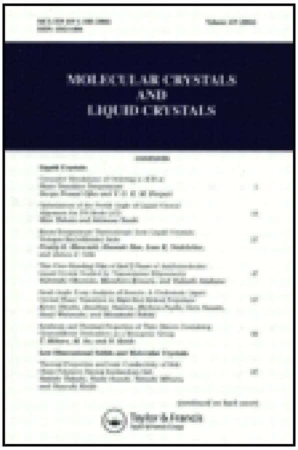

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Enantiocontrol of Photoreactions in the Solid State

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ENANTIOCONTROL OF PHOTOREACTIONS IN THE SOLID STATE

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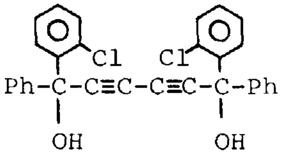
Abstract Irradiation of crystalline complexes of prochiral guest compounds and optically active host compounds in the solid state gave optically active photoreaction products. For example, irradiation of the complexes of tropolone alkyl ether, nitrones, and oxoamides with optically active 1,6-di(o-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol, (1), in the solid state gave optically pure 1-alkoxy-bicyclo[3.2.0]hepta-3,6-dien-2-one, oxaziridines, and β-lactam, respectively. Irradiation of complexes of cycloocta-2,4,6-trienenone and cycloocta-2,4-dienone with the same host compound, (1), in the solid state also gave opticaly active photoreaction products, bicyclo[4.2.0]octa-4,7-dien-2-one and anti-tricyclo[8.6.0.$0^{2,9}$]hexadeca-7,11-diene-3,16-dione, respectively. The most exciting result of the enentiocontrol reaction is the photoreaction of chiral crystals of achiral oxoamide, N,N-diisopropylphenylglyoxylamide in the solid state which gives optically active β-lactam. This result is important in relation to the generation of chirality on Earth.

INTRODUCTION

Development of preparation methods of optically active compounds from optically nonactive compounds is one of the most important targets in Organic Chemistry. The enantioselective reactions have mostly been studied in solution, so far using chiral reagents containing metal ions. This method is, however, not always successful because interaction between reactant and chiral reagent is not very effective in solution. Contrarily, reaction in the solid state is expected to proceed more selectively because molecules are arranged regularly in crystalline lattices. We report some examples of enantioselective reaction in the solid state.

Stereocontrol of photoreactions of guest compounds have been achieved by irradiation of host-guest complexes in the solid state. For example, irradiation of inclusion complexes of chalcone,[1] dibenzoylacetone,[2-3] 9-acylanthracene,[2-4] and pyridone[2-5] with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol in the solid state gave their photodimers regio- and stereoselectively. When an optically active host compound is used instead of an achiral host compound, enantioselective photoreaction is expected. We report some such examples.

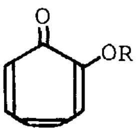
Irradiation of a 1:1 complex of (-)-1,6-di(o-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol, (1a)[6] and tropolone methyl ether, (2a), in the solid state gave (-)-3a of 100% ee.[7,8] By the same procedure, 2b gave (-)-3b, 100% ee.[7,8] The mechanism of the efficient enantioselective reaction has been studied by X-ray crystal structure analysis of a 1:1 complex of 1a and 2a. The data show that the disrotatory cyclization of 2 occurs only in one direction in accord with the steric effect of 1a.[9]



1

a: (-)-form

b: (+)-form



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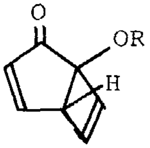
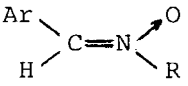


3

a: R=Me

b: R=Et

Optically active oxaziridines are useful reagents for enantioselective oxidation of olefins. However, all the preparative methods which have been reported so far can give optically active oxaziridines of less than 30% ee.[10] We succeeded in preparing oxaziridines (**5**) of 100% ee by enantioselective photocyclization of nitrones (**4**) in a crystalline inclusion complex with **1a**.[11] Powdered **4a** and **4b** were irradiated and the reaction mixtures were chromatographed on silica gel (benzene) to give **5a** of 100% ee (51%) and **5b** of 94% ee (52% yield), respectively. In the case of **4c**, complexation of racemic **4c** with **1a** gave (-)-**4c** of 100% ee in 31% yield. Irradiation of a 1:1 complex of **4c** of 100% ee and **1a** gave **5c** of 100% ee in 31% yield. This is not due to chiral induction by the optically active alkyl group, because irradiation of **4c** of 100% ee in benzene gave **5c** of only 12% ee.



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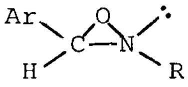
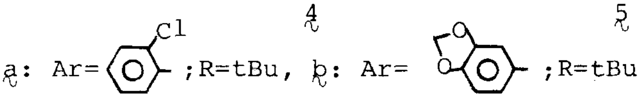


5



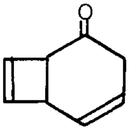
c: Ar=Ph ;R=CH(CHMe$_2$)Me

Cycloocta-2,4,6-trien-1-one (**6**) exists as an equilibrium mixture of two rapidly flipping isomers (**6a** and **6b**). By complexing with **1a**, the flipping equilibrium of **6** was frozen as one optical isomer. When an ether-hexane (1:1) solution of **1a** and two molar amounts of **6** was kept at room temperature for 12 h, a 1:2 complex of **1a** and **6** was obtained as pale yellow prisms in 76% yield. In order to know whether one enantiomer, (6a or 6b), is included selectively or a racemic mixture (6a and 6b) is included, photoconversion of 6 in the complex to 7 was carried out. Irradiation of the complex in the solid state gave (-)-7 in 28% yield ($[\alpha]_D$ -62.9° (c 0.12, $CHCl_3$). Although optical purity of this product was not determined, it is clear that one of the two enantiomers, 6a or 6b, is included selectively or at least predominantly. Since photoreaction of 6 in pentane solution is known to give racemic 7 in 31% yield after irradiation for 21 days,[13] the photoreaction of 6 in the complex with 1a is clearly shown to proceed not only enantioselectively but also much more efficiently.

Irradiation of 8 in pentane solution for 1 h gives racemic 9 in 10% yield along with polymeric material.[14] However, irradiation of a 2:1 complex of 1a and 9 for 48 h in the solid state gave (-)-9 of 78% ee in 55% yield. Since one unit of the complex contains one molecule of 8 and two molecules of 1a, at least two of these units should take part the photodimerization of 8. It is not clear at present whether this has something to do with the relatively high enantioselectivity of the photodimerization or not.

Photoreaction of 10 in MeOH gives a mixture of racemic 11, 6, and cyclohepta-1,3,5-triene.[15] However, irradiation of a 2:1 complex of 10 and 1a for 24 h gave racemic 11 in 71% yield. Neither 6 nor cyclopenta-1,3,5-triene was detected in this reaction. However, optically pure (+)-11 was

6a 6b



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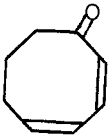

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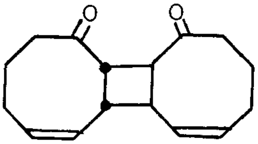

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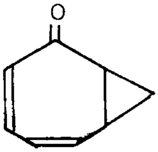
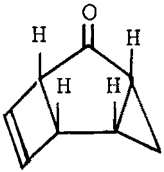


10



11

easily obtained by complexation of racemic 11 with 1a.

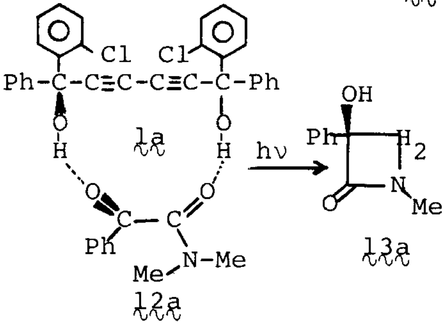
Irradiation of a 1:1 complex of 12a and 1a in the solid state gave optically active β-lactam 13 of 100% ee in 82% yield.[9] X-Ray crystal structure study of the complex showed that the complex has a cyclic structure. Thus the photocyclization of 12a in the complex should give chiral β-lactam (13).[9]

$Ph\text{-}CO\text{-}CO\text{-}NR_2$

12

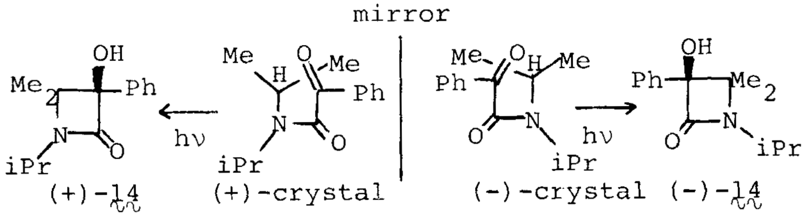
a: R=Me

b: R=iPr



We found that the achiral oxoamide **12b** forms chiral crystals, which upon irradiation in the solid state give the optically active β-lactam **14**. in high optical and chemical yields. Recrystallization of **12b** from benzene afforded colorless prisms. That each crystal (5-10 mg) was chiral was shown by photochemical conversion into optically active **14**. Crystals of (+)- and (-)-**12b** can easily be prepared in large quantities by seeding with finely powdered crystals of (+)- and (-)-**12a** during recrystallization of **12a**. Irradiation of crystals of (+)-**12a** with occasional grinding (agate pestle and motar) at room temperature for 40 h gave (+)-**14** of 93% ee in 74% yield.[16] Irradiation of (-)-**12a** under the same conditions gave (-)-**14** of 93% ee in 75% yield.[16] Purification to 100% ee of the (+)- and (-)-**14** can easily achieved by recrystallization from benzene. The results are valuable in that an optically active compound is produced in bulk from achiral material. Moreover, the results may throw some light on the generation of optically active amino acids on Earth, since the photocyclization of **12b** proceeds efficiently in sunlight and hydrolysis of the optically active **14** gives an optically active β-amino acid.

A possible mode of formation of optically active **14** from achiral **12b** in the chiral crystal is shown in Scheme 1. Since the molecular motion of **12b** is restrained in the crystal lattice, photoreactions in the chiral (+)- and (-)-crystals proceed stereoselectively.[16]



Scheme 1. A possible mode of formation of optically active **14** from achiral **12b** in its chiral crystal. The relationship between the depicted absolute configuration and sign of $[\alpha]_D$ is arbitrary.

REFERENCES

1. F. Toda and K. Tanaka, J. Chem. Soc., Chem. Commun., 1983, 593.
2. K. Tanaka and F. Toda, Nippon Kagaku Kaishi, 1984, 141.
3. M. Kaftory, K. Tanaka, and F. Toda, J. Org. Chem., 85, 2154 (1985).
4. M. Kaftory, Tetrahedron-Symposium-in-Print, 43, 1503 (1987).
5. M. Kuzuya, A. Noguchi, N. Yokota, T. Okuda, F. Toda, and K. Tanaka, Nippon Kagaku Kaishi, 1986, 1746.
6. F. Toda, Top. Curr. Chem., 140, 43 (1987).
7. F. Toda and K. Tanaka, J. Chem. Soc., Chem. Commun., 1986, 1429.
8. F. Toda, Top. Curr. Chem., in press.
9. M. Kaftory, K. Tanaka, and F. Toda, J. Org. Chem., in press.
10. A. Forni, I. Moretti, and G. Torre, J. Chem. Soc., Perkin Trans. 2, 1987, 699; F. A. Davis, J. P. McCauley, Jr., S. Chattopadhyay, M. E. Harakal, J. C. Towson, W. H. Watson, and I. Tavanaiepour, J. Am. Chem. Soc., 109, 3370 (1987); D. R. Boyd, R. M. Campbell, P. B. Coulter, J. Grimshaw, D. C. Neill and M. B. Jennings, J. Chem. Soc., Perkin Trans. 1, 1985, 849.
11. F. Toda and K. Tanaka, Chem. Lett., 1987, 2283.
12. F. Toda, K. Tanaka, and M. Oda, Tetrahedron Lett., in press.
13. G. Buchi and E. M. Burgess, J. Am. Chem. Soc., 84, 3104 (1962).
14. T. S. Cantrell and J. S. Solomon, J. Am. Chem.

Soc, 92, 4656 (1970).

15. L. A. Paquette and O. Cox, J. Am. Chem. Soc., 89, 5633 (1967).
16. F. Toda, M. Yagi, and S. Sōda, J. Chem. Soc., Chem. Commun., 1987, 1413.