Photochemical Asymmetric Synthesis. Irradiation of Mannitol Hexacinnamate

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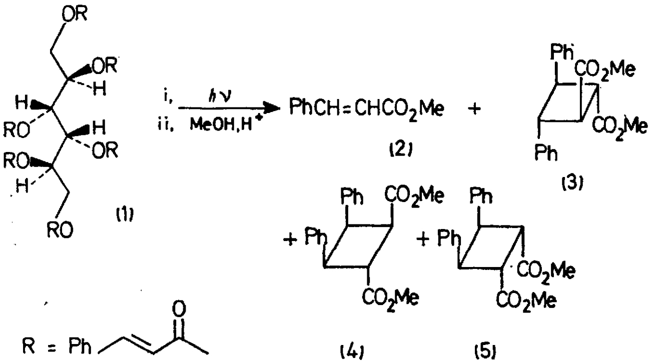
Summary Intramolecular photocycloaddition takes place when a solution of mannitol hexacinnamate is irradiated ($\lambda > 290$ nm) and, after ester exchange with excess of methanol and chromatographic separation, methyl cinnamate, dimethyl β-truxinate, (±)-dimethyl neo-truxinate, and (+)-dimethyl δ-truxinate are isolated; the optical yield of the latter is as high as 46%.

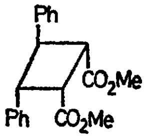
DESPITE lively interest in asymmetric synthesis[1] the use of photochemical reactions to achieve asymmetric synthesis has, apart from the use of circularly polarized light,[2] remained almost unexplored.[3] We are currently examining the utility of 2 + 2 photocycloadditions as routes to optically active cyclobutane derivatives, where the asymmetric induction is provided by simple, readily available chiral materials such as carbohydrate derivatives, and we report herein the first example in this study.[4]



The absolute configuration of (3) is not yet known

A solution of mannitol hexacinnamate (1)[5] in benzene (2 g per 150 ml) was irradiated (450 W medium-pressure Hg immersion apparatus; Pyrex) for periods of 5—50 h. After evaporation, the residue was treated with boiling methanolic HCl and the resulting methyl esters were separated by chromatography on silica gel. There were thus obtained, in order of elution, *cis*- and *trans*-methyl cinnamate (**2**), (+)-dimethyl δ-truxinate (**3**) [25—40%, yields based on recovered (**2**)], (±)-dimethyl neo-truxinate (**4**) (*ca.* 10%), and dimethyl β-truxinate (**5**) (*ca.* 20%). From the rotation of (**3**), $[\alpha]_D$ 4·3°, 4·7°, and 5·1° (acetone), an optical yield of 38—46% can be calculated.[6] Comparable optical yields of (+)-(**3**) are obtained when the irradiation of (**1**) is performed in EtOAc or in aqueous $HCONMe_2$. Irradiation of molten (**1**) (at *ca.* 110°) also affords (+)-(**3**); crystalline (**1**) is light-stable.

The first conclusion from these results is that such photochemical reactions show distinct promise in asymmetric synthesis. The optical induction, we feel, results primarily from preferred ground-state conformations. For each of the many transient conformations of (**1**) there may be a variety of 'sites', intramolecular arrangements with pairs of cinnamate residues aligned with good olefinic π-orbital overlap and *ca.* 4 Å separation between centres of C=C bonds,[7] appropriate for the formation of (+)-δ-, (−)-δ-, or β-truxinate derivatives. Surprisingly, the optical yield is not markedly dependent on irradiation time and is about the same when less than one cyclobutane ring has been formed, on the average, for each molecule of (**1**) and when, on the average, two have been formed. This implies that reaction at one 'site' does not appreciably change the conformational arrangements at other 'sites.'



(6)

Finally, it is noteworthy that the product of a *cis* + *trans* photoaddition, (**4**), is formed yet, unlike (**3**), it is racemic, and that ξ-truxinate (**6**), which could also have been produced by a *cis* + *trans* addition, is absent. These results suggest that *trans* → *cis* photoisomerization competes with addition in 'sites' that afford (**5**) and that in these sites both the cinnamate residues have an equal probability of undergoing photoisomerization [photoisomerization and subsequent photoaddition in a site that afforded (**3**) would have yielded optically active (**4**)]; the cinnamate photoisomerization involves rotation of the carboxy-group about the double bond [leading to (**4**)] in preference to movement of the phenyl group, which would have led to (**6**).

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[1] J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions,' Prentice-Hall, Englewood Cliffs, New Jersey, 1971; J. W. Scott and D. Valentine, *Science*, 1974, **184**, 943.

[2] G. Balavoine, A. Moradpour, and H. B. Kagan, *J. Amer. Chem. Soc.*, 1974, **96**, 5152, and refs. cited therein; O. Buchardt, *Angew. Chem. Internat. Edn.*, 1974, **13**, 179.

[3] Chiral photosensitizers: G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, 1965, **87**, 3256; G. Balavoine, S. Juge, and H. B. Kagan, *Tetrahedron Letters*, 1973, 4159; C. S. Drucker, V. G. Toscano, and R. G. Weiss, *J. Amer. Chem. Soc.*, 1973, **95**, 6482. Other reports: D. Elad and J. Sperling, *J.C.S. Chem. Comm.*, 1969, 234; D. Seebach and H. Daum, *J. Amer. Chem. Soc.*, 1971, **93**, 2795; R. H. Martin, *Angew. Chem. Internat. Edn.*, 1974, **13**, 649.

[4] For an asymmetric synthesis involving a 2 + 2 photocycloaddition reaction in the solid state, where the chiral crystal structure is the sole source of dissymmetry, see: A. Elgavi, B. S. Green, and G. M. J. Schmidt, *J. Amer. Chem. Soc.*, 1973, **95**, 2058.

[5] E. Fischer and R. Oetker, *Chem. Ber.*, 1913, **46**, 4029.

[6] R. Stoermer and F. Bachér, *Chem. Ber.*, 1922, **55**, 1860.

[7] This conclusion is reached from the extensive work on solid-state photodimerization of cinnamates (G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647; *cf.* J. K. Frank and I. C. Paul, *J. Amer. Chem. Soc.*, 1973, **95**, 2324), and the fact that, owing to their short excited-state lifetime, cinnamates do not dimerize even in the neat liquid. Only when the cinnamate residues are linked together can intramolecular photocycloaddition become efficient (J. Rennert, S. Soloway, I. Waltcher, and B. Leong, *J. Amer. Chem. Soc.*, 1972, **94**, 7242; R. T. Lalonde and C. B. Davies, *Canad. J. Chem.*, 1969, **47**, 3250) as in the case of (**1**).