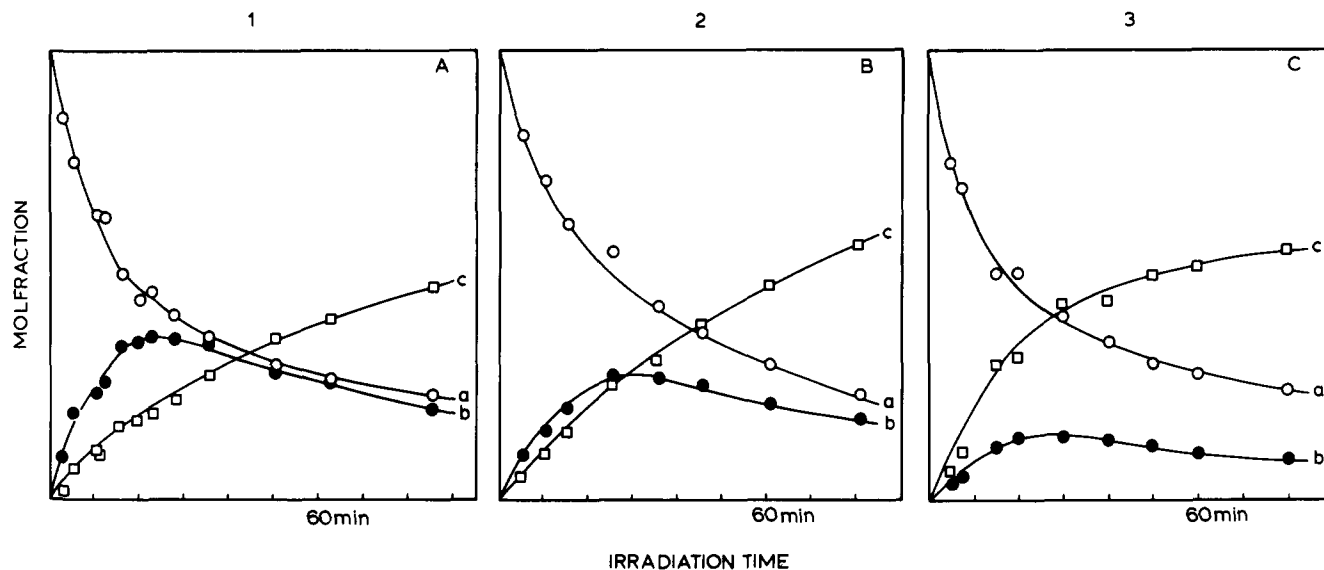
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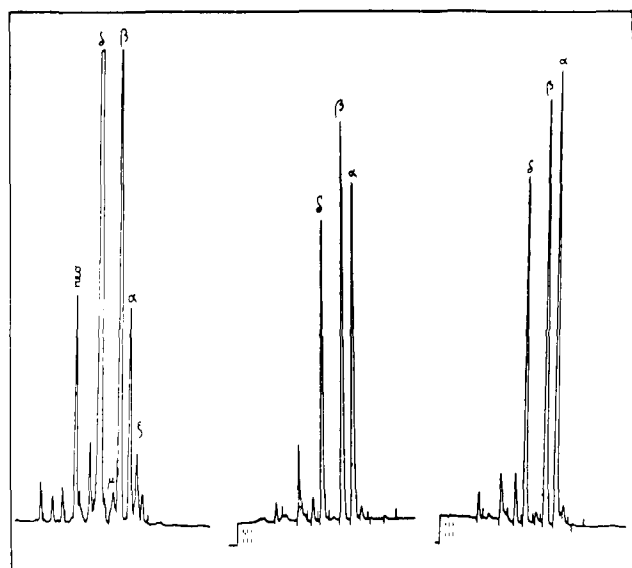
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Figure 1. Progress of cis–trans isomerization and of cycloaddition in irradiated ethyl cinnamate: (a) in the liquid state at 25 °C; (b) in thee solid glass at –80 °C; and (c) in the solid glass at –196 °C.

Figure 2. Gas chromatograms of the photolysis product of ethyl cinnamate: (a) in the liquid state at 25 °C; (b) in the solid glass at –80 °C; and (c) in the solid glass at –196 °C.

is established between the geometric isomers, from which cyclization proceeds as a secondary event. As a result, both the cis and the trans form of ethyl cinnamate contribute to the formation of dimers.

In principle, ethyl cinnamate can form 11 cyclic dimers. Six of these have been positively identified in the products, and two more may be present in trace amounts. The product distribution is shown in the chromatogram of Figure 2 and in the data of Table II. It is noted that δ-truxinate and β-truxinate account for more than 75% of the cyclodimers, α-truxillate, neotruxinate, and ζ-truxinate making up most of the remainder.

A point of interest is the strong prevalence of head-to-head dimers over head-to-tail dimers, the ratio of truxinates to truxillates being 9:1. A regioselectivity of this kind is not uncommon in cycloaddition reactions;[25] it has been observed in the photodimerization of cinnamates,[26] phenylvinyl esters,[27] and substituted

styrenes[28-30] and rationalized, e.g., by the use of frontier orbitals.[31,32] Steric factors must also play a role in determining the reaction probabilities of the various encounter configurations. From an inspection of molecular models it appears that δ-truxinate corresponds to the encounter pair which offers the least steric resistance to the mutual approach of the –C=C– double bonds; δ-truxinate is indeed the main product of the photoreaction in the liquid system.

A last point concerns the three cis:cis cyclodimers, *peri*-truxillate and μ- and ω-truxinate. They correspond to the reaction of an excited *cis*-cinnamate with an adjacent *cis*-cinnamate in the ground state, and their absence from the photolysis products may be caused by a shorter lifetime of the excited state of the cis form.[33,34] In this context it is of interest to note that crystalline *cis*-cinnamic acid does not produce cyclodimers on irradiation, although the lattice geometry is favorable, but rather undergoes inversion to *trans*-cinnamic acid and eventually generates the photoproducts of the trans form.[35]

In summary, irradiation of *trans*-ethyl cinnamate leads to cycloaddition products in high yield. δ-Truxinate is the most important cyclodimer formed, followed by β-truxinate; other isomers are present in small quantities. A marked regioselectivity in favor of head-to-head dimerization and the absence of cis:cis cyclodimers are noted.

Photolysis of Ethyl Cinnamate Glasses. Gerasimov and co-workers[36] have shown that rapid cooling of ethyl cinnamate below the melting point of its crystals (12 °C) produces a glass which has a secondary phase transition at –103 °C and which liquefies at about 10 °C. This glass is highly photoreactive and represents a useful low molecular weight model of a photopolymer matrix.

Thin films of ethyl cinnamate glass were irradiated in Pyrex flasks at –20 °C, –45 °C, –80 °C, and –196 °C, and the reaction products were analyzed as before. It was found that up to 90%

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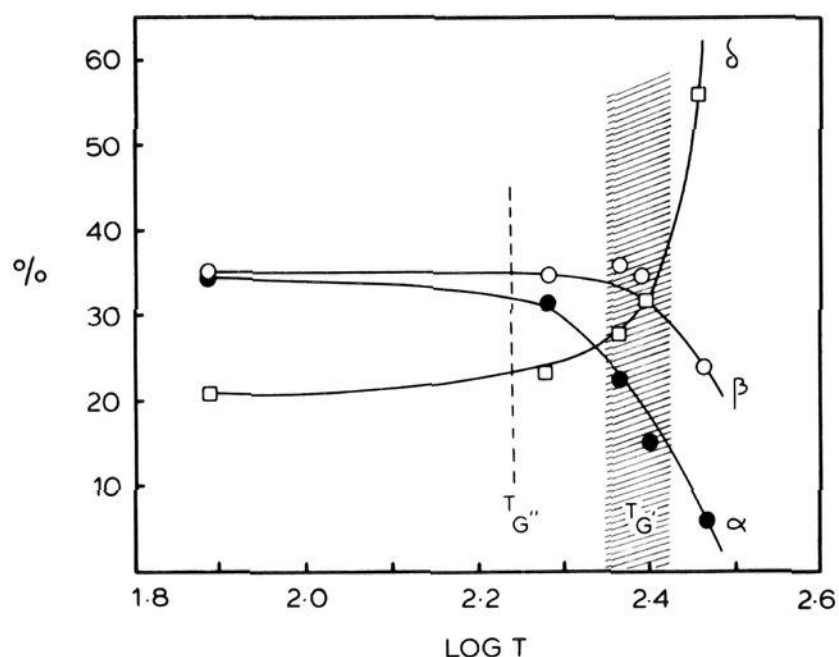
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Figure 3. The contributions of δ-truxinate, β-truxinate, and α-truxillate to the photoproducts at various temperatures of irradiation.

of the cinnamoyl groups had undergone cyclization.

The product distribution observed in the solid-state experiment is different from the result of the liquid-phase photolysis (see the data of Table II). The new feature is a large increase in the fraction of α-truxillate, and a decrease in that of δ-truxinate.

The change in product distribution is not caused by the effect of temperature on the reactivity of the various product pathways, but by its effect on the mobility of the chromophores. This is illustrated in Figure 3 where the contributions of the principal photoproducts are plotted logarithmically as a function of temperature. It can be seen that the transition from the liquid to the

completely rigid matrix is not abrupt, but proceeds via a succession of glasses in which the local mobility of the chromophores is gradually inhibited.

If reactant configurations are fixed in the solid environment, the final product distribution in the matrix is determined not by the reactivities of the various encounter pairs, but by the frequency of occurrence of the corresponding local geometries. The data in Table II show a high content of α and β isomers in the products and indicate therefore a preference for the α- and β-pair configurations in the solid matrix. We note at this point that the head-to-tail dimer, α-truxillate, is formed in spite of a strong regioselectivity in favor of head-to-head dimerization. Its appearance in the products therefore supports the topochemical *interpretation of the matrix reaction.*

The strict topochemical correlation between local geometry in the original solid and the stereochemistry of the final products can apply only if the site configurations in the matrix are maintained throughout the period of irradiation. This is not the case *in ethyl cinnamate glasses where cis-trans isomerization does occur.* The progress of isomerization in the solid matrices is shown in Figure 1B,C which refers to irradiation at −80 °C and at −196 °C. It can be seen that at −80 °C (above the secondary glass transition) isomerization competes on fairly equal terms with cycloaddition. In the hard glass at −196 °C *isomerization is largely inhibited,* but even here enough free volume is available to allow some degree of molecular inversion. As a consequence, the product distribution in solid-state photolysis does not strictly reflect the site geometries in the undisturbed matrix, but relates to a photoperturbed system.

Although photoisomerization loosens the link between original site geometry and the structure of the final products, the data in the last column of Table II are nevertheless incompatible with
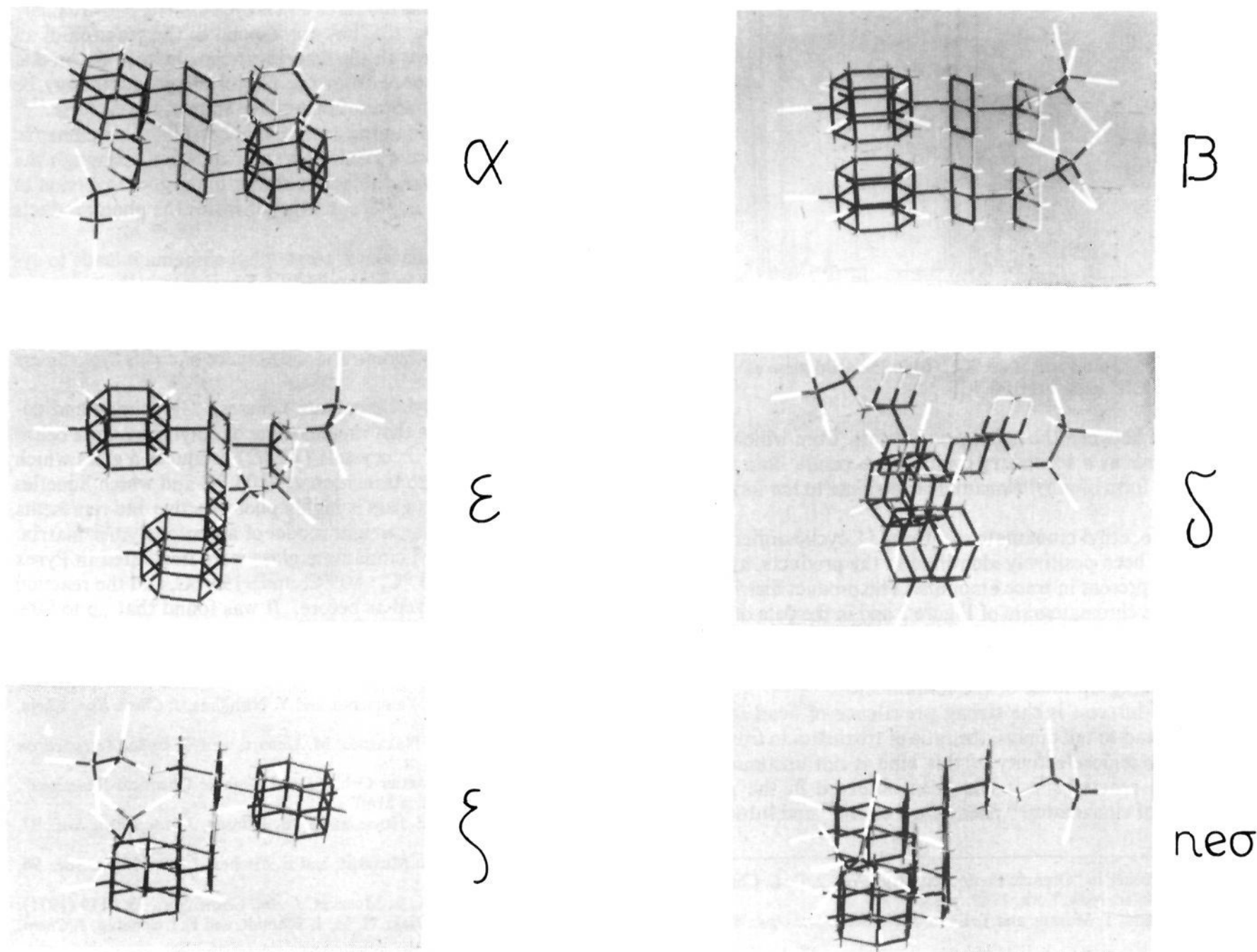
Figure 4. Molecular models of the ground-state pair configurations corresponding to the principal products in the photolysis of ethyl cinnamate.

a view of the matrix as a random collection of reactant configurations. The high content of α-truxillate and β-truxinate in the products rather indicates a strong preference for two specific site configurations. The reason why these contact geometries are important in the solid, we believe, is the tendency of the cooling liquid to optimize its molecular packing. The point is illustrated in Figure 4 which shows molecular models of the ground-state-pair configurations corresponding to the principal cyclodimers. Clearly, the α and β configurations are the most compact and will be favored as the packing density of the liquid increases.

In ethyl cinnamate glasses a reactant conversion of up to 90% can be achieved. In that case the product distribution presents a fairly complete account of the site geometries present in the matrix. In ethyl cinnamate the experimental data reveal thus the existence of a type of molecular organization which is short range and inexact, and yet clearly distinct from a random ensemble of configurations. The driving forces which bring about this intermolecular correlation are the dipolar interactions which in favorable circumstances lead to liquid crystal behavior.[37] The

potentially mesogenic nature of the cinnamoyl grouping is illustrated, e.g., by 4-methoxycinnamic acid[38] which forms a nematic mesophase between 171 °C and 189 °C.

In summary, by virtue of the rich stereochemistry of the cyclobutane ring, photocycloaddition can act as an effective probe into the micromorphology of a photoreactive solid. In ethyl cinnamate glasses the high content of α-truxillate and β-truxinate in the photoproducts indicates a preference for the two contact geometries which correspond to the most compact reactant pair configurations in the ground state. The predominance of these site geometries in the matrix reveals a considerable degree of intermolecular correlation.

Photocycloaddition as a structural probe is particularly useful in the study of some photoreactive polymers where local morphology determines the chemical, and the photographic, properties of the material. We have reported on that aspect in earlier communications.[39,40]

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Solvolysis of 2-(Trifluoromethyl)-2-propyl Trifluoromethanesulfonate. Solvent, Salt, and β-Deuterium Isotope Effects. Substituent Effect of a Strongly Deactivating Group and Rate-Limiting Solvent-Assisted Elimination[1]

Michael P. Jansen, Kalavelil M. Koshy, Nevindra N. Mangru, and Thomas T. Tidwell*

Contribution from the Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada, M1C 1A4. Received October 21, 1980

Abstract: Solvolysis rates of 2-(trifluoromethyl)-2-propyl trifluoromethanesulfonate (**2c**) in a variety of solvents did not show a correlation with rates for 2-adamantyl tosylate in the same solvents. The effect of added salts on the rates of **2c** and 2-propyl tosylate in 80% EtOH was very similar, with significant rate increases for nucleophilic/basic salts. Methyl CD$_3$ isotope effects on the rate of **2c** in three solvents showed average values $k(d_0)/k(d_3) = 1.78$ and $k(d_0)/k(d_6) = 3.80$. The initial observed product from **2c** was CF$_3$C(CH$_3$)=CH$_2$ (**4**) in all cases. The rate ratio $k(i\text{-PrOTf})/k(\mathbf{2c})$ ranges from a high of 4×10^6 in TFA to a low of 1.5×10^4 in EtOH and shows a high degree of destabilization of a cationic transition state by the CF$_3$ group. The results are interpreted in terms of rate-limiting solvent or salt attack on an intimate ion pair formed from **2c**. The observed average product ratio CF$_3$C(CD$_3$)=CH$_2$/CF$_3$C(CH$_3$)=CD$_2$ of 1.9 from **2c**-d_3 in CF$_3$CO$_2$D, HFIP, and CD$_3$CO$_2$D is consistent with this conclusion.

The study of substituent effects on solvolytic reactions leading to carbonium ion intermediates has historically been limited to systems as shown in eq 1, where X is hydrogen or some more

$$X-\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}}-Y \longrightarrow X-\overset{\overset{R}{\diagup}}{\underset{\diagdown R'}{C^+}} + Y^-$$ (1)
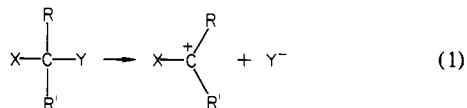
electron-donating substituent such as alkyl, aryl, vinyl or some heteroatom-substituted group such as R''S or R''O. However, quite recently there has developed a strong interest in the study of systems where X is more electron withdrawing than hydrogen[2–8]

and the effects of α substituents such as CHROTs,[4] CH=O,[5] and CN[7,8] have been examined, both experimentally and theoretically.[7c,8]

Our own interest in the effect of strongly deactivating groups on solvolytic reactivity arose from studies of the rates of pro-

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