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Solid State Di-π-Methane Type Photorear-Rangements and a Case of Efficient Spontaneous Chiral Crystallization

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SOLID STATE DI-π-METHANE TYPE PHOTOREARRANGEMENTS AND A CASE OF EFFICIENT SPONTANEOUS CHIRAL CRYSTALLIZATION

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Abstract Photochemical solid state di-π-methane type photorearrangements of a seemingly homo-chirally crystallized achiral α,δ-dienone (**1**) give preparative quantities of two optically active di-π-methane photoproducts (**2** and **3**) of synthetic value. Considerable changes in product selectivity are observed for runs in homogeneous solution *vs.* the solid state and form the basis of mechanistic pathway interpretations and propositions. Notably, the starting dienone **1** adopts chiral packing (space group $P2_12_12_1$) with some relatively short intermolecular distances. The photorearrangements proceed so that the products are obtained in respective enantiomeric excesses of ≤96 % (**2**) and ≤34 % (**3**). Reaction selectivity changes have been followed as a function of conversion for both irradiations of crystal batches and single crystals. Extensive structural modifications of **1** (**4**-**7**) have been made for a study of the crystallization and reaction properties of this class of compounds.

INTRODUCTION

Spontaneous crystallization and the use thereof in asymmetric synthesis[1-3] have established simple and inexpensive routes to the preparation of optically enriched compounds. In these cases, a molecularly achiral substrate adopts a chiral orientation during crystallization. The chirality of such substrates in the crystal can then be trapped through solid state reactions to form stereogenic centers in the products.

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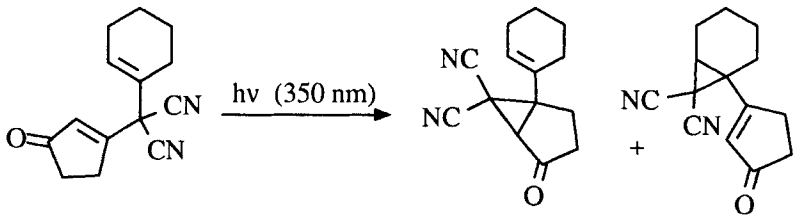
PHOTOCHEMISTRY OF CHIRALLY CRYSTALLIZED **1**

In a project aiming at novel synthetic access to mixed linearly and angularly fused natural products, we uncovered preparatively useful solid state di-π-methane type photorearrangements[3] of seemingly homo-chirally crystallized **1** to give the photoproducts **2** and **3** (TABLE I). A considerable change in product selectivity is observed for these rearrangements for runs in homogeneous solution *vs.* the solid state.[4] Whereas irradiation of **1** in CH_3CN gives a 1 : 3.2 ratio of **2** : **3**, a neat single crystal affords a ratio of 2.1 : 1. Interestingly, **1** adopts chiral packing (space group $P2_12_12_1$ secured for both enantiomorphs) and a helical molecular conformation; the X-ray analysis, including extensive data, has been recently published.[3] Attempts to unequivocally determine the absolute configuration of **1** as well as of the products **2** and **3** or their antipodes by anomalous scattering have thus far been unsuccessful. The product mixtures from the irradiation of single crystals of **1** (suspension in water) showed that **2** and **3** are obtainable in enantiomeric excesses (ee's) of ≤ 96 %

TABLE I. Di-π-methane Type Photorearrangements of **1** to **2** and **3**



1 **2** **3**

Aliquot **1**	Irrad. condtns	Conv. (%)	Ratio **2** : **3**	Isol.yield / ee (%) **2**	**3**
7g	CH_3CN, 18°C 0.1 M, 32 h	100	1 : 3.2	20/0	64/0
7g fine crystals	H_2O, 18°C 0.09 M, 168 h	52	1.2 : 1	26/86	23/26
single crystal (3x1mm)	H_2O, 0-3°C	10	2.1 : 1	- / 96	- / 34

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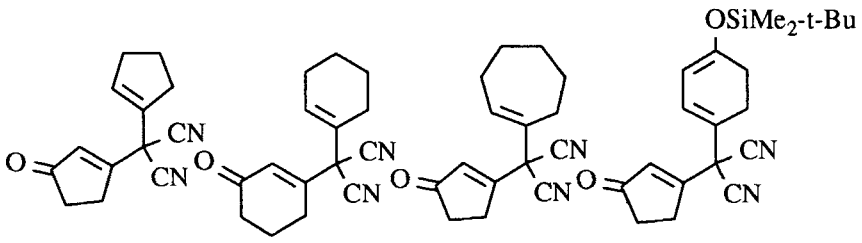
and ≤ 34 %, respectively, and that the ee's decrease proportionately with conversion.[3] The large majority of crystallization batches of **1** afforded dextrorotatory photoproducts indicating preferential enantioselectivity during crystallization which is most likely due to the presence of an undefined nucleating agent. Notably, preparative batches (second entry in TABLE I) even allow isolation of product **2** with an ee as high as 86 % at a conversion of starting material of 52 %. This constitutes the first case of a truly preparative example and a second general case of asymmetric synthesis through solid state di-π-methane type rearrangements, preceded only by the examples of Scheffer and co-workers.[2f]

CRYSTALLIZATION AND PHOTOREACTIONS OF STRUCTURAL MODIFICATIONS OF 1 (4 - 7)

FIGURE I. Structural Modifications of **1**: Di-π-methane Reactive Analogs **4**-**7**.

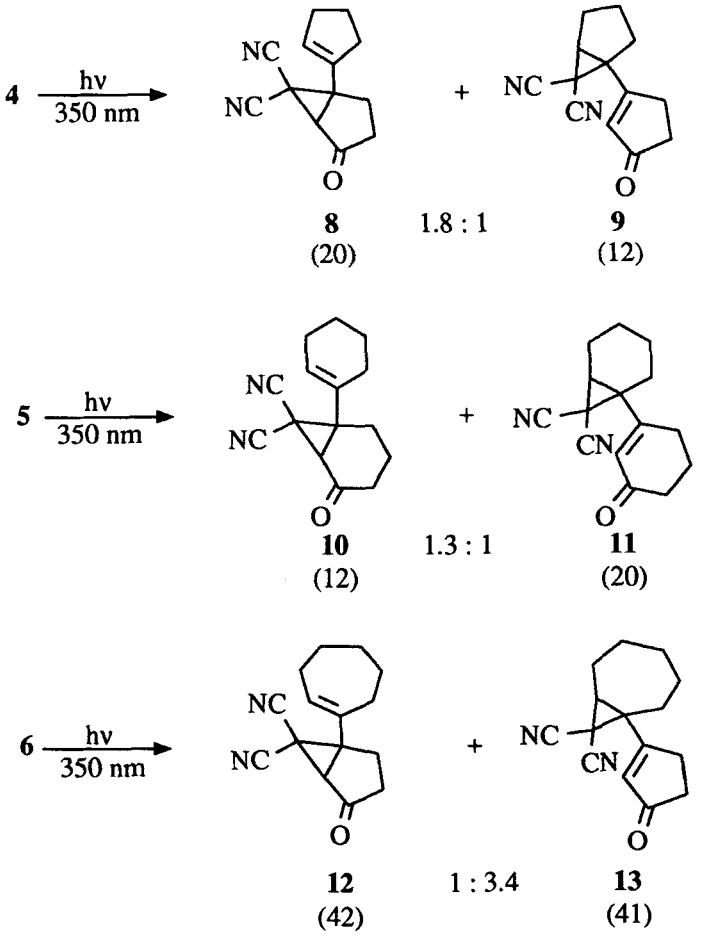


4 **5** **6** **7**

Comparison of the reaction course of **1** in homogeneous solution *vs.* the solid state has served as a basis for mechanistic pathway propositions.[3] In this context two results of the X-ray analysis were comparatively interpreted: (a) the conformational rigidity of the cyclopentenone moiety of **1** due to short intermolecular interactions in the crystal, and (b) the relative flexibility of the cyclohexene unit. We were therefore seeking for gradual modifications of the ring sizes and of the structural pattern.[5] Modification of the cycloalkene part of **1** was achieved by new syntheses of model compounds **4** and **6**. Alternatively, enlargement of the cycloalkenone (→ **5**) and flattening of the cyclohexene (→ **7**) were probed. Especially **4** was hoped to exhibit more conformational rigidity than **1**, due to the cyclopentene, and hence be another candidate for extended intermolecular interactions initiating chiral crystallization.

However, **1** is so far the sole prominent substrate crystallizing chirally; the analogs **4** - **7** - albeit crystalline - pack in achiral space groups. Interestingly, a relative rare packing ($P4_2/n$) is adopted by **7**. In order to still be able to plan synthetic concepts invoking enantiomerically enriched or pure materials, inclusion complexes of **4** - **6** in β-cyclodextrin[2g,6] have been prepared and subjected to 350 nm-irradiation. In the cases of the substrates **4** and **5**, chemoselection and chiral induction *en route* to **8** / **9** and **10** / **11**, respectively, are low to mediocre (FIGURE II: see product ratios and ee

FIGURE II. Photoproducts **8** - **13** of β-Cyclodextrin Complexes of **4** - **6** (2 h irradiation at λ_{irr}= 350 nm; 10 - 40 % conversions of **4** - **6**). Enantiomeric excesses in parentheses.



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values given in parentheses). Both the chemoselection (1 : 3.4) and enantioselectivity (42/41% ee) are remarkably high for the transformation **6** → **12** + **13**.

Furthermore it is of interest to note that the product ratios favoring the ketones **8** and **10** from **4** and **5**, respectively, resemble the results obtained in the crystal of **1** (cf. TABLE I) while the rearrangement of **6** parallels the chemistry of **1** in homogeneous solution. Hence one is tempted to propose a switch in mechanism between the rearrangements **4** / **5** and **6**; this could be rationalized by different complexation modes depending on the ring size.

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