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A NEW STEREOSELECTIVE SYNTHESIS OF RACEMIC DISPARLURE, THE SEX PHEROMONE OF GYPSY MOTH (<u>PORTHETRIA DISPAR</u> L.)

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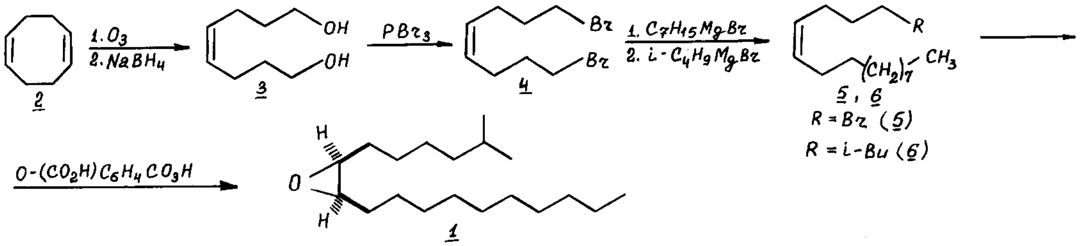
One of the crucial steps in the synthesis of (Z)-7,8-epoxy-2-methyloctadecane (disparlure, 1) includes generation of cisoid C=C bond in the molecule. A number of approaches have been reported to solve this problem involving Wittig olefination[1], selective hydrogenation of disubstituted acetylenes[2], or protodesilylation of the appropriate vinylsilane[3]. We wish to report here new, stereocontrolled synthesis of 1 starting from readily available cyclooctadiene (2). One of its Z double bonds was employed in present approach for the construction of epoxide moiety as outlined in Scheme.

Selective ozonolysis[4] of 2 using 0.9 mol equiv. of O_3 in cyclohexane at ca. 5° in the presence of 1 mol equiv. of MeOH with subsequent treatment of ozonide with 1.3 mol equiv. of $NaBH_4$ in MeOH at ca. 20° gave (85%) 4Z-octene-1,8-diol (3)[5], b.p. 78°/0.001 mm Hg, n_D^{20} 1.4760. Reaction of 3 with 0.8 mol equiv. of PBr_3 in Et_2O solution in the presence of Py (Ar, 1h at 5° then 12h at ambient temperature) yielded (45%) the dibromide (4)[5], b.p. 96-97°/1 mm Hg, n_D^{20} 1.5220. Treatment of 4 with 2 mol equiv. of $C_7H_{15}MgBr$ (THF solution, Ar, 5 min at 25-40°)[6] followed by column chromatography of the reaction mixture on alumina (pentane) furnished (90%) the bromide (5)[5], b.p. 114-115°/ 1 mm Hg, n_D^{20} 1.4753. The bromide 5 was treated with 4 mol

Scheme



equiv. excess of i-C_4H_9MgBr (THF solution, Ar, 5 min at 25-40°)^6 to give (80%) the olefin (6)^5, b.p. 135-136°/1 mm Hg, n_D^{20} 1.4430. Its epoxidation with monoperphtalic acid (Et_2O solution, 1h at -10-5°, then 12h at ambient temperature) resulted in after column chromatography on alumina (low-boiling petroleum ether - Et_2O, 10:1) d,l-disparlure (1)^5 with a yield of 90%, b.p. 142-143°/1mm Hg, n_D^{20} 1.4460, cf^7. Thus the transformations mentioned above represent the five step stereoselective synthesis of racemic disparlure in 25% overall yield calculated from the starting butadiene dimer.

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5. Elemental analysis and spectral (IK, NMR, MS) data are in agreemant with this structure.
6. After addition of 60 mmol of the Grignard reagent 3 ml of 0.1M Li_2CuCl_4 solution (cf. M.Tamura, J.Kochi, Synthesis, 1971, 303) was added at -5° and the resulting mixture was kept at ca. 20° for 15h.
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