Asymmetric Induction In the Solid State Photochemistry of 4-(2t,3t-Dibenzoylcyclopropyl)benzoic acid

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Enantiomerically pure substances have a great deal of importance in a number of fields, particularly in the pharmaceutical industry. Therefore, chemists are faced with the challenge of developing new, generally applicable, enantioselective synthetic methods to meet the growing demand for these products. Asymmetric induction in crystalline state photochemical reactions can be achieved via the lonic Chiral Auxiliary approach, wherein an achiral, photoreactive carboxylic acid (or amine) and an optically pure amine (or acid) can be joined through acid-base chemistry to form a salt. The optically pure substrate forces the compound to crystallize in a chiral space group, thus differentiating between the enantiomeric transition states. Enantiomeric excess of the photoproduct can then be achieved via kinetic control of the reaction. This technique has been applied to the cis-trans photoisomerization of 4-(2t, 3t-dibenzoylcyclopropyl)benzoic acid (Scheme 1).



For the 12 chiral salts tested, a range of enantiomeric excesses from 0-65% was obtained, with the maximum ee achieved for the (1S,2S)-(+)-thiomicamine salt irradiated for 7 hours at -5 °C.