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(7) Major mesylate: ^{1}H NMR (C_6D_6) δ 1.34 (d, 3 H, $J_{9,10}$ = 6.5 Hz, H_{10}), 2.67 (dd, 1 H, $J_{6,7}$ = 1.8 Hz, $J_{7,9}$ = 4.5 Hz, H_7), 4.80 (dq, 1 H, $J_{9,10}$ = 6.5 Hz, $J_{7,9}$ = 4.5 Hz, H_9). Minor mesylate: ^{1}H NMR δ 1.30 (d, 3 H, $J_{9,10}$ = 6.5 Hz, H_{10}), 2.61 (dd, 1 H, $J_{6,7}$ = 1.8 Hz, $J_{7,9}$ = 8.0 Hz, H_7), 4.82 (dq, 1 H, $J_{9,10}$ = 6.5 Hz, $J_{7,9}$ = 8.0 Hz, H_9).
(8) Ene-lactam from major mesylate: ^{1}H NMR ($CDCl_3$) δ 2.00 (d, 3 H, J = 7.5 Hz, H_{10}), 5.70 (q, 1 H, J = 7.5 Hz, H_9). Ene-lactam from minor mesylate: ^{1}H NMR δ 1.73 (d, 3 H, J = 7 Hz, H_{10}), 6.10 (q, 1 H, J = 7 Hz, H_9).
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(12) Procedure developed by Dr. J. Fahey.
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(17) Identification was made by carrying the pure crystalline 8*S** epimer of **2** (R = H; R′ = CH_2CH_2OH; R″ = $CH(OCO_2CH_2C_6H_4$-*p*-$NO_2)CH_3$), through the same sequence of reactions.
(18) Recovered **7b** was recycled several times to improve the overall conversion, the final yield being 47% based on recovered **7b**.

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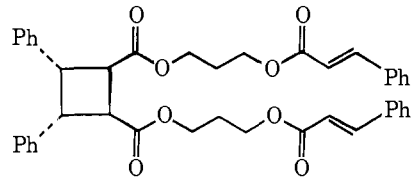
Internal Photocycloaddition between Chromophores Separated by 17 Bonds

Sir:

Intramolecular photochemical interaction between two chromophoric units bridged by more than four bonds has been studied by a few groups[1-3] with a view to determine the formation of exciplexes and/or products. Internal formation of exciplexes and emission from such transients has been observed in molecules with separations between the chromophores which extend up to 23 bonds.[2] Compound formation between internal chromophores which may be subject to more restrictive conditions (and certainly is less easy to detect) has been successfully studied by De Schryver and his coworkers in the cases of 7,7′-polymethylenedioxycoumarins with separations up to 14 bonds,[1] polymethylenedicarboxylic acid (7-coumarino) diesters (s = 12),[1] as well as polymethylene bis-2-anthroates (s = 14).[1b]

We wish to report the internal photochemical [2 + 2] addition reaction in the α,ω-dicinnamate **1** which leads to the tricyclic molecule **2** (eq 1), a reaction which represents photochemical addition between chromophores separated by 17 bonds. Internal photocycloaddition in α,ω-dicinnamates has been studied by Rennert et al.[4-6] in **3** and **4** and Rennert[5] has mentioned that similar [2 + 2] photocycloaddition between internal chromophores has been observed in dicinnamates with longer methylene chains separating the ester groups but no details were given. The photodimerization of cinnamic acid and its derivatives in the solid state which has been extensively studied[7] has also been used to construct macrocyclic rings.[8]



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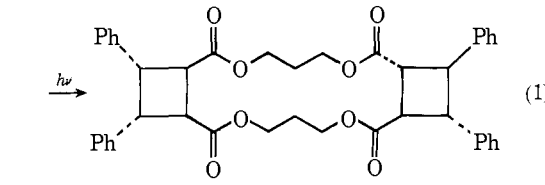

(1)

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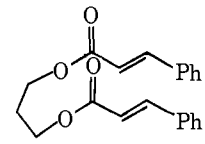
This will be discussed toward the end of this communication.



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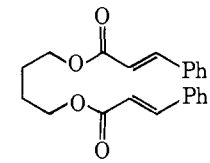

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1 was synthesized from β-truxinic acid[9] by esterifying first with an excess of propylene glycol in the presence of toluenesulfonic acid followed by cinnamoylation of the dihydric diester alcohol with cinnamoyl chloride. A sample of **1**, which had been purified by chromatography, in its NMR spectrum[10] showed 20 aromatic protons in two well-separated groups of 10 H each (δ 7.18 and 6.92, complex), two pairs of olefinic protons centered at δ 7.85 and 6.50 (J = 16 Hz), protons belonging to the central methylene chain at δ 1.9 (4 H, quintet) and 4.28 (8 H, triplet, J = 6 Hz), and cyclobutane protons in two groups at δ 4.5–4.7 and 3.7–3.9. The protons thus were distributed into three distinct entities of relative areas 24 (downfield), 12 (midfield), and 4 (upfield). On irradiation in ether at 300 nm (direct irradiation) with cuprous chloride as catalyst, the NMR spectrum first showed a rapid change corresponding to the trans → cis isomerization of the olefinic bonds. On prolonged irradiation, a white crystalline solid **2** slowly separated from solution (mp 159–161 °C, 32% isolated yield, mol wt 672[11]). Its NMR spectrum showed a distribution of 10, 16, and 4 protons in the down-, mid-, and upfield regions. Since this compound was isomeric with **1**, the chemical reaction corresponded to the disappearance of the 4 olefinic protons in **1** and their replacement by new absorptions at δ 4.18 and 3.30 attributable to cyclobutane protons. The spectral evidence is therefore consistent with **2** being the internal [2 + 2] photoadduct of **1**. The stereochemistry at the point of closure was readily seen by a comparison of the chemical shifts and coupling of the newly formed cyclobutane protons to those of authentic samples of α-truxillic, β-truxinic, and δ-truxinic acids and their esters.[12]

It may be noted that, in the solid state,[7] photodimerization of cinnamic acid and its derivatives leads to α-truxillic or β-truxinic acid derivatives only.[7] In solution, **3** was found to give[4,5] a mixture of the internal diester of β-truxinic acid (90%) and δ-truxinic acid (10%), while **4** gave the diester of the δ acid exclusively. The stereochemistry of the closure in the present instance is therefore consistent with these observations in solution phase. Quantum yields for the closure reaction as well as the trans ⇄ cis isomerization of **1** were measured under a variety of conditions. These are listed in Table I relative to the photoisomerization of *trans,trans*-1,3-propanediol dicinnamate to the cis,trans diester which was measured by Rennert et al.[6] The absolute value of this quantum yield was reported by them to be 0.473. The analogue of **1** derived from α-truxillic acid

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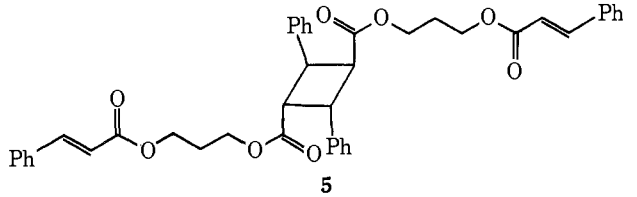
Table I. Relative Quantum Yields for Photoisomerization and Cyclization[a]

Compd	Reaction	Solvent	Wavelength, nm	Catalyst	Rel quantum[b] yield
3[c]	Cyclization	$(C_2H_5)_2O$	300	None	0.05
1[c]	Trans → cis	$(C_2H_5)_2O$	300	None	0.90
1[c]	Cyclization	$(C_2H_5)_2O$	300	None	0.02
1[c,d]	Cyclization	$(C_2H_5)_2O$	300	CuCl	0.20
1[c,d]	Cyclization	$CHCl_3$	350	Ph_2CO	0.10
5[c]	Trans → cis	$(C_2H_5)_2O$	300	None	0.90

[a] Standard: photoisomerization (trans → cis) of 1,3-propanediol-dicinnamate = 1.0 in diethyl ether at 300 nm. [b] Values are extrapolated to zero conversion. These values can be converted to absolute quantum yields by the use of 0.47 for the quantum yield of the standard.[6] [c] Concentration 5×10^{-5} M. [d] Concentration 10^{-4} M.

which has the structure **5** was found not to undergo internal photocycloaddition under any of the experimental conditions that were tried. Reaction 1 is of interest from two points of view which follow.



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(i) One concerns the factors which control the probability of a successful encounter between two cinnamate groups in a given molecule. The two important considerations according to the present investigation are the rate of a diffusive encounter between the chromophoric groups and the lifetime of the excited state of the molecule. Direct irradiation of **1** or **3** or **5** seems to lead to reaction from a singlet state as triplet sensitization gives quite different results. In this singlet state, trans → cis isomerization proceeds with about equal efficiency in all three instances (which is reasonable), but cyclization is twice as efficient in **3** ($s = 8$) as in **1** ($s = 17$), while **5** which has nearly the same separation between the chromophores as **3** does not cyclize at all to any detectable extent. The decrease in reactivity in going from **3** to **1** parallels the reported[3] decrease in the quantum yields for the closure of bis anthroates with separations of 7 and 14 bonds and is attributable to decreased probability of an encounter between the ends of the chain with increasing chain length. The sharp contrast in behavior between **3** and **5** which have nearly the same separation suggest yet another consideration. Molecular models show that a [2 + 2] internal adduct of **5** would not suffer from angle strain whatever the stereochemistry of the addition may be, but severe limitations on its conformational mobility are placed by its *trans*-1,3-cyclobutane geometry. Therefore, separations between chromophores are comparable only when the geometries of the molecules are strictly similar.

For a given reactant molecule, the number of encounters between the ends is undoubtedly increased by going from a singlet to a triplet excited state. The marked effectiveness of triplet sensitizers on the photoreaction of various cinnamate esters (including polyvinyl cinnamate) is well documented in the literature.[13,14] The data in Table I also bear this out. Cuprous chloride may also function by promoting the intersystem crossover through a heavy atom effect.[15]

(ii) A second point of interest is the stereochemistry of the addition in reaction 1. In the solid state it has been shown[4] that a [2 + 2] photocycloaddition between cinnamate groups will give exclusively α-truxillic or β-truxinic acids or their derivatives. The conditions which govern the formation of one or the other have been elegantly worked out. In contrast, in solution, as already mentioned, the δ-truxinic ester is a product of the photocyclization of **3** and is the only product from **4.** The present work suggests that the latter mode persists with even longer molecular separation between cinnamate groups. It may be noted that all three dicarboxylic acids are derived from *trans*-cinnamic acids. The stereochemistry that prevails in the photo cross linking of polyvinyl cinnamate which is usually irradiated as an amorphous film is an interesting question. In our earlier work,[16] we had looked for only α-truxillic and β-truxinic acids among the hydrolysis products of the photolyzed materials. After establishing the stereochemistry in **2,** the earlier data were reexamined to see if we could have overlooked the presence of δ-truxinic acid. It was confirmed that an amorphous film of polyvinyl cinnamate gives only α-truxillic acid as we determined before. This indicates that the behavior of the cinnamate groups in the film is similar to those in a crystal rather than a fluid solution. The structure of the film deserves further examination.

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Sirohydrochlorin. Prosthetic Group of a Sulfite Reductase Enzyme and Its Role in the Biosynthesis of Vitamin B_{12}

Sir:

Recent work in these laboratories[1,2] and independently at Cambridge[3] and Stuttgart[4] has confirmed the role of uro'gen III (**1**) in the biosynthesis of vitamin B_{12} (**2**). It has also been shown[5] that, during the bioconversion of both uro'gen III (**1**) and the "ring C heptacarboxylic acid" (**4**) to cobryinic acid (**3**), formaldehyde can be trapped from the δ-meso (C-20) carbon of **1** and **4.** The relatively low but intact conversion of **4** to **3** (ca.

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