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SYNTHESIS OF (+)-DISPARLURE USING THE REACTION OF 6-METHYLHEPTYL PHENYL SULPHONE WITH TRIMETHYLSILYL ETHYLENE OXIDE AND ASYMMETRIC EPOXIDATION

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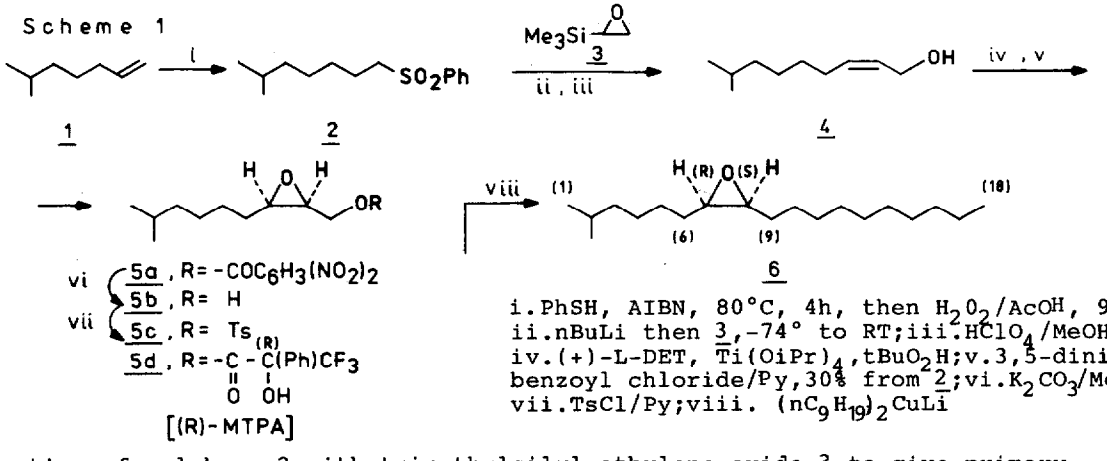
Summary: Lithiated sulphone 2 was reacted with trimethyl(oxiranyl)silane 3 to yield allylic alcohol 4; the latter was epoxidized by the Sharpless procedure and the corresponding hydroxy-epoxide 5b was transformed into (+)-disparlure 6 via tosylate 5c.

Disparlure (6, Scheme 1), an attractant of gypsy moth, is one of the most popular targets of the contemporary synthetic studies in the field of pheromones.[1] Optically active compound 6, in both enantiomeric forms, has been prepared[2,3] using as intermediates (Z)-allylic alcohols corresponding to the C_1-C_9 or C_6-C_{18} fragments of its carbon skeleton and applying Sharpless asymmetric epoxidation.[4] In this context the availability of primary (Z)-allylic alcohols is of utter importance for the efficiency of the synthetic route to the compound under consideration and to some other natural products. We have recently found[5] that (Z)-allylic alcohols may be prepared with high selectivity by the reaction of alkyl aryl sulphones with trimethyl(α,β-epoxyalkyl)silanes. Now, we report an efficient synthesis of natural (+)-disparlure, involving the

Scheme 1



i.PhSH, AIBN, 80°C, 4h, then H_2O_2/AcOH, 95% ii.nBuLi then 3,-74° to RT;iii.$HClO_4$/MeOH; iv.(+)-L-DET, $Ti(OiPr)_4$,$tBuO_2H$;v.3,5-dinitr benzoyl chloride/Py,30% from 2;vi.K_2CO_3/MeOH vii.TsCl/Py;viii. $(nC_9H_{19})_2CuLi$

reaction of sulphone 2 with trimethylsilyl ethylene oxide 3 to give primary allylic alcohol 4, as well as transformation of the latter into enantiomerically pure hydroxy-epoxide 5b.

Sulphone 2 was obtained by radical addition of thiophenol to 6-methyl-

-hept-1-ene[6] (1), followed by oxidation (Scheme 1). Epoxide 3 was obtained from trimethylvinylsilane via bromhydrin.[7] The reaction of compound 2 (lithium derivative) and 3, followed by acid hydrolysis,[5] gave allylic alcohol 4 in a 65% yield,[8] E:Z = 1:13. This product was submitted to Sharpless epoxidation, and the crude hydroxy-epoxide was esterfied with 3,5-dinitrobenzoyl chloride.[2] Single crystallization of the obtained mixture (hexane-ether) furnished pure ester 5a (45% yield from 4). The latter ester was hydrolyzed and the alcohol 5b[9] was converted into tosylate 5c. This derivative was treated with n-nonyllithiumcuprate according to the procedure of Mori and Ebata.[2] The required product 6 displaying the expected physical properties, was obtained.

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6. This compound was prepared by coupling of i-amylmagnesium bromide and allyl chloride
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8. Distilled product
9. Enantiomeric purity of this product was confirmed by ^{1}H NMR spectra of its ester with (R)-3,3,3-trifluoro-2-methoxy-2-phenylpropionic acid [(R)-MTPA] (J.A.Dale, H.S.Mosher, J.Am.Chem.Soc., 1973, 95, 512)

Selected physical and spectroscopic properties of the products:

Sulphone 2, bp 138°C/0.05 mmHg, correct elemental analysis;
3,5-Dinitrobenzoate 5a, mp 80°C, $[\alpha]_D$=-11.03 (c=1.35, Et_2O); ^{1}H HMR ($CDCl_3$, Bruker Am 500): δ (ppm) 0.88(d,6H, J=6,6Hz, $2CH_3$), 1.18-1,24(m,2H),1.35-1.66(m,7H), 3.13(ddd, 1H, J_1=J_2=6.2, J_3=4.4 Hz, C_3-H), 3.37 (ddd, 1H, J_1=4.2, J_2=4.2, J_3=7.6Hz, C_2-H), 4.41(dd, 1H, J_1=3.7, J_2=12.1Hz) and 4.73(dd, J_1=7.6, J_2=12Hz, $2C_1$-H), 9.21(d, J=2.1Hz) and 9.25 (t,J=2.1Hz, aromat.H)
(R)-MTPA-ester 5d, ^{1}H NMR, diagnostic signals: δ (ppm) 4.35 (dd, 1H, J_1=6.8, J_2=12.0Hz, C_{1a}-H) and 4.51 (dd, 1H, J_1=4.6, J_2=12.0Hz, C_{1b}-H)
Alcohol 5b, ^{1}H NMR δ (ppm)).865(d,6H, J=6.6Hz, $2CH_3$), 1.14-1.19(m,2H,CH_2), 1.25-1.40(m,4H,CH_2), 1.52(9 lines, J=6.6, C_8-H), 2.06(dt,2H,J_1=J_2=ca.7Hz C_4-H), 4.19(d,2H, J=6.3Hz, C_1-H, 5.52(dt, 1H, J_1=7,J_2=10.9Hz, C_3-H), 5.62(dt, 1H, J_1=6.3, J_2=10.9Hz, C_2-H)
(+)-Disparlure (6), ^{1}H NMR δ (ppm) 0.87 (d overlaping t, 9H, CH_3), 1.15-1.55 (m, 27H), 2.9(m, 2H).

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