

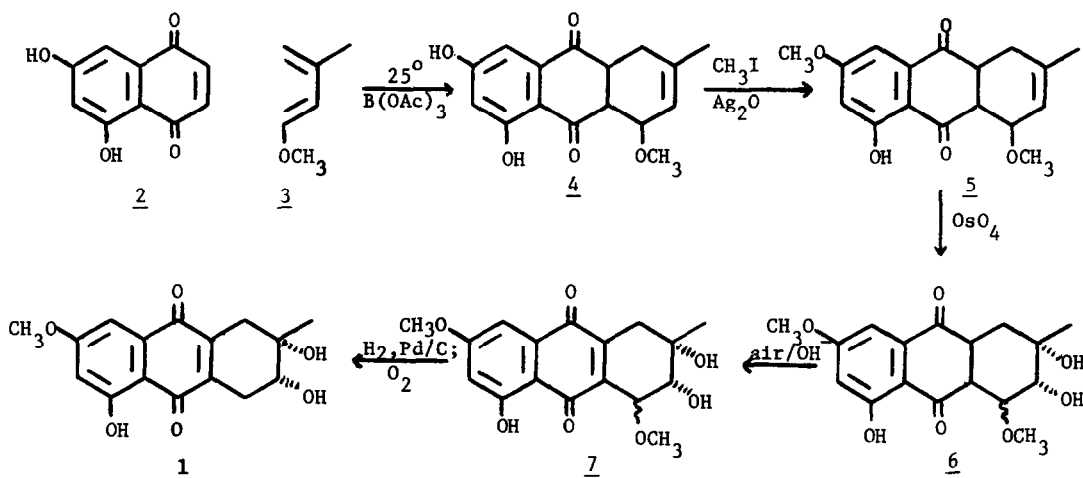
A REGIOCHEMICALLY-CONTROLLED SYNTHESIS OF ALTERSOLANOL B

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The structure of Altersolanol B (1) was reported by Stoessl in 1969.<sup>1</sup> In conjunction with our examination of the effect of Lewis acid catalysis on the regiochemical outcome on Diels Alder reactions of oxygenated naphthoquinones, which is described in the accompanying communication, we now report an efficient, regiochemically-controlled synthesis of (+)-1 (Scheme 1). Thus, Diels Alder reaction of 2<sup>2</sup> and excess 3<sup>3</sup> in ether at 25° in the

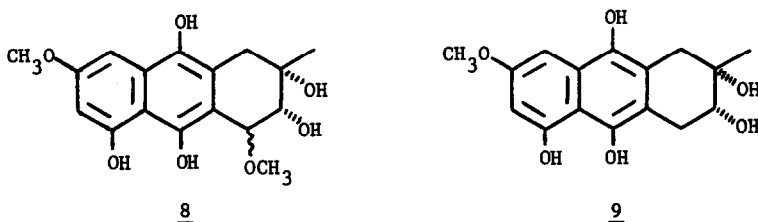
Scheme 1



presence of 2 equivalents B(OAc)<sub>3</sub> affords 4 (mp 138-9° from CH<sub>2</sub>Cl<sub>2</sub>) in greater than 80% yield.\* The regioselectivity of this B(OAc)<sub>3</sub>-mediated reaction between 2 and 3 is ≥95%.\* Methylation of 4 (Ag<sub>2</sub>O, CH<sub>3</sub>I in CH<sub>2</sub>Cl<sub>2</sub>) gave 5 (mp 125-6° from Et<sub>2</sub>O/pet. ether) in nearly quantitative yield. Reaction of 5 with OsO<sub>4</sub> in CCl<sub>4</sub> (2-4 hrs at 25°) followed by dilution with THF and treatment with ~3 equivalents of 10% aqueous NaHSO<sub>3</sub> (2 hrs, 25°) gave 6, which was not isolated. Rather, the reaction solution was made slightly basic (5% aq. NaOH) and stirred in the presence of air for ½ hr. After neutralization (excess pH 7 buffer) and isolation (extract 3 times with a 1:1 Et<sub>2</sub>O:THF mixture; dry over Na<sub>2</sub>SO<sub>4</sub>; concentrate *in vacuo*),

\*For the assignment of regiochemistry to 4, and a discussion of the role of B(OAc)<sub>3</sub>, see the accompanying paper.

chromatography on a silica gel SEP-PAK "column"<sup>4</sup> (elute first with  $\text{CHCl}_3$ , then 90:10  $\text{CHCl}_3$ : EtOH) afforded 7 (mp 172-4°). The conversion of 2 to 7 can be conveniently conducted without purification of any intermediates in 60% overall yield. Hydrogenolysis of 7 [ $\text{H}_2$  (1 atm), 5% Pd/C in EtOH, 6 hrs), followed by exposure to air, gave, presumably<sup>5</sup> via 8 and 9, ( $\pm$ )-1



(mp 199-201°) in 66% yield after recrystallization from EtOH. The ( $\pm$ )-Altersolanol B so obtained is identical in all appropriate respects with an authentic sample of 1 by direct comparison.<sup>6</sup>

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#### References and Notes

1. A. Stoessl, *Can. J. Chem.*, **47**, 767 (1969); M. Gordon, A. Stoessl and J.B. Stothers, *ibid.*, **50**, 122 (1972).
2. See footnote 4 in the accompanying paper.
3. T.R. Kelly, *Tetrahedron Letters*, 1387 (1978).
4. Manufactured by Waters Associates. We Thank Mr. Patrick King for introducing us to these useful devices.
5. Compare T. Noda, T. Take, T. Watanabe and J. Abe, *Tetrahedron*, **26**, 1339 (1970).
6. The nmr spectra (internal TMS) of the compounds described are (only distinctive peaks are given): 4 (in  $\text{CDCl}_3$ ),  $\delta$  1.80 (3H, s,  $\text{CH}_3$ ), 2.98 (3H, s,  $\text{OCH}_3$ ), 3.99 (1H, m,  $\text{CHOCH}_3$ ), 5.75 (1H, m, olefinic H), 6.57 and 7.00 (2H, dd,  $J=2\text{Hz}$ , aromatic H's), 12.56 (1H, s, *peri* OH); 5 (in  $\text{CCl}_4$ ),  $\delta$  1.90 (3H, s,  $\text{CH}_3$ ), 3.02 (3H, s,  $\text{OCH}_3$ ), 3.95 (3H, s, aromatic  $\text{OCH}_3$ ), 3.95 (1H, m,  $\text{CHOCH}_3$ ), 5.80 (1H, m, olefinic H), 6.55 and 6.98 (2H, dd,  $J=3\text{Hz}$ , aromatic H's), 12.29 (1H, s, *peri* OH); 7 (in  $\text{CDCl}_3$ ),  $\delta$  1.36 (3H, s,  $\text{CH}_3$ ), 3.65 (3H, s,  $\text{CHOCH}_3$ ), 3.90 (3H, s, aromatic  $\text{OCH}_3$ ), 4.50 (1H, br d,  $J=3$ ,  $\text{CHOCH}_3$ ), 6.65 and 7.15 (2H, dd,  $J=3$ , aromatic H's), 12.28 (1H, s, *peri* OH). The NMR spectra of our ( $\pm$ )-1 and authentic 1 (both recorded on the same instrument) are superimposable and in agreement with that reported previously.<sup>1</sup>

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