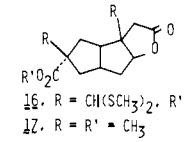
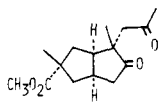
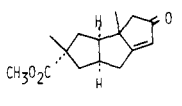
The keto ester was transformed into the lactone **14**,[3,4] mp 158–159.5 °C (K_2CO_3, CH_3OH, H_2O, RT, 2 h; $NaBH_4$, C_2H_5OH, THF, 0 °C, 1 h; Ph_3P, $CH_3O_2CN{=}NCO_2CH_3$, THF, RT, 4 h; overall 92%).[8] The olefinic carbons of the latter, after conversion of the nitrile to the carbomethoxy group (dry HCl, CH_3OH, ether, 96%) were directly converted to methyl groups without isolating any intermediates. Thus, after ozonolysis (CH_3OH, CH_2Cl_2, −78 °C, and then $(CH_3)_2S$), methyl mercaptan and boron trifluoride etherate were added to form the bisthioacetal **16** which was directly subjected to desulfurization with W-5 Raney nickel to give the tricyclic lactone **17**,[3,4] mp 45–47 °C, in 75% yield. The acid **18**[3] (1 N aqueous KOH, THF, reflux, 2 h, and then acidify, 84%, mp 126.5–128 °C) was converted to the known methyl ketone **19**[2a] by standard methods (CH_3Li, THF, −78 °C; CH_2N_2, ether, 0 °C; $C_5H_5NH^+$-CrO_3Cl^-, CH_2Cl_2, NaOAc, RT; 70% yield) and subsequently treated with base (KOC_4H_9-*t*, *t*-C_4H_9OH, RT, 79% yield) to effect an intramolecular aldol reaction to give the known tricycle **20**.[2a] Comparison of its spectral data



16, R = $CH(SCH_3)_2$, R' = CH_3
17, R = R' = CH_3
18, R = CH_3, R' = H



19



20

with those of an authentic sample of **20** confirmed their identity. Furthermore, tricyclic enone **20** was converted to hirsutic acid by the method of Matsumoto et al.[2a] Again, comparison of our synthetic sample of racemic hirsutic acid C with an authentic sample of the natural product by IR, 270-MHz ^1H NMR, ^{13}C NMR, and chromatography confirmed their identity except for optical rotation.[9]

Not only does this route rigorously control relative stereochemistry but it also offers an opportunity to explore control of absolute stereochemistry which is created in the conversion of achiral cyclohexenone **5** to chiral bicyclo[3.2.1]octanone **6**. Treatment of **5** with (−)-quinine gave the bicyclic ketone **6** in 83% yield with $[\alpha]^{25}_D$ −68° (*c* 0.84 acetone). Use of 25 mol % of the chiral shift reagent Eu(hfbc)$_3$[11] separates the methyl ester signals of the two enantiomers (δ 4.17 and 4.21) at 270 MHz to allow determination of the ratio as 65% (−) enantiomer and 35% (+) enantiomer, respectively. This degree of asymmetric induction is delightfully high for a Michael reaction with a carbon nucleophile[10] and offers the promise of a chiral synthesis of this interesting class of compounds.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs. We thank Professor G. Mellows for a generous gift of hirsutic acid C and Professor Matsumoto for copies of the spectral data of tricyclic enone **20.** We also express our appreciation to Dr. V. Reutrakul for his early contributions to this project.

References and Notes

(1) Comer, F. W.; McCapra, F., Qureshi, I. H.; Scott, A. I. *Tetrahedron* **1967**, *23*, 4761; Comer, F. W.; Trotter, J. *J. Chem. Soc. B* **1966**, 11. For biosynthesis see Felini, T. C.; Mellows, G. *J. Chem. Soc., Chem. Commun.* **1974**, 63. For related compounds see the following. Ayanoglu, E.; Gebreyesus, T.; Beechan, C. M.; Djerassi, C.; Kaisin, M. *Tetrahedron Lett.* **1978**, 1671. Nakamura, H.; Takita, T.; Umezawa, H. *J. Antibiot.* **1974**, *27*, 301.

(2) A nonstereocontrolled synthesis has been reported. See the following. (a) Hashimoto, H.; Tsuzuki, K.; Sakan, F.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1974**, 3745. Sakan, F.; Hashimoto, H.; Ichihara, A.; Shirahama, H.; Matsumoto, T. *ibid.* **1971**, 3703. (b) Lansbury, P. T.; Wang, N. Y.; Rhodes, J. E. *ibid.* **1972**, 2053; **1971**, 1829. (c) Hayano, K.; Ohfune, Y.; Shirahama, H.; Matsumoto, T. *ibid.* **1978**, 1991.

(3) This compound has been fully characterized by spectroscopic means and elemental composition established by elemental analysis and/or high resolution mass spectroscopy.

(4) **5:** IR 2252, 1728, 1715 cm^{-1}; NMR δ 2.78 (2, H, s), 3.76 (3 H, s). **6:** IR 2250, 1716, 1663 cm^{-1}; NMR δ 3.46 (1 H, m), 3.71 (3 H, s), 5.88 (1 H, t, J = 3 Hz). **7:** IR 2247, 1722 cm^{-1}; NMR δ 1.7–3.0 (12 H, m), 3.64 (3 H, s). **9:** IR 2400–3600, 2240, 1718, 1655 cm^{-1}; NMR δ 1.6–3.0 (11 H, m), 3.64 (3 H, s), 4.39 (1 H, t, J = 4 Hz), 5.68 (1 H, s). **11:** IR 3630, 3510, 2242, 1719, 1630, 1603 cm^{-1}; NMR δ 1.1–3.0 (8 H, m), 3.53 (2 H, m), 3.66 (3 H, s), 4.36–4.64 (0.7 H, m), 5.48 (0.3 H, s), 5.66 (0.7 H, s), 6.07 (0.7 H, d, J = 9.5 Hz), 6.39 (1 H, d, J = 9.5 Hz), 7.36 (0.3 H, d, J = 9.5 Hz). **13:** IR 2246, 1735 cm^{-1}; NMR δ 1.9–3.2 (10 H, m), 3.60 (3 H, s), 5.10 (1 H, d, J = 9 Hz), 6.20 (1 H, d, J = 9 Hz); ^{13}C NMR δ 214.3, 170.9, 135.1, 126.5, 122.2, 55.5, 51.6, 48.8, 44.9, 42.2, 37.6, 37.5, 37.3, 35.2. **14:** IR 2256, 1775, 1648 cm^{-1}; NMR δ 1.8–3.1 (8 H, m), 2.56 (2 H, s), 4.49 (1 H, d, J = 6 Hz), 5.45 (1 H, d, J = 9.5 Hz), 6.10 (1 H, d, J = 9.5 Hz); ^{13}C NMR δ 174.6, 134.6, 127.6, 122.4, 90.6, 55.2, 49.7, 49.1, 41.4, 40.1, 38.0, 37.5 and 36.6. **17:** IR 1787, 1734 cm^{-1}; NMR δ 1.1–2.9 (8 H, m), 1.19 (3 H, s), 1.28 (3 H, s), 2.39 (s, 2 H), 3.63 (3 H, s), 4.50 (1 H, dd, J = 6, 2 Hz).

(5) See the following for example. Woodward, R. B.; Singh, T. *J. Am. Chem. Soc.* **1950**, *72*, 494. Stork, G.; Tomasz, M. *ibid.* **1962**, *84*, 310.

(6) In this compound, the exocyclic double bond is an *E,Z* mixture, but, since this stereochemistry is inconsequential to the synthesis, no attempt to separate the two isomers was made.

(7) Stetter, H.; Kuhlmann, H. *Chem. Ber.* **1976**, *109*, 2890. Stetter, H.; Basse, W.; Wiemann, K. *ibid.* **1978**, *111*, 431.

(8) For use of this reaction in macrolactonization, see the following. Fukuyama, Y.; Kirkemo, C. L.; White, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 646. Seebach, D.; Seuring, B.; Kalinowski, H.-O.; Lubosch, W.; Renger, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 264. Kurihara, T.; Nakajima, Y.; Mitsunobo, O. *Tetrahedron Lett.* **1976**, 2455.

(9) The overall yield of 3.6% to tricyclic enone **20** demonstrates the efficiency of this approach compared with that of the earlier nonstereocontrolled synthesis.

(10) Cf. the following. Wynberg, H.; Helder, R. *Tetrahedron Lett.* **1975**, 4057. Helder, A.; Arends, R.; Bolt, W.; Hiemstra, H.; Wynberg, H. *ibid.* **1977**, 2181. Also see Hashimoto, S.-i.; Komeshima, N.; Yamada, S.-i.; Koga, K. *ibid.* **1977**, 2907.

(11) The symbol hfbc represents 2-heptafluorobutyrylcamphor: Goering, H. L.; Eikenberry, J. N.; Koermer, G. S.; Lattimer, C. J. *J. Am. Chem. Soc.* **1974**, *96*, 1493.

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Stereoselective Energy Transfer Induced by Circularly Polarized Light

Sir:

Generation of optical activity in the absence of added chemical or biochemical chiral agents is a fascinating problem of fundamental importance. Photolysis by circularly polarized light (CPL) has been the most successful approach to date.[1,2] Partial photoresolution,[3] asymmetric destruction,[4] and synthesis[5] initiated by CPL have been reported. All of these experiments relied upon the determination of enantiomeric selectivities generated, often in relatively small amounts, in the products or that remained in the reactants subsequent to photodecomposition. We report here the direct consequences of irradiating with CPL. Intramolecular energy transfer, induced by CPL, showed remarkable stereoselectivity.

Emission spectra of D-tryptophan (D-Trp) and L-tryptophan (L-Trp) excited at 284 nm in methanol by unpolarized and by left and right CPL[6] are shown in Figure 1. No difference was observed in the emission spectra between equal concentrations and optical purities of D-Trp and L-Trp if irradiated by unpolarized light. Irradiation by left CPL, however, resulted in appreciably higher fluorescence efficiency of D-Trp than L-Trp. Irradiation with right CPL produced the same difference between D-Trp and L-Trp in the opposite direction (Figure 1). This observation lends credence to the purities of our samples and the equivalence of left and right CPL in our instrument and substantiates the observed effect. Differences in fluores-

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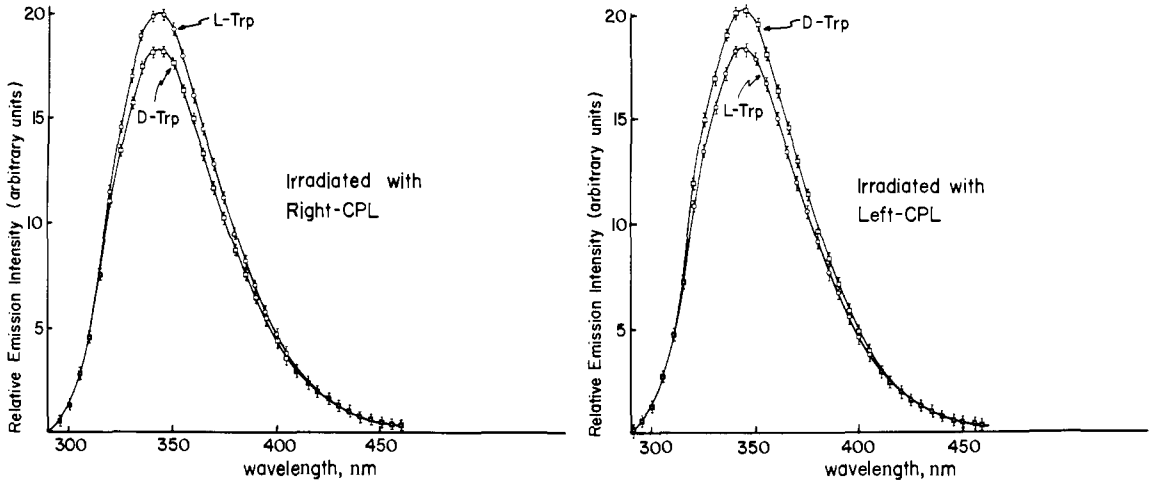
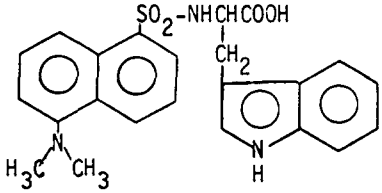


Figure 1. Emission spectra of air-saturated 5.0×10^{-5} M D-Trp (□) and L-Trp (○) in MeOH excited by right and left CPL. See note 6 for experimental details.

cence intensities are the consequence of the different orientations of the electric and magnetic dipoles of the optically active tryptophan relative to the vector potential and direction of propagation of the light wave. This effect has been recognized and is related to fluorescence detected circular dichroism (FDCD).[7] Relative fluorescence efficiencies[8] are collected in Table I. Stereoselectivities induced by CPL in methanol are substantially greater than those in glycerol.[10] This is a direct consequence of the reduced rotatory Brownian motion during the lifetime of excited tryptophan in glycerol which results in decreasing the anisotropic population. Analogous photoselection has been previously documented in FDCD.[9]

Stereoselective energy transfer is believed to be the most significant aspect of the present work. Intramolecular Förster-type excitation energy transfer from tryptophan to 5-dimethylaminonaphthalene-1-sulfonamide was examined. Preparation and purification of 5-dimethylaminonaphthalene-1-sulfonyl-L-tryptophan (dansyl-L-Trp, **1**) and 5-dimethylaminonaphthalene-1-sulfonyl-D-tryptophan (dansyl-D-Trp, **1**), as well as the experimental approach in following energy transfer, corresponded to those reported for dansyl-L-Trp.[11] Once again, there was no difference in the emission spectra of the dansyl moiety between equal concentrations and optical purities of dansyl-D-Trp and dansyl-L-Trp if unpolarized light is used as the excitation source. Marked difference in fluorescence efficiencies between the enantiomers are seen, however, upon exciting the tryptophan moiety by CPL (Figure 2). It is pleasing to observe the opposite effect of left and right CPL. The data can be more quantitatively discussed in terms of energy transfer efficiencies, T values (Table II). Correction has been made for the different absorptions of the CPL by dansyl-D-Trp and dansyl-L-Trp, excited by unpolarized light; these agree well with previously published data (T = 54% in ethanol, T = 83% in glycerol).[11] In methanol, excitation by right CPL increased the transfer efficiency of dansyl-L-Trp (from (50.6 ± 1.3) % to (55.0 ± 2.9) %), but it decreased that



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dansyl-D-Trp or dansyl-L-Trp

Table I. Fluorescence Efficiencies of D-Trp and L-Trp, ϕ_{Trp}, Excited by CPL[a]

excitation source	solvent	$\phi_{D\text{-}Trp}$	$\phi_{L\text{-}Trp}$	% stereoselectivity[b]
right circularly polarized light[c]	MeOH	0.211	0.231	4.53
left circularly polarized light[c]	MeOH	0.224	0.206	4.19
right circularly polarized light[c]	glycerol	0.615	0.652	2.92
left circularly polarized light[c]	glycerol	0.610	0.596	1.16

[a] Determined on newly prepared air-saturated solutions of 5.0×10^{-5} M D-Trp and L-Trp. Fluorescence efficiencies are related to that of 5.0×10^{-5} M naphthalene (an achiral molecule) in the same solvent irradiated by CPL. Emission spectra of 5.0×10^{-5} M naphthalene obtained upon excitation with left CPL was identical with that excited by right CPL. Naphthalene fluorescence efficiency was related to that of L-Trp (excited by unpolarized light), assuming the latter to be 0.20 in water. See note 6 for experimental details. [b] Defined as $100\|\phi_{L\text{-}Trp} - \phi_{D\text{-}Trp}\|/(\phi_{L\text{-}Trp} + \phi_{D\text{-}Trp})$. [c] Looking toward the light source clockwise rotation corresponds to right and counterclockwise to left circularly polarized light.

of dansyl-D-Trp (from (51.0 ± 1.3) % to (49.6 ± 2.6) %). Irradiation by left CPL has the opposite effect. The observed stereoselectivities of intramolecular energy transfer on excitation by CPL is up to 5.3%. The magnitude of this differentiation far exceeds anything previously observed for *asymmetric synthesis* induced by CPL.[5] The rate constant of transfer through resonance interaction, k_T, is expressed by the Förster equation[12]

$$k_T = \frac{9(\ln 10)K^2}{128\pi^5 N n^4 \tau R^6} \int F_D(\lambda)\epsilon_{A(\lambda)}\lambda^4 \, d\lambda \qquad (1)$$

or in terms of experimental parameters

$$k_T = T/\phi_D\tau \qquad (2)$$

where K = dipole-dipole orientation factor, N = Avogadro's number (mol^{-1}), n = refractive index of the medium, R = distance between donor and acceptor (cm), $\int F_{D(\lambda)}\epsilon_{A(\lambda)}\lambda^4 \, d\lambda$ = overlap integral ($cm^6\ mol^{-1}$), k_T = the rate constant for the transfer, ϕ_D = donor fluorescence efficiency in the presence of the transfer, and τ = the natural lifetime of the donor. The calculated overlap integrals for energy transfer for dansyl-D-Trp and dansyl-L-Trp were the same within the limits of our experimental error and they were unaffected by the origin of the excitation.[13] Molecular models did not indicate an appreciable difference in the distances between chromophors on comparing dansyl-D-Trp with dansyl-L-Trp. Similarly, the

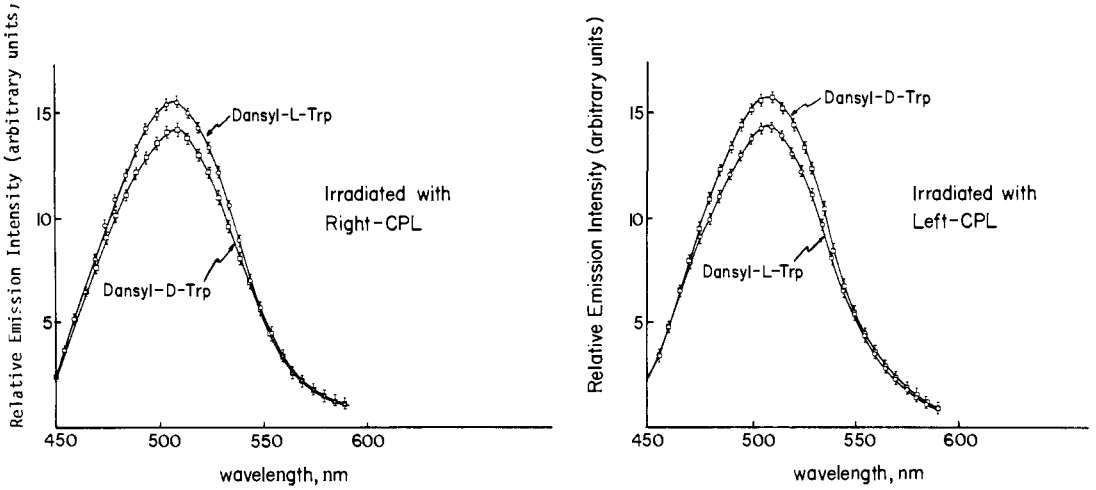

Figure 2. Emission spectra of 5.0×10^{-5} M dansyl-D-Trp (□) and dansyl-L-Trp (○) in MeOH excited by right and left CPL. See note 6 for experimental details.

Table II. Energy Transfer Efficiencies[a]

excitation source	solvent	% T, dansyl-D-Trp	% T, dansyl-L-Trp	% stereoselectivity[b]
unpolarized light	MeOH	51.0 ± 0.2	50.6 ± 0.4	0.39 ± 0.42
right circularly polarized light[c]	MeOH	49.6 ± 1.2	55.0 ± 1.0	5.21 ± 1.30
left circularly polarized light[c]	MeOH	55.7 ± 1.1	50.9 ± 1.1	4.51 ± 1.35
unpolarized light	glycerol	85.0 ± 1.1	84.9 ± 1.3	0.06 ± 1.02
right circularly polarized light[c]	glycerol	76.3 ± 2.6	84.9 ± 1.7	5.33 ± 1.92
left circularly polarized light[c]	glycerol	82.9 ± 1.1	76.0 ± 1.0	4.34 ± 0.95

[a] Calculated from $T = (A_A/A_D)[(I/I_A - 1]^{14}$ where A_D and A_A are the absorbances of unpolarized, left CPL, or right CPL of dansyl-D-Trp or dansyl-L-Trp and dansylglycine at 284 nm, respectively; I and I_A are emission intensities of dansyl-D-Trp or dansyl-L-Trp and dansylglycine at 510 nm, excited by unpolarized, left CPL, or right CPL at 284 nm, respectively. Data for each system represent the mean of five independent determinations for newly prepared air-saturated solutions of 5.0×10^{-5} M dansyl-D-Trp, dansyl-L-Trp, and dansylglycine at 25.0 °C. Errors were calculated as described in Y. Beers, "Introduction to the Theory of Errors", Addison Wesley, Inc., Cambridge, 1953, p 26. Concentrations and optical purities of pairs of enantiomers agreed within 0.5%. See note 6 for experimental arrangements. [b] Defined as $100|T_{\text{dansyl-D-Trp}} - T_{\text{dansyl-L-Trp}}|/(T_{\text{dansyl-D-Trp}} + T_{\text{dansyl-L-Trp}})$. [c] Looking toward the light source clockwise rotation corresponds to right and counterclockwise to left circularly polarized light.

orientation factor is expected to be the same for both enantiomers. The stereoselective energy transfer predominantly originates, therefore, in differences in the concentrations of excited-state enantiomers, formed by CPL (Table I).

Stereoselectivities for energy transfer are seen to be somewhat enhanced with respect to stereoselective fluorescence efficiencies (compare Tables I and II). This effect cannot originate in differences in τ since, once absorbed, the chirality of the light is lost and the lifetimes of the excited states of the enantiomers should be identical. Different conformers of dansyl-Trp (D or L) may, however, absorb the chiral light differently.[15] This would, in turn, result in stereodiscriminations in the excited-state concentrations (i.e., irradiation by left CPL would further enhance [dansyl-D-Trp]* and irradiation by right CPL would further enhance [dansyl-L-Trp]*). Additional stereoselectivities could arise in the energy transfer step if the lifetimes of given conformers are longer than the lifetimes of their excited states.[16] The pronounced stereoselective energy transfer in glycerol could be the consequence of the decreased rate of conformational changes in this solvent. Currently, we are designing experiments which will allow time resolution of these processes on suitable models. Our goal is to obtain substantially enhanced CPL induced stereoselectivities through a proper understanding of the photophysics involved.

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References and Notes

(1) O. Buchard, *Angew. Chem., Int. Ed. Engl.*, **13**, 179 (1974).
(2) Y. Izumi and A. Tai, "Stereodifferentiating Reactions", Academic Press, New York, 1977.
(3) K. L. Stevenson and J. F. Verdieck, *J. Am. Chem. Soc.*, **90**, 2974 (1978); K. L. Stevenson and J. F. Verdieck, *Mol. Photochem.*, **1**, 271 (1969); B. Norden, *Acta Chem. Scand.*, **24**, 349 (1970); K. L. Stevenson, *J. Am. Chem. Soc.*, **94**, 6652 (1972).
(4) W. Kuhn and F. Braun, *Naturwissenschaften*, **17**, 227 (1929); W. Kuhn and E. Knopf, *Z. Phys. Chem., Abt. B*, **7**, 292 (1930); W. Kuhn and E. Knopf, *Naturwissenschaften*, **18**, 183 (1930); P. Boldt, W. Thielecke, and H. Luthe, *Chem. Ber.*, **104**, 353 (1971); A. Moradpour, J. F. Nicoud, G. Balavoine, H. Kagan, and G. Tsoucaris, *J. Am. Chem. Soc.*, **93**, 2353 (1971); G. Balavoine, A. Moradpour, and H. B. Kagan, *ibid.*, **96**, 5152 (1974); H. B. Kagan, G. Balavoine, and A. Moradpour, *J. Mol. Evol.*, **4**, 41 (1974); J. F. Nicoud, C. Eskenazi, and H. B. Kagan, *J. Org. Chem.*, **42**, 4270 (1977); B. Norden, *Nature (London)*, **266**, 567 (1977).
(5) G. Tsoucaris, G. Balavoine, A. Moradpour, J. F. Nicoud, and H. B. Kagan, *C.R. Hebd. Seances Acad. Sci.*, **272**, 1271 (1971); A. Moradpour, J. F. Nicoud, G. Balavoine, and H. Kagan, *J. Am. Chem. Soc.*, **93**, 2353 (1971); A. Moradpour, H. Kagan, M. Baes, G. Morren, and R. H. Martin, *Tetrahedron*, **31**, 2139 (1975); J. F. Nicoud and H. B. Kagan, *Isr. J. Chem.*, **15**, 78 (1976/77); W. J. Bernstein, M. Calvin, and O. Buchardt, *J. Am. Chem. Soc.*, **94**, 494 (1972); W. J. Bernstein, M. Calvin, and O. Buchardt, *ibid.*, **95**, 527 (1973).
(6) A 150-W Xenon lamp was used as the excitation source. The beam was passed through a double grating 0.22-m excitation monochromator (set at 284 nm, using a 2-nm band path and a 5-mm slit) and split into two portions. The smaller portion was allowed to impinge upon a Rhodamine-B quantum counter. The major part of the beam excited the sample (by unpolarized light). Circularly polarized light was obtained by passing the major part of the beam through a UV Glan-Thompson polarizer and a cemented zero-order quarterwave plate (284 nm) whose axis is set at +45 or −45° corresponding to the axis of the polarizer prior to impinging upon the sample. Sample solutions were thermostated at 25 °C. Circular polarization of the light was established by observing no changes in the light intensities on rotating a polacoat ultraviolet polarizing filter (analyzer) placed after the quarterwave plate. Emitted light was observed at 90° to the excitation beam. It was passed through an UV scrambler (depolarizer) and a double grating 0.22-m emission monochromator (using a 2-nm band path and a 1.25-mm slit). Three photomultipliers were used to determine light intensities emerging from the quantum counter, those transmitted (180°) and emitted (90°) by the sample. A colored glass cut-off filter was placed in the path of the transmitted light beam to prevent fluorescence and light

scattering reaching the photomultiplier used for monitoring the transmitted light. Using photon counting, ratios of emissions over references (E/R) were electronically recorded and analyzed on a PDP-11 minicomputer. All reported spectra are excitation corrected.
(7) In FDCD, the optically active sample is irradiated by right and left CPL using, typically, a photoelastic modulator (instead of the quarterwave plate). Information is obtained by monitoring the difference in fluorescence intensities for left and right circularly polarized excitation by scanning, usually, the excitation spectrum.[8] In contrast to FDCD, the sample in the present work is excited only at one wavelength (by CPL), and the emission is scanned. We note in passing that none reportedly looked at FDCD for both enantiomers of a given optically active molecule.[9]
(8) I. Z. Steinberg in "Methods in Enzymology", in press: R. S. Richardson and J. P. Riehl, *Chem. Rev.*, **77**, 773 (1977); T. G. White, Y.-H. Pao, and M. M. Tang, *J. Am. Chem. Soc.*, **97**, 4751 (1975); I. Tinoco, Jr., and D. H. Turner, *ibid.*, **98**, 6453 (1976); I. Tinoco, Jr., B. Ehrenberg, and I. Z. Steinberg, *J. Chem. Phys.*, **66**, 916 (1977).
(9) D. H. Turner, I. Tinoco, Jr., and M. F. Maestre, *J. Am. Chem. Soc.*, **96**, 4340 (1974); D. H. Turner, I. Tinoco, Jr., and M. F. Maestre, *Biochemistry*, **14**, 3794 (1975); B. Ehrenberg and I. Z. Steinberg, *J. Am. Chem. Soc.*, **98**, 1293 (1976).
(10) Although optical rotations of D-Trp and L-Trp were found to be identical in methanol and glycerol, fluorescence efficiencies in the latter solvent was 0.6 (compared to 0.2 in methanol). The enhanced fluorescence efficiency in glycerol is the consequence, of course, of the greater viscosity of the solvent and hence the reduction in the overall quenching processes which depopulate the excited state.
(11) R. H. Conrad and L. Brand, *Biochemistry*, **7**, 777 (1968).
(12) T. Förster in "Modern Quantum Chemistry, Part III", O. Sinanoglu, Ed., Academic Press, New York, 1965.
(13) The overlap integrals calculated in the present work agree well with that given in ref 11.
(14) P. W. Schiller in "Biochemical Fluorescence: Concepts", Vol. 1, R. F. Chen and H. Edelhoch, Eds., Marcel-Dekker, New York, 1975, Chapter 5.
(15) This effect is related to photoselectivity and the procedure used to calculate T values (see footnote *a* in Table II) is unlikely to correct for it. Concentrations of given conformers are, of course, the same for dansyl-D-Trp and dansyl-L-Trp.
(16) Transfer efficiencies are extremely sensitive to intrachromophoric distances (see eq 1 and ref 11). R values in given conformers are, of course, the same for dansyl-D-Trp and dansyl-L-Trp.

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Regiochemistry of the Addition of DCl to *trans*-1,3-Pentadiene

Sir:

We report here the first clear evidence on the regiochemistry of addition of a Brønsted acid to a 1,3-diene proceeding through a symmetrically substituted intermediate allylic carbenium ion. The data show a characteristic preference for 1,2 over 1,4 addition and thus reveal the operation of association effects in the mechanism. The results provide a needed basis for the interpretation of related observations involving unsymmetrical ions. They have significance as well to the question of carbocation structure in the addition of acids to norbornene.

Competitive 1,2 and 1,4 additions of electrophilic agents to conjugated dienes have received considerable attention.[1] The fundamental case of reaction of a Brønsted acid with a diene whose protonation should afford a symmetric allylic cation, however, has been addressed previously only once. Hammond and Warkentin[2] in 1961 examined the course of polar addition of DBr to 1,3-cyclohexadiene in pentane. Their results, however, admitted the possibility of dominant interconversions of first-formed products.

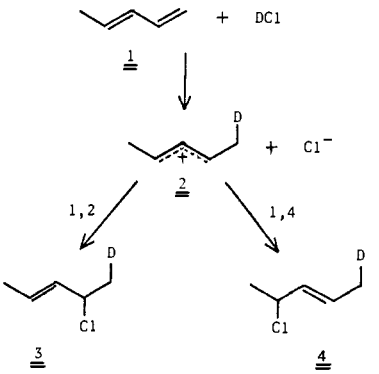
trans-1,3-Pentadiene (**1**) is the prototype of addition substrates parent to allylic ions free per se from electronic and steric bias, as shown in Scheme I. Diene **1** adds DCl in no solvent, pentane, acetic acid-*O*-*d*, or nitromethane over a range of temperatures to produce mixtures of *trans*-4-chloro-2-pentene-*5*-*d* (**3**) and -*1*-*d* (**4**); <4% cis isomers are formed. The reactions were carried out using ~0.75 equiv of DCl (from D_2O and benzoyl[3] or acetyl chloride) and were monitored by ^1H NMR. When addition was determined to be almost complete

Table I. Regiochemistry of DCl Addition to *trans*-1,3-Pentadiene[a]

solvent	temp, °C	% trans products[b]	% 1,2 product (**3**)[c]	% 1,4 product (**4**)[c]
none	−78[d]		75.5	24.5
	0	97.6	72.4	27.6
	25		61.5	38.5
pentene	−78	97.7	77.7	22.3
	0	96.3	68.1	31.9
	25		63.8	36.2
CH_3CO_2D[e]	25[d]	96.8	65.0	35.0
CH_3NO_2	0		71.5	28.5
	25		67.7	32.3

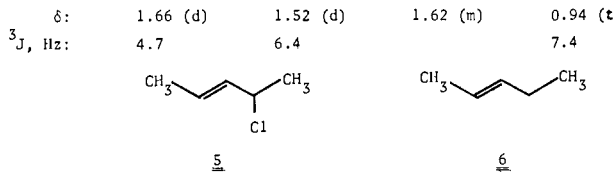
[a] Reactant (ChemSampCo) was 99% trans, 1% cis. [b] By gas chromatographic analysis after reduction of the products to 2-pentenes; remainder was cis. [c] As percentages of the *trans*-chloropentenes, **3** + **4**. [d] Recovered excess diene was found by ^2H NMR to have incorporated no deuterium (<2%). [e] Containing 2% (weight) of acetic anhydride.

Scheme I

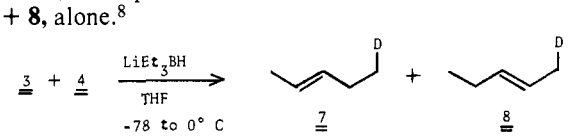


residual DCl was removed in a stream of dry nitrogen to stabilize the products. The final solutions were colorless, or nearly so, and their NMR spectra indicated yields of **3** + **4** of 90% or better.

Label analysis of the products was conducted initially by complementary 15.4-MHz proton-decoupled ^2H NMR measurements.[4] Following solvent removal at subambient temperature (pentane by distillation at 60 mmHg, acetic acid by neutralization in cold $NaHCO_3$ solution, pentane extraction, and distillation), the spectrum of the chloropentenes was recorded and the partially overlapping deuterium signals were integrated with the aid of a curve resolver.[5] The upfield absorption was assigned to the *5*-*d* isomer, **3**, from the comparative methyl-group chemical shifts in the ^1H spectra[6] (CCl_4, 60 MHz) of *trans*-4-chloro-2-pentene (**5**) and its dechlorination product, *trans*-2-pentene (**6**). Corroborative data were



obtained by prompt reduction of the **3** + **4** mixture with lithium triethylborohydride[7] to *trans*-2-pentene-*5*-*d* (**7**) and -*1*-*d* (**8**), respectively, and integration of these isomers' fully separated ^2H NMR signals. Upon the observation of close agreement (±3%) between the analyses of **3** + **4** and **7** + **8** for three reactions, subsequent measurements were made on the olefins, **7** + **8**, alone.[8]



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