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Control of Solid-State Photodimerization of trans-Cinnamic Acid by Double Salt Formation with Diamines

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Abstract: By double salt formation, diamines can steer the solid-state [2+2] photodimerization of trans-cinnamic acid (1). Thus, the yields for the photodimerization were significant only in three double salts, i.e., the ones with tn and t- and c-chxn, which are assumed to have an overlap structure. The resultant photodimer is generally β -truxinic acid, although in one case, ε -truxillic acid was formed. α -Truxillic acid was not produced from any of the double salts studied. The X-ray crystal structures of three double salts of low photoreactivity (1-en, 1-pen, 1-hen) were consistent with Schmidt's rule.

Photochemical [2+2] cycloaddition of alkenes in the crystalline state is synthetically very useful, because it usually produces only one stereoisomer predicted from the alkene crystal structure.¹ On the other hand, this stereospecificity of the reaction can be a disadvantage because of inaccessibility to other stereoisomers. Therefore, solid-state photocycloadditions are not widely used for syntheses.² In order to circumvent this problem, we are exploring methods to control solid-state [2+2] photodimerizations, e.g., double salt formation with diamines (and some tri- and tetraamines) for controlling the photodimerization of transcinnamic acid and analogs. The idea behind this research is that, neglecting for the time being the presence of neighboring double salt molecules, the double salt may be reactive in an overlap configuration but may be unreactive in a non-overlap configuration (Scheme 1). Here we describe the effect of varying the amine structure on the photodimerization of trans-cinnamic acid (1). The results are important, since techniques to control solid-state reactivity (crystal engineering for solid-state reactions) are still not well developed.^{3,4}



The amines we employed are shown above. Upon mixing 2 mole equivalents of trans-cinnamic acid (1) with 1 mole equivalent of diamine (or 0.67 and 0.5 mole equivalent of dien and hmta, respectively) in a suitable solvent, the corresponding carboxylic acid/amine salts precipitated readily in most cases. The precipitated salts were recrystallized and then dried *in vacuo* at room temperature. The solvent employed for mixing and recrystallization was usually ethereal methanol or ethereal ethanol. The molar ratios of cinnamic acid to amine in the resultant salts, which were determined by elemental analyses, were 2 : 1 in all cases, demonstrating formation of the corresponding double salts. It is interesting that even dien and hmta afforded only the double salts. The series of double salts we prepared and their melting points are listed in Table I. The asymmetric (v_s) stretching frequencies of the COO⁻ group for several double salts are shown in Table II. For a series of the double salts derived from the straight-chain α, ω -diaminoalkanes (en to hen), the values for mp, v_{as} or v_s depended on the chain length in a zigzag pattern.

The double salt crystals obtained as above were ground into powders and 15 mg of the powder was spread between two Pyrex plates. This was placed in our solid-state photolysis vessel⁶ and irradiated for 10 h with a 400-W high-pressure mercury lamp under an argon atmosphere. During the irradiation, the vessel was cooled by running water. After the photolysis, the reaction mixture was dissolved in MeOH or DMSO-d₆ for HPLC and NMR analyses, respectively, and the yields for products and recoveries ([2+2] dimers and cis- and trans-cinnamic acids) were estimated. The results are summarized in Table I. The amine underwent no photodecomposition (by NMR). In several cases, experiments on a larger scale were carried out in order to separate the [2+2] dimers. Because of their low solubilities, their isolation was actually very easy.⁷

The most stable crystal modification of 1 is known to be an α -structure,⁸ which is photochemically converted into α -truxillic acid with high efficiency ($\Phi = 0.7$).¹⁰ Trans-cis photoisomerization of 1 does not take place in the solid state but does occur efficiently in solution ($\Phi = 0.62$).¹¹ Inspection of Table I shows that the double salts of 1 with various amines are not so photoreactive.¹² Many of them are either photostable (i.e., 1-en and 1-hmta) or only slightly photoreactive to give cis-cinnamic acid (i.e., 1-ten, 1-pen, 1-dmen, and 1-pi). However, the double salts 1-tn, 1-hen and 1-c-chxn produced β -truxinic acid in low to reasonable yields (10, 6 and 64 %, respectively), and 1-t-chxn gave ε -truxillic acid in 43 % yield. The yield for δ -truxinic acid from 1-t-chxn (5 %) is also not negligible. α -Truxillic acid was not formed from any of the double salts studied. Thus, it seems that when the double salts are photoreactive, β -truxinic acid is usually produced.

amine used	double salt mp °Cb	product yield and recovery, %		
bp (or mp) °C ^a		[2+2] dimer ^C	cinnamic acid ^d	
en, 118	colorless plates, 173-184	no reaction		
tn, 140	colorless prisms, 146-151	β 10	cis 25, trans 64	
ten, (27-28)	colorless powder, ^e 177.5-178.5	0	cis 1, trans 96	
pen, 178-180	colorless prisms, 139-160	0	cis 3, trans 97	
hen, (42-45)	colorless needles, 182-186	β6	cis 0.5, trans 94	
pn, 119-120	colorless prisms, 122-123	β2	cis 5, trans 93	
t-chxn, 79-81/15	colorless prisms, 163-170	ε 43, δ 5	cis 23, trans 29	
c-chxn, 92-93/18	colorless small crystals, 122-123	β 64, δ 3	cis 11, trans 20	
dmen, 119	colorless prisms and plates, 103-108	0	cis 6, trans 94	
dien, 199-209	colorless needles, 145-151.5	β2,δ1	cis 8, trans 76	
pi, (108-110)	colorless needles, 216.5-223	0	cis 10, trans 90	
dabco, (158-160)	colorless plates, 161.5-173	β1,δ1	cis 8, trans 88	
hmta, (280 (subl))	colorless plates, 142.5-144.3	no reaction		

Table I. Double Salts Derived from trans-Cinnamic Acid (1) and Various Amines and Their Solid-State Photolyses.

^atrans-cinnamic acid (1), mp 133-134 °C. ^bAll the double salts gave correct C, H and N analyses (within $\pm 0.3 \%$) as (1)₂(amine) except (1)₂(ten)(H₂O)_{0.4} and (1)₂(dmen)(H₂O)_{0.2}. ^c[(moles of dimer)/(moles of double salt employed)] x 100 %. ^d[(moles of cinnamic acid)/(moles of double salt employed)] x 0.5 x 100 %. ^eNeedles before drying in vacuo.

diamine	vas	v _s	dia	amine	v _{as}	v _s
en	1520	1384		pn	1527	1383
tn	1564	1406	đ	men	1521	1383
ten	1525	1378	t-0	chxn	1519	1384
pen	1542	1386	C	chxn	1523	1390
ĥen	1524	1375				
*H ₃ N \ NH ₃ * (-	000c~Ph);	hv, Ar, 10 h	 No reaction 		HO	
1•	e n				~ +=	illio ocid
	DOC_Ph)2	hv, Ar, 10 h	HO ₂ C CO ₂ H	Ph LCO ₂ H Ph HO ₂ C	+ (^{Рћ} соон	+ Ph HO ₂ C
1•c- c l	חצח	ſ	β-truxinic acid 64 %	δ-truxinic acid 3 %	11 %	20 %
NH3 ⁺ NH3 ⁺	⁰⁰⁰ Ph) ₂	hv, Ar, 10 h	$- \begin{array}{c} Ph \\ Ph \\ CO_2H + \\ O_2C \end{array}$	Ph LCO ₂ H Ph HO ₂ C	+ (^{Рћ} соон	+ Ph HO ₂ C
1-1-01		ε·	-truxillic acid 43 %	o-truxinic acid 5 %	23 %	29 %

Table II. The Asymmetric (v_{as}) and Symmetric (v_s) Stretching Frequencies of the COO⁻ Group for the Double Salts 1-diamine in KBr; cm⁻¹.

Since trans-cinnamic acid (1) photoreacts very efficiently in both the solid and solution phases, 10,11 it is interesting that such a high photoreactivity for 1 was completely suppressed by salt formation with en. The X-ray structure analyses of the double salts 1-en, 1-pen, and 1-hen were successfully carried out.¹³ Figure 1 displays a stereoview of the crystal packing for 1-en and 1-hen. The layered structure of 1-en is characteristic and en adopts an anti conformation. While pen is partially coiled (not shown), hen is in a fully extended conformation. It is found in all three crystals that the molecules of 1 do not overlap each other and that the nearest neighbor double bonds are more than 4.8 Å away. Since these distances are well beyond Schmidt's critical distance (4.2 Å), ^{1c} their observed low reactivities for photodimerization (Table I) are not surprising. Furthermore, the packing for 1-en seems more compact than that for 1-pen and 1-hen, since their crystal densities D_x are 1.226, 1.169, and 1.181 g/cm³, respectively. This compactness may be the reason why 1-en neither photodimerizes nor photoisomerizes at all.

Despite many trials, the highly photoreactive double salts 1-t-chxn and 1-c-chxn did not grow into crystals of good quality, hampering their X-ray studies. However, from consideration of the ring structure constraint of the component diamine,¹⁴ they are likely to adopt an overlap configuration. The relatively reactive double salt 1-tn did not give good crystals either, but a three-methylene spacer in tn reminds us of the n = 3 rule in intramolecular excimer formation.¹⁵ Similarly, the rate of photocyclization of polymethylene dicinnamate was enhanced by a trimethylene chain,¹⁶ implying an overlap configuration of the dicinnamate.

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References and Notes

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- 2 For example, *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, Chapter 2.
- 3 (a) Desiraju, G. R. Crystal Engineering: The Design of Organic Solids; Elsevier: Amsterdam, 1989. (b) Ramamurthy, V.; Venkatesan, K. Chem. Rev. 1987, 87, 433-481.

- 4 This paper is a part of our project for the design of photoreactive multi-component crystals by using noncovalent forces.⁵
- 5 Ito, Y.; Asaoka, S.; Ohba, S. Tetrahedron Lett. 1994, 35, 8193-8196. Fu, T. Y.; Liu, Z.; Scheffer, J. R.; Trotter, J. J. Am. Chem. Soc. 1993, 115, 12202-12203.
- 6 A vessel slightly modified from the original one (Ito, Y. Mol. Cryst. Liq. Cryst. 1992, 219, 29-36) was used.
- 7 For example, a white powder (158 mg) obtained from photolysis of the double salt 1-t-chxn was fractionally recrystallized by using 10 mL of methanol, resulting in the isolation of pure colorless plates of the 1:1 (from NMR) ε-truxillic acid/t-chxn salt; yield 57 mg, mp 146-150 °C. In addition, 2 mg of white crystals of the 1:1 δ-truxinic acid/t-chxn salt contaminated with a small amount of the above double salt was obtained. Free ε-truxillic acid was recovered by dissolving 3 mg of the double salt in 1 mL of water, followed by acidifying the solution with 1 M HCl to pH 1, as white needles (1.5 mg), mp 200-202 °C (lit mp 192 °C).
- 8 trans-Cinnamic acid (1) can occur in two crystal modifications (α and β), but the α form is usually obtained under normal recrystallization conditions.⁹
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- 12 Under the same reaction conditions, trans-cinnamic acid (1) was entirely converted into α -truxillic acid. The low reactivity of the double salts is probably due to the effect of crystal packing. In fact, solutionphase photolyses of 1 (0.01-0.125 M) in the presence of en (0.003-1.0 M) in methanol led to efficient trans-cis photoisomerization, being as efficient as in the absence of en. Hence, the quenching of excited 1 by en is unlikely to occur.
- 13 Crystal data. 1•en: triclinic $P\overline{I}$, a = 8.8840, b = 24.560, c = 8.8527 Å, $\alpha = 91.208^{\circ}$, $\beta = 91.021^{\circ}$, $\gamma = 10.021^{\circ}$, γ
- 88.665°, Z = 4, $D_x = 1.226$ g/cm³, R = 0.039. 1•pen: triclinic $P\overline{I}$, a = 14.390, b = 16.380, c = 10.335Å, $\alpha = 95.72^{\circ}$, $\beta = 97.31^{\circ}$, $\gamma = 108.59^{\circ}$, Z = 4, $D_x = 1.169$ g/cm³, R = 0.054. 1•hen: orthorhombic *Ccc2*, a = 15.647, b = 19.221, c = 7.789 Å, Z = 4, $D_x = 1.181$ g/cm³, R = 0.035. The details of their crystallographic determinations will be reported elsewhere.
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Figure 1. Stereoview of the crystal packing and ORTEP view for (a) 1-en and (b) 1-hen.

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