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COMMUNICATION

A new simple chiral helicene 3,4-bis(diphenylmethylene)-N-methylsuccimide in its chiral crystal. A generation of chirality

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Chiral crystals of the achiral title compound, prepared in large quantities, were irradiated in the solid state to give the optically active photocyclization product.

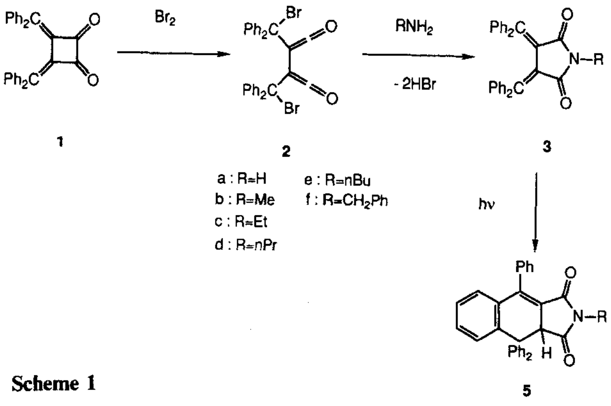
Achiral molecule of the title compound (**3b**) was found to arrange in a chiral form in crystal. The chirality of **3b** in crystal was frozen by photoirradiation in the solid state to give optically active photocyclization product **5b**. However, some 3,4-bis(diphenylmethylene)-succimides which have hydrogen or other alkyl group than methyl on the nitrogen formed only racemic crystal and their photoirradiation gave the corresponding racemic photocyclization product.

3,4-bis(diphenylmethylene)succimide (**3a**) and its N-alkyl derivatives (**3b–f**) were prepared by the reaction of 3,4-bis(diphenylmethylene)cyclobutanedione (**1**)[1] with ammonia or amine in CCl_4 in the presence of Br_2 according to the reported procedure (Scheme 1).[2]

Recrystallization of **3b** from acetone formed chiral crystal as orange hexagonal plates (**A**, converts to **C** by heating at 260 °C) and two racemic crystals as orange rectangular plates (**B**, mp 302 °C) and yellow rectangular plates (**C**, mp 297 °C). These can easily be separated by picking up. In one piece of **A** crystal, for example, (+)-**3b** molecules are pucked and (−)-**3b** molecules are pucked in another piece of **A** crystal. These chiral crystals are tentatively named as (+)-A and (−)-A crystal, respectively. The chirality of **3b** in the crystal **A** was proven by photoirradiation of the crystal to give the optically active photocyclization product **5b**. For example, irradiation of powdered (+)-A crystal (50 mg) by 100 W high-pressure Hg-lamp for 50 h gave (+)-**5b** of 64% e.e. (50 mg, 100% yield, mp 285–287 °C, $[\alpha]_D + 102°$ (c 0.05, $CHCl_3$)). Similar irradiation of (−)-A crystal gave (−)-**5b**. The optical purity was determined by HPLC on the chiral solid phase Chiralpak AS.[3]

The chiralty of **3b** in crystal **A** is probably attributed to the steric prohibition of an inter-conversion between the two phenyl rings a and a′ (Scheme 2). Namely, **3b** is a simple chiral helicene, although the chirality appears only in the crystalline state. Nevertheless, the chirality of the helicene can be transferred to the stable **5b** by photoreaction. This is an example of the generation of chirality.[4] The formation of chiral crystals of the achiral oxo amide N,N-diisopropylphenylglyoxylamide, and their photoconversion in the solid state to the optically active β-lactam 3-hydroxy-1-isopropyl-4,4-dimethyl-3-phenyl-azetidin-2-one have also been reported by us.[5,6] In the pesent case, however, it is the interesting point that the generation of chirality was observed for the simple helicene molecule **3b**. This result may throw some light on the generation of chirality on Earth.[7]

The enantioselective photoconversion of the chiral helicene **3b** to the optically active **5b** consists of two



Scheme 1

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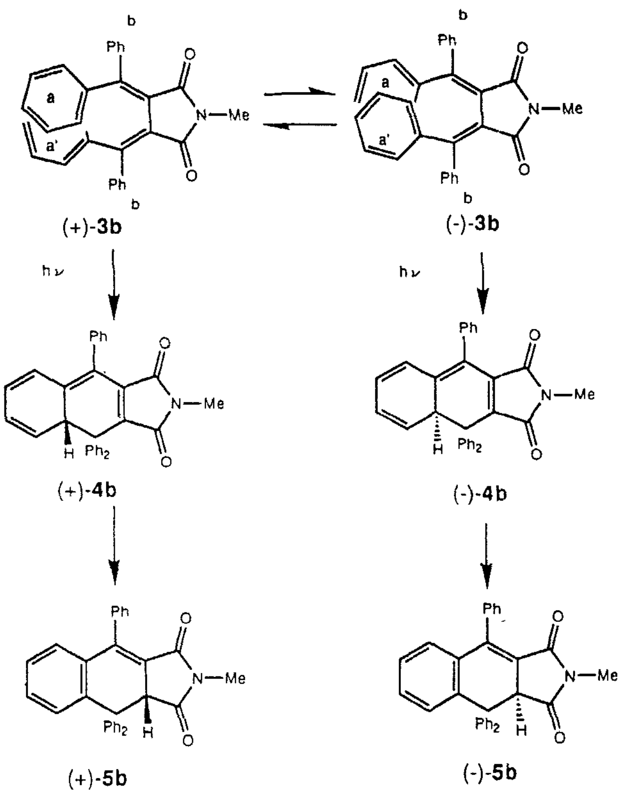
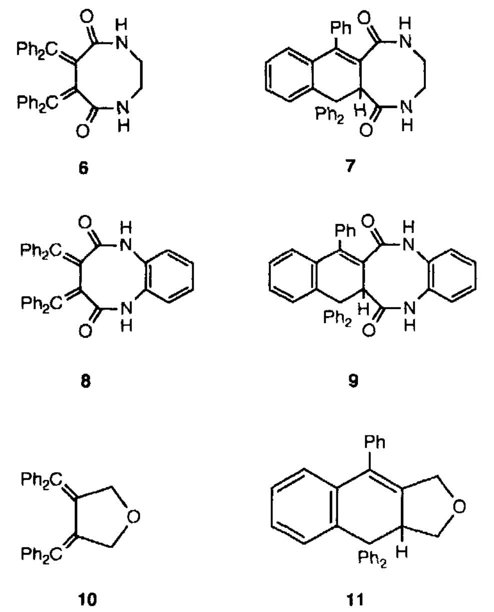


Scheme 2



Scheme 3

stereoselective steps, the conrotatory ring closure of **3b** to the intermediate **4b** and the 1,5-hydrogen shift of **4b** to give the product **5b** (Scheme 2). In this reaction, optically active **5b** of 64% e.e. was obtained. It is not clear which step is less stereo-selective.

Photoirradiation of crystals **B** and **C** gave racemic **5b**. In these racemic crystals, (+)-**3b** and (−)-**3b** molecules would be pucked in a 1:1 ratio. Interconversion among the three crystals **A**, **B**, and **C** and that between (+)-**A** and (−)-**A** crystals occur easily. By heating at 260 °C, **A** is converted to **C**. Addition of one piece of (+)-**A** crystal as seed crystal during the recrystallization of **C** (100 mg) from acetone (20 ml) gave (+)-**A** (66 mg), **B** (15 mg), and **C** crystal (10 mg). Addition of one piece of (−)-**A** crystal during the recrystallization of (+)-**A** crystal (50 mg) from acetone gave (−)-**A** (23 mg), **B** (4 mg), and **C** crystal (8 mg).

However, **3a** and **3c–f** formed only racemic crystals and their photoirradiation on the solid state gave racemic photocyclization products **5a** and **5c–f**, respectively, in quantitative yields. The data show that the formation of chiral helicene depends delicately on the N-substituent of **3**.

We further investigated chiral crystals of some other heterocyclic compounds bearing two adjacent diphenylmethylene groups such as **6** (pale yellow prisms mp 258–260 °C) prepared according to the reaction shown in Scheme 1, **8** (pale yellow prisms mp 279–283 °C),[8] and **10** (yellow prisms, mp 178–181 °C) prepared by an etherification of the corresponding diol. They formed, however, only racemic crystals and their photoreaction in the solid state gave the corresponding photocyclization products in quantitative yields, **7** (colorless prisms, mp 206–208 °C), **9** (colorless prisms, mp 297–302 °C), and **11** (colorless prisms, mp 142–145 °C) in racemic forms. Nevertheless, it is interesting that the photocyclization of **10** to **11** occurs efficiently in the solid state, although **10** has no carbonyl group which is usually necessary to activate C = C bond in the phtoreaction.

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REFERENCES

1 Toda, F.; Akagi, K.; *Tetrahedron* **1971**, *27*, 2801.
2 Toda, F.; Fujita, J.; *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1928.
3 Chiralpak AS is available from Daicel Chemical Industries Ltd., Himeji, Japan.
4 Green, B.S.; Lahav, M.; Rabinovich, D.; *Acc. Chem. Res.* **1979**, *12*, 191.
5 Toda, F.; Yagi, M.; Soda, S.; *J. Chem. Soc., Chem. Commun.* **1987**, 1413.
6 Sekine, A.; Hori, K.; Ohashi, Y.; Yagi, Y.; Toda, F.; *J. Am. Chem. Soc.* **1989**, *111*, 697.
7 Addadi, L., Lahav, M.; in *Origins of Optical Activity in Nature* (Walker, D.C., ed.), Elsevier, New York, **1979**, p. 124.
8 Ro, Z.; Tanaka, K.; Toda, F.; *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3193.