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Regioselective Hula-twist photoisomerization of cinnamate esters in organic glass

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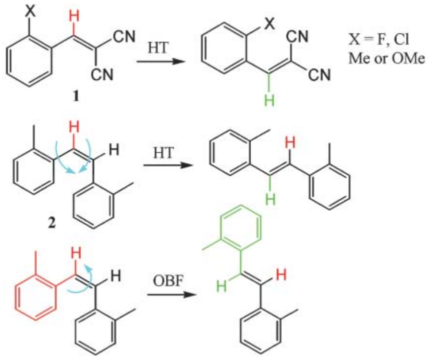
Received (in Corvallis, OR, USA) 15th July 2004, Accepted 2nd September 2004
First published as an Advance Article on the web 18th October 2004

Irradiation of ethyl *cis-o*-fluorocinnamate and related compounds in organic glass led to two HT-isomerization processes that exhibit a strong preference at C-β than at C-α as shown by low temperature UV absorption spectroscopy and supported by *ab initio* calculations.

Earlier, studies of photoisomerization of substituted styrene[1] and stilbenes[2] in low temperature organic glass were reported. Their photochemical behavior was shown to be different from that in solution at room temperature. The results were consistent with the thesis that one-bond flip (OBF), or conventional torsional relaxation, is the predominant process in solution, while the volume conserving Hula-twist (HT)[3] process is the predominant process in the confined medium of frozen organic glass.

The design of the systems for these initial studies (*e.g.*, **1** and **2**) was such that there was only one possible mode of HT:



Now we wish to report the result of photoisomerization of a cinnamate ester (**3**) in an organic glass. Clearly, for the mono-ester there are two possible modes of HT (at center α and center β relative to the ester group). Regioselectivity for these two modes of isomerization has now been examined.

Similar to *trans*-1,2-diarylethylenes in frozen media,[4] *trans* ethyl *o*-fluorocinnamate (*trans*-**3**)[5] was found to be unreactive when irradiated in EPA glass.[6] When the *cis* isomer of ethyl *o*-fluorocinnamate (*cis*-**3**)[5] was irradiated (> 310 nm) in EPA glass,[6] a simple one-to-one conversion to a red-shifted photoproduct was observed (isosbestic points at 225 and 248.5 nm) during early stages of irradiation (to 160 s) (Fig. 1a). Prolonged irradiation (> 900 s), however, led to a substantial drift of the isosbestic point, a further red-shift of the absorption spectrum and a prominent display of vibrational fine structures (Fig. 1b). The secondary photoproduct was marked by a new peak (310 nm) at the red-edge of the absorption bands. That two separate photochemical processes are involved in different periods of irradiation is also revealed in changes of absorbance *versus* time (see the semi-log plot in insert of Fig. 1) and in difference absorption spectra (not shown). The initial straight line exhibited considerable curvature (green dots) at the later stage of irradiation.

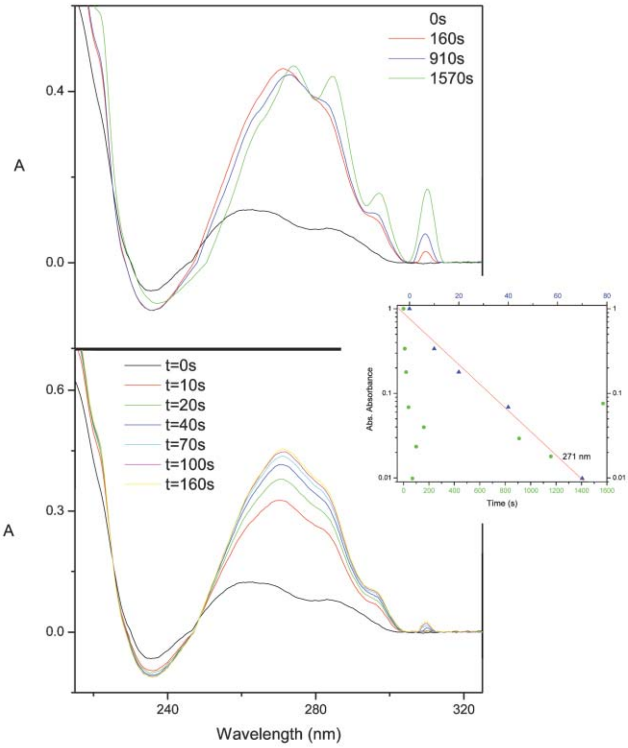


Fig. 1 Irradiation of *cis*-ethyl *o*-fluorocinnamate (*cis*-**3**) in EPA glass at liquid nitrogen temperature (> 310 nm, Corning 0-54 filter) in an Oxford low temperature cryo-tip cell. (Lower) Absorption curves before and after irradiation of 10, 20, 40, 70, 100, 160 s. (Upper) Absorption curves after irradiation of 160, 910, 1570 s. The insert is a semi-log plot showing disappearance of *cis*-**3** against time (green points for the lower timescale; blue points for the expanded earlier time period).

The 310-peak turned out to be part of the well structured lowest transition band of the *trans* isomer of **3** (*trans*-**3**) as demonstrated in the following experiment. A sample of *cis*-**3** after irradiation for 910 s was warmed to room temperature and re-cooled to −196 °C. The spectra before and after warming are shown in Fig. 2a. Also shown in the figure are absorption spectra of pure *trans*-**3** at −196 °C and simulated spectra containing 54% *trans*-**3** and 46% *cis*-**3** (Fig. 2a). Clearly, the maxima of the irradiated and re-cooled sample are identical to those of an authentic sample of *trans*-**3**. And, from the 160 s irradiated sample, we calculated the absorption spectrum of the initial photoproduct (minus 5% of *trans*-**3**). Its weakly structured broad band is very different from that of the stable *trans*-**3**. This structureless feature plus its ready conversion to the stable *trans* led to the assignment of the more crowded *Z*-conformer (*trans*-**3′**) to the new photoproduct. The sample of 1570 s appeared to be largely *trans*-**3** although possibly with the presence of small amounts of both *cis*-**3** and *trans*-**3′** (note that *trans*-**3** is photochemically unreactive).

Hence, the initial period of irradiation must involve the establishment of a photo-equilibrium between the initial *cis* isomer and the unstable *trans*-**3′**. This is, however, a pseudo

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† On leave from U. Pittsburgh at Johnston, January 1 – May 31, 2004.

DOI: 10.1039/b411306n

Table 1 Calculated structures of energy-minimized cinnamate *cis*-**3**

Method of calc.[a]	Ring/chain conformation Input	 Calculated	Enone Calculated[b]	Rel. energy & absorption max. Calc. rel. E[c]	 Calc. abs. max.[c]
Cis-**3**					
RHF/6-31G(d)	s-*E*, 0°	s-*E*, 21.4°	s-*cis*, 21.4°	3.27 kcal mol^{-1}	270, 282 nm
RHF/6-31G(d)	s-*Z*, 30°	s-*E*, 21.4°	s-*cis*, 21.4°		
B3LYP/6-31G*	s-*E*, 22°	s-*E*, 13.1°	s-*cis*, 13.1°		
trans-**3**				0.00	271, 287 nm

[a] M. J. Frisch .. (33 others) .. and J. A. Pople, Gaussian 94, Revision E.2, Gaussian, Inc., Pittsburgh PA, 1995. [b] The calculated energy difference between s-*cis* and s-*trans* of the ene-ester fragment was found to be 1.13 kcal mol^{-1} favoring the s-*cis*. [c] By ZINDO configuration interaction based on MOPAC PM3 geometries, dihedral angles initially at DFT optimized values. [d] DHf = −91.45 kcal mol^{-1}.

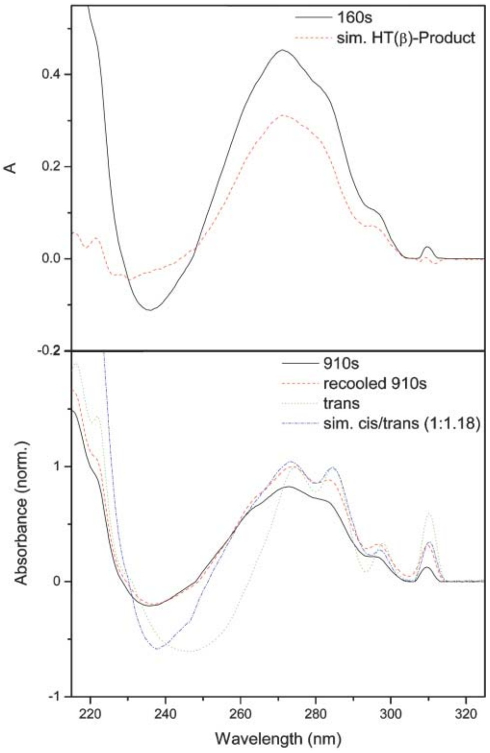
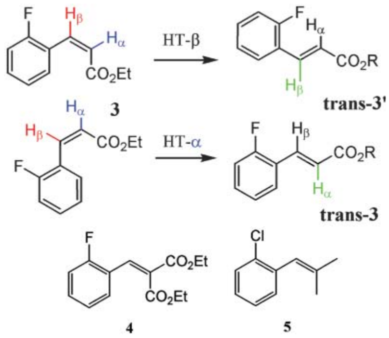


Fig. 2 (Lower) Absorption spectrum (—) of *cis*-**3** after 910 s of irradiation at −196 °C superimposed with that of the same sample but after warming to room temperature and re-cooled to −196 °C (———) superimposed with that of the pure *trans*-**3** (⋯..) and the simulated spectrum of a sample containing 55% *trans*-**3** and 45% *cis*-**3** (-.-.-.). (Upper) Absorption spectrum of *cis*-**3** after 160 s of irradiation (—) superimposed with that of the calculated spectrum of the photoproduct (- - -).

photo-equilibrium because of the ensuing conversion to the thermally stable *trans* isomer. Given the confined conditions (solid glass) for these photochemical reactions, it should be safe to assume that the isomerization reactions proceeded by way of the volume conserving HT processes.[3] In fact, the results are consistent with an efficient initial HT-process at center β (to the ester), in a way similar to the disubstituted compounds of the general formula **1**, to give, in this case, the unstable conformer *trans*-**3**′. The second less efficient photochemical reaction must then be HT at center α, giving the more stable *trans*-**3**.[7] The relative efficiencies of HT-β to HT-α are ~10 : 1.

The above explanation implies that *cis*-**3** exists primarily in one conformation. To obtain corroborative evidence we carried out *ab initio* calculations for the compound. The results based on two different levels of calculation are shown in Table 1. As expected the data show that the compound is likely to exist in a ring/chain twisted (~21°) s-*E* conformation. Notice the absence of the stable s-*Z* conformer regardless of whether we started the calculation with the s-*E* or the s-*Z* conformation. The same energy minimized s-*E* structure was obtained.



We have also carried out low temperature photoisomerization of the diester **4**[5] under the same confined conditions. Its spectral changes clearly revealed a simple one-to-one conversion as reflected by the sharp isosbestic points similar to the dicyano-analog (**1** where X = F) reported earlier.[1] Clearly, the removal of Hα has simplified the photochemical transformation. The result also says that, given the similar steric crowding in *cis*-**3** and **4**, conformational changes of the ester functional group(s) do not play a role in the observed different photochemical changes of the two compounds.

We have also found that the dimethyl analog **5** failed to exhibit any photochemical changes under the same conditions. The negative result is consistent with the activated energies (approaching 7 kcal mol^{-1}) recently reported for photoisomerization of simple styrene derivatives (all hydrocarbons).[8] Thus, the combined results suggest that for styryl derivatives, HT can take place only in derivatives containing at least one electron withdrawing group.

Supported by a grant from the National Science Foundation (CHE-32250). T. Kawahara assisted in the synthesis of **3**–**5**.

Notes and references

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2 Y. Imamoto, T. Kuroda, M. Kataoka, S. Shevyakov, G. Krishnamoorthy and R. S. H. Liu, *Angew. Chem., Int. Ed.*, 2003, **42**, 3630–3633.
3 (*a*) R. S. H. Liu and A. E. Asato, *Proc. Natl. Acad. Sci. USA*, 1985, **82**, 259–263; (*b*) R. S. H. Liu and G. S. Hammond, *Proc. Natl. Acad. Sci. USA*, 2000, **97**, 11153–11158; (*c*) R. S. H. Liu, *Acc. Chem. Res.*, 2001, **34**, 555–562.
4 (*a*) M. V. Alfimov, V. F. Razumov, A. G. Rachinsky, V. N. Listvan and Yu. B. Sheck, *Chem. Phys. Lett.*, 1983, **101**, 593–597; (*b*) N. Castel and E. Fisher, *J. Mol. Struct.*, 1985, **127**, 159–166.
5 Compounds **3**–**5** were prepared *via* standard condensation with *o*-fluorobenzaldehyde (from Aldrich). Structures were confirmed by ^{1}H NMR and UV spectra.
6 An Oxford Optistat photochemical cell coupled with a Hg-Xe arc lamp; absorption spectra recorded on a PE λ-19 spectrometer.
7 A reviewer suggested direct conversion from *trans*-**3**′ to *trans*-**3**. Although we do not have experimental evidence to rule out this possibility, such a process is more volume-demanding than the unobserved OBF process around the C=C bond. Also, a photochemical process involving single bond rotation does not agree with the NEER postulate.
8 F. Lewis and X.-B. Zuo, *J. Am. Chem. Soc.*, 2003, **125**, 8806–8813.