

## First Photosensitized Enantiodifferentiating Polar Addition: Anti-Markovnikov Methanol Addition to 1,1-Diphenylpropene

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Enantiodifferentiating methanol addition to 1,1-diphenylpropene sensitized by chiral naphthalene(di)carboxylates gave optically active 1,1-diphenyl-2-methoxypropane in optical yields up to 27%, indicating the intervention of an intimately interacting exciplex or contact ion pair.

Much interest has recently been focused on the photosensitized enantiodifferentiating reactions.<sup>1-15</sup> Photosensitizations with optically active compounds enable catalytic chirality transfer and multiplication through apparently weak and short-lived interaction in the excited state by using a small amount of optically active sensitizer, and also provide valuable mechanistic and structural insights into the intervening exciplex or radical ion pair.<sup>1,5</sup> In contrast to the considerable efforts devoted to the unimolecular enantiodifferentiating photoisomerizations,<sup>2-13</sup> only a few attempts have

been reported so far on the bimolecular enantiodifferentiating [4 + 2] or [2 + 2] photocycloaddition/dimerization reactions, which, however, give relatively low optical yields around 1% at ambient temperature<sup>14,15</sup> and 9-15% at even lower temperatures.<sup>14</sup> The situation seems even worse for the photosensitized enantiodifferentiating polar addition, since the use of a polar solvent is usually a prerequisite for the facile formation of free radical cation to which addition occurs.<sup>16-19</sup> We now report our results on the first enantiodifferentiating polar addition of methanol to 1,1-diphenylpropene **1** sensi-

**Table 1** Enantiodifferentiating methanol addition to 1,1-diphenylpropene **1** photosensitized by chiral 1-, 2,6- or 1,8-naphthalene(di)carboxylates (**3–5**) at 25 °C

| Run | Sensitizer | Solvent      | [MeOH]/<br>mol dm <sup>-3</sup> | Irrad.<br>time/h | Conv. (%) | Yield (%) | [α] <sub>D</sub> <sup>20</sup><br>(c, CHCl <sub>3</sub> ) | op (%) <sup>a</sup> |
|-----|------------|--------------|---------------------------------|------------------|-----------|-----------|-----------------------------------------------------------|---------------------|
| 1   | <b>3a</b>  | Pentane      | 1.5                             | 82               | 29        | 8.3       | -0.9 (1.50)                                               | 1.8                 |
| 2   |            | Benzene      | 1.5                             | 85               | 20        | 6.8       | -1.4 (0.37)                                               | 2.7                 |
| 3   | <b>3b</b>  | Pentane      | 1.5                             | 133              | 13        | 5.6       | -1.0 (1.56)                                               | 2.0                 |
| 4   | <b>4a</b>  | Pentane      | 1.5                             | 16               | 80        | 48        | -0.3 (1.80)                                               | 0.6                 |
| 5   | <b>4b</b>  | Pentane      | 1.5                             | 46               | 95        | 53        | +1.2 (1.37)                                               | 2.3                 |
| 6   |            |              | 0.5                             | 36               | 47        | 26        | +1.3 (1.50)                                               | 2.5                 |
| 7   |            |              | 0.3                             | 84               | 38        | 5.9       | +2.3 (1.10)                                               | 4.4                 |
| 8   |            |              | 0.2                             | 86               | 18        | 8.7       | +2.9 (1.32)                                               | 5.5                 |
| 9   |            | Benzene      | 1.5                             | 38               | 55        | 45        | +0.6 (1.27)                                               | 1.1                 |
| 10  |            |              | 0.5                             | 109              | 40        | 17        | +1.2 (1.10)                                               | 2.3                 |
| 11  |            | Acetonitrile | 1.5                             | 17               | 99        | 60        | -0.2 (1.95)                                               | 0.4                 |
| 12  | <b>4c</b>  | Pentane      | 0.5                             | 23               | 39        | 26        | +0.3 (1.47)                                               | 0.6                 |
| 13  | <b>5a</b>  | Pentane      | 0.5                             | 165              | 14        | 4.2       | -6.2 (1.15)                                               | 11.7                |
| 14  | <b>5b</b>  | Pentane      | 0.5                             | 139              | 12        | 2.2       | -7.3 (0.35)                                               | 13.8                |
| 15  | <b>5c</b>  | Pentane      | 0.5                             | 204              | 6.1       | 1.9       | -14.1 (0.50)                                              | 26.8                |

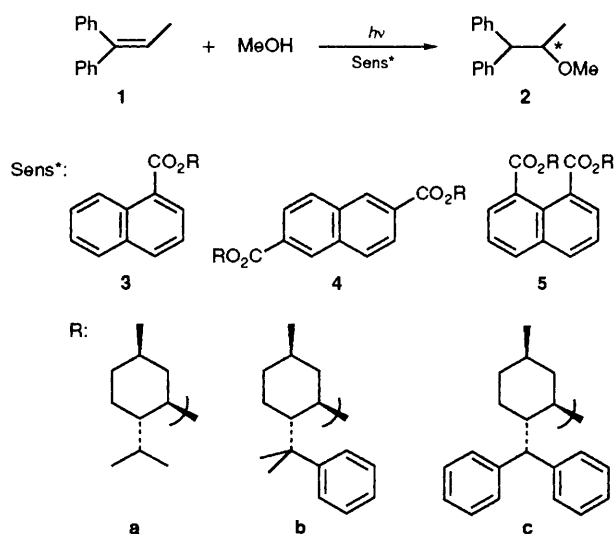
<sup>a</sup> Optical purity of **2**, determined by comparing product's optical rotation with that of the optically pure (-)-(*S*)-**2**: [α]<sub>D</sub><sup>20</sup> -52.5 (CHCl<sub>3</sub>).

tized by chiral alkyl naphthalene(di)carboxylates (Scheme 1), which gives the adduct 1,1-diphenyl-2-methoxypropane **2** in good optical purity up to 27% at 25 °C.

Photosensitized methanol additions to **1** (20 mmol dm<sup>-3</sup>) were performed<sup>†</sup> at 25 °C in pentane, benzene and/or acetonitrile containing 0.2–1.5 mol dm<sup>-3</sup> of methanol in the presence of optically active 1-, 2,6- and 1,8-naphthalene(di)carboxylates **3**, **4** and **5**, respectively (3 mmol dm<sup>-3</sup>), which were prepared<sup>20</sup> from the corresponding acid chloride and (-)-(1*R*,2*S*,5*R*)-menthol **a**, (-)-(1*R*,2*S*,5*R*)-8-phenylmenthol **b**<sup>21</sup> and (+)-(1*R*,2*S*,5*R*)-2-diphenylmethyl-5-methylcyclohexanol **c**.<sup>22</sup> The optical purity (op) of adduct **2** isolated from the photolysate by MPLC and GC<sup>‡</sup> was determined by the direct comparison of product's specific rotation (error ±0.1°) with that of the authentic specimen of (-)-(*S*)-**2** synthesized independently.<sup>§</sup> The reaction conditions and the results are summarized in Table 1.

Although arene(poly)carboxylates have not frequently been used as sensitizer–electron acceptors in photoinduced electron-transfer reactions as compared with (poly)cycanoarenes,<sup>16,19</sup> most of the chiral naphthalene(di)carboxylates afforded the adduct **2** in moderate to good chemical yields even in pentane, as was the case with 1,9-dicyanoanthracene in benzene or acetonitrile.<sup>19</sup>

It is interesting to note that the solvent polarity and the methanol content significantly affect the product's op. With increasing solvent polarity from pentane to benzene, and then to acetonitrile, the op of adduct **2** gradually decreases from 2.3

**Scheme 1**

<sup>†</sup> Irradiation with a 300 W high-pressure mercury arc were conducted at >300 nm under an argon atmosphere in an annular Pyrex vessel immersed in a thermostatted water bath at 25 °C.

<sup>‡</sup> Chemically pure **2** was isolated from the photolysate by MPLC over silica gel and the subsequent preparative GC over OV-101. The product **2** thus isolated was >99% pure and free from the chiral sensitizers and their possible fragments as indicated by GC analysis and <sup>1</sup>H NMR spectroscopy.

<sup>§</sup> Authentic specimen of the optically active (-)-(*S*)-**2** was independently prepared from 1,1-diphenylacetone. The racemic 1,1-diphenylpropan-2-ol obtained by LiAlH<sub>4</sub> reduction was converted to the corresponding hydrogen phthalate, which was in turn resolved optically through recrystallization of its brucine salt (R. Haller and H. J. Schneider. *Arch. Pharm.*, 1973, **306**, 846): [α]<sub>D</sub><sup>20</sup> -52.5.

to 0.4% in the photosensitizations with **4b**; compare runs 5, 9 and 11. Similarly, the use of higher methanol contents in pentane affords lower product's op (runs 5–10). These observations may indicate that the diastereoisomeric exciplex or contact ion pair produced from the chiral sensitizer and **1** becomes 'looser' in the solvents of higher polarities, making the subsequent attack by methanol less enantioface selective.

The product's op is also a critical function of both position and bulkiness of the alkoxy carbonyl substituent(s) introduced to naphthalene. As far as the less-congested 1- or 2,6-naphthalene(di)carboxylates **3** or **4** is concerned, the bulkiness of chiral alkoxy group does not significantly affect the product's op. However, the op is dramatically enhanced by the increased bulkiness in the sterically congested 1,8-naphthalenedicarboxylate **5**. Mutual interaction between two highly bulky alkoxy groups (**b** and **c**) located closely at the *peri* positions may fix the conformation in the excited state, differentiating the two diastereoisomeric exciplexes or contact ion pairs more effectively.

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