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# PREPARATION, STRUCTURE AND ASYMMETRIC DIELS-ALDER REACTIONS OF 10-ARYLSULFONYLISOBORNYL ACRYLATES

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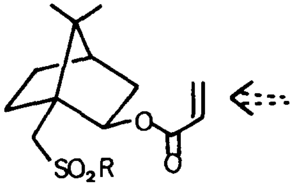
*Abstract:* The crystalline chiral auxiliaries 4 and 5 were readily prepared from camphorsulfonic acid. Their acrylates underwent the Diels-Alder reactions 6 → 7 with modest asymmetric induction consistent with an X-ray study of 6a.

In the preceding communication we reported efficient and practical acrylate-stereoface-differentiations in $TiCl_2(OiPr)_2$-mediated [4+2]-additions of cyclopentadiene to sulfonamides A, R=N$(iPr)_2$[1], R=N(cyclohexyl)$_2$[1a,c].

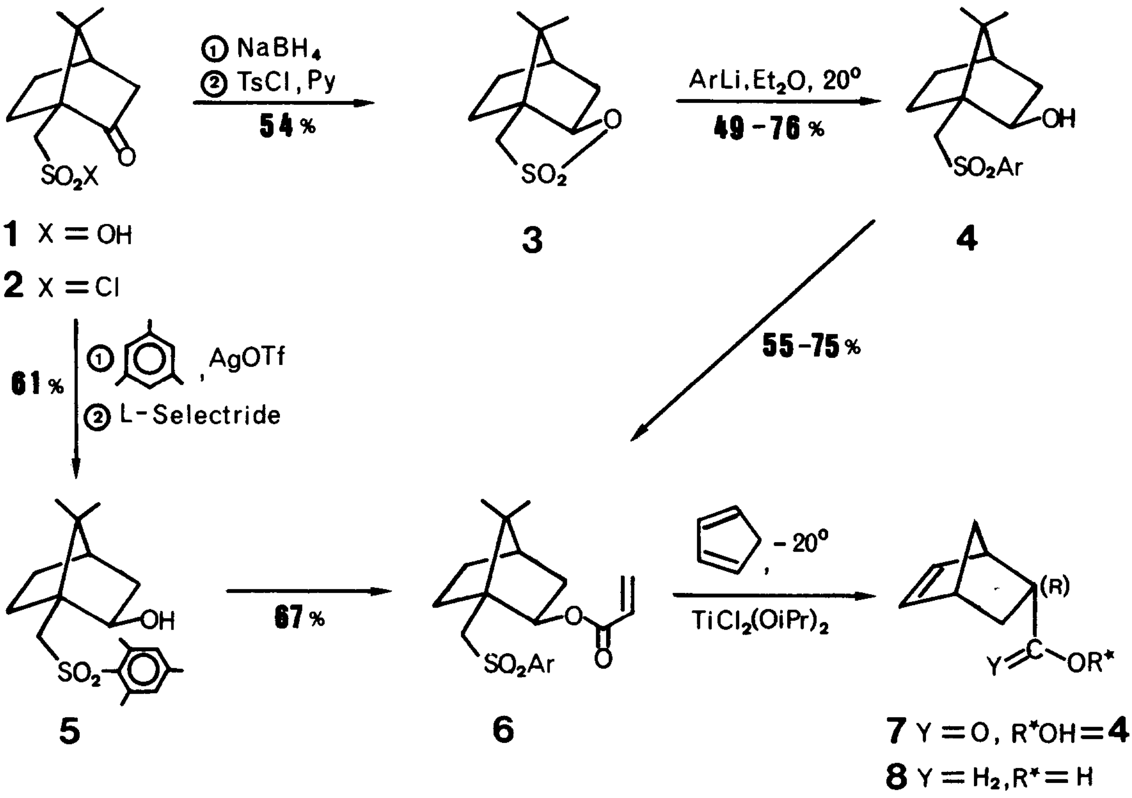
*Scheme 1*



**A**

The purpose of this work was to improve and to rationalize the comparatively modest phenylsulfone-derived shielding in A, R=Ph[1b,c].

*Scheme 2*



| entry | aryl | 4, yield% (m.p. °C) | 6, yield% (m.p. °C) | 7 yield%[a] | 7 endo% | 7 d.e.%[b] |
|---|---|---|---|---|---|---|
| a | phenyl | 73 (141.5-3.5) | 66 (70-1, 83-4[c]) | 97 | 95 | 66 (66) |
| b | 1-naphthyl | 76 (126-9) | 64 (127-30.5) | 99 | 96 | 64 (63) |
| | 8 recrystallizations of 7b (toluene/hexane) | | | 49 | ~100 | ≥ 99.5 |
| c | 2-naphthyl | 71 (128.5-30) | 55 (164-7) | 98 | 95 | - (64) |
| d | 9-phenanthryl | 49 (182.5-4) | 58 (159-64) | 92 | 95 | 69 (69) |
| e | 2,4,6-trimethylphenyl | 5 (131.5-3) | 67 (207-9) | 99 | 95.6 | 66 (64) |

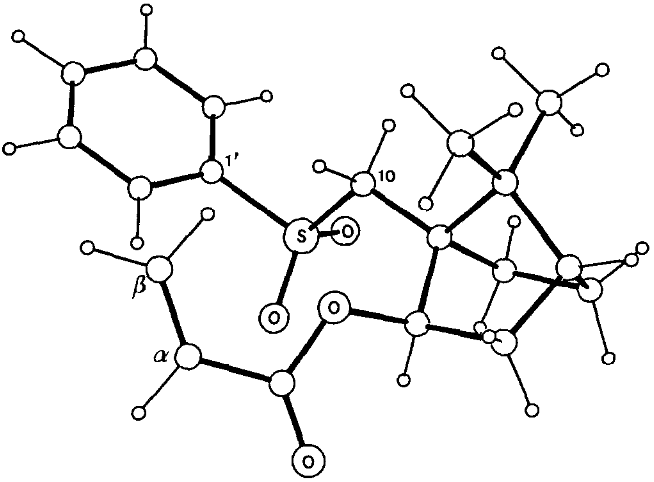
*a)* based on 6.

*b)* determined by HPLC of the carbamate derived from (R)-α-naphthylethyl isocyanate (by $^1$H NMR integration of the methyl signals of crude 7).

*c)* (hexane) m.p. 70-1° (plates), resolidifies, m.p. 83-4° (needles).

To increase the aromatic surface of the blocking group the 1-naphthyl-, 2-naphthyl- and 9-phenanthryl sulfones 4b [2], 4c [2] and 4d [2] were conveniently prepared by nucleophilic ring opening of sultone 3 [3] with the corresponding aryllithium reagent [4]. Alternatively, the sterically demanding mesityl group was introduced by a modified Friedel-Crafts reaction [5] of 2 with mesitylene to give, after carbonyl reduction, the alcohol 5 [2,4]. *Mukaiyama* acylation [4,6] of alcohols 4 and 5 furnished acrylates 6 [2] which were subjected to $TiCl_2(OiPr)_2$-promoted cyclopentadiene additions. These additions 6 → 7 [2], the reductions 7 → 8 ($LiAlH_4$) and stereochemical analyses of 8 were carried out under standard conditions [1]. Moreover, the $^1H$ NMR spectra of crude 7 showed clearly the extent of asymmetric induction. Our results are summarized in the Table. Disappointingly, enlargement of neither the aromatic surface (b,c,d) nor the steric bulk (e) led to an acrylate-stereoface differentiation exceeding 69% d.e. This result, which outweighs several practical advantages of the control elements 4 and 5, is consistent with an X-ray analysis of the uncomplexed phenylsulfonyl acrylate 4a [7].

*Scheme 3.*



Notable features are the antiplanar disposition of the $C_\alpha,C_\beta$- and the C=O bond (almost identical to that found in sulfonamide A, $R=N(cyclohexyl)_2$ [1a,c]), the staggered conformation of the $C(10)H_2$ relative to the camphor skeleton and to the $SO_2$ group and, last but not least, the perpendicular orientation of the C(10)-S-C(1')- and the benzene planes as well as the bisection of the O-S-O-plane by the C(1')-phenyl-p-orbital [8]. Consequently, the sulfone-conjugated aryl plane is perpendicular to the $C_\alpha$-*re*-face which explains the less distinct shielding.

This paper and the preceding one support the hypothesis that conjugation-derived conformational constraints play an important role in "low temperature" asymmetric Diels-Alder reactions which may be of predictive value for the rational design of new, chiral control elements.

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## NOTES AND REFERENCES

[1] a) Preceding paper. b) *W. Oppolzer*, *C. Chapuis* and *M.J. Kelly*, Helv. Chim. Acta 66, 2358 (1983). c) Presented (*W.O.*) at the Symposium "Pericyclic Reactions, Theory and Applications in Synthesis", Wageningen, March 1984 and at the "1984-Euchem Conference on Asymmetric Synthesis", Port-Camargue, April 1984.

[2] All new compounds were characterized by IR, $^1$H-NMR and MS.

[3] *D. Solas* and *J. Wolinsky*, J. Org. Chem. 48, 1988 (1983).

[4] The following procedures (carried out with stirring under argon) are representative: 3 → 4: add 1.4N BuLi(hexane, 2.0 ml) to the aryl bromide (3 mmol) in $Et_2O$ (15 ml) at RT; after 10 min. add sultone 3 (325 mg, 1.5 mmol) in $Et_2O$ (5 ml); after 45 min at RT, aq. work-up, chromatography ($SiO_2$) and crystallization ($CH_2Cl_2$/hexane). 2 → 5: i) add 2 (193 mg, 0.77 mmol) in mesitylene (3 ml) to silver triflate (198 mg, 0.77 mmol) RT 16 h, then aq. work-up and crystallization of the resulting sulfonyl ketone (192 mg, 72% m.p. 119.5-120.5°); ii) add 1M L-selectride (THF, 5.1 ml) to the sulfonyl ketone (1.367 g, 4.1 mmol) at -78°; 30 min -78° then → RT, then RT, 1h, usual work-up[1], crystallization (hexane, 84%). For the conversions 4 → 6, 6 → 7 and 7 → 8: see ref. [1].

[5] *K. Huthmacher*, *G. König* and *F. Effenberger*, Chem. Ber. 108, 2947 (1975).

[6] *K. Saigo*, *M. Usui*, *K. Kikuchi*, *E. Shimada* and *T. Mukaiyama*, Bull. Chem. Soc. Jpn. 50, 1863 (1977).

[7] Comments and methods are identical with those cited in ref.[1a] except: The crystals (m.p. 70-1°) are orthorhombic, $a$=8.703(2), $b$=13.238(2), $c$=16.273(2) Å, space group $P2_12_12_1$, $z$=4, $d_c$=1.234 g. cm$^{-3}$. The enantiomorph-polarity parameter $x$=-0.39(32). The final $R$-factor, based on 1300 observed reflections was 0.055.

[8] Spectral (a) and X-ray (b)-evidence for similar spatial arrangements of alkylarylsulfones: a) *M. Mohraz*, *W. Jian-qi*, *E. Heilbronner*, *A. Solladié-Cavallo* and *F. Matloubi-Moghadam*, Helv. Chim. Acta 64, 97 (1981); b) *C. Rérat* and *G. Tsoucaris*, Bull. Soc. Fr. Min. Cristallogr. 87, 100 (1964); *F. Mo* and *A. Gaasdal*, Acta Cryst. B 36, 2349 (1980).

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