

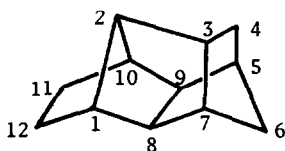
METHANOMETHENONAPHTHALENES BY BASE-PROMOTED EPOXIDE ISOMERIZATION. A CONVENIENT SYNTHESIS OF EXO-4-PENTACYCLO[6.4.0.0^{2,10}.0^{3,7}.0^{5,9}]DODECANOL

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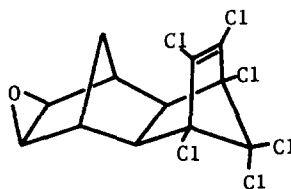
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The twist-bridged framework of pentacyclo[6.4.0^{2,10}.0^{3,7}.0^{5,9}]dodecane (1) has significance in several connections. It is the principal skeleton generated by the photoisomerization¹ as well as metabolism² in diverse organisms of the insecticides dieldrin (2) and aldrin (2, C=C instead of oxirane). Ethylated 1 has been found by Schleyer *et al* to be a successful if relatively inaccessible precursor to diamantane under acid-catalyzed rearrangement,³ while the parent hydrocarbon (1) under the same conditions gives a disproportionation mixture containing 2,4-ethanoadamantane.⁴ Secondary-alcohol derivatives of 1 have been instructive substrates in solvolysis studies by Winstein *et al*.⁵



1



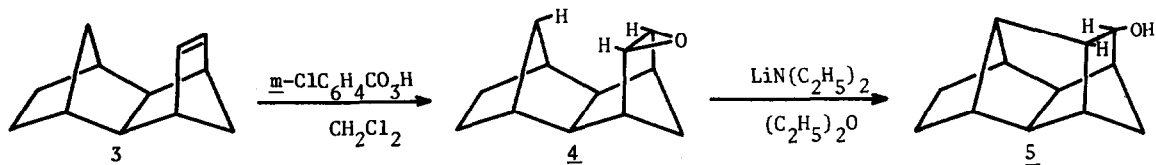
2

For entry to an investigation in progress we required a quantity of alcohol 5 (decahydro-2,4,7-metheno-1H-cyclopenta[a]pentalen-3-ol).⁶ The compound has been previously synthesized^{5a} but by a relatively long and low-yield procedure, and a more direct route was sought. It appeared from the work of Cope and coworkers⁷ and later Crandall and coworkers⁸ that transannular carbonoid insertion upon treatment of the readily available epoxide 4 with strong base might produce 5 in high yield. This hypothesis has been realized.

Reaction of the Diels-Alder adduct⁹ (3) of norbornene and cyclopentadiene with *m*-chloroperbenzoic acid in methylene chloride at 10-15 °C gave in 98% crude yield (10.0-g scale) the epoxide 4,¹⁰ which without further purification was treated with 2.5 equivalents of lithium diethylamide in ether⁸ at 0-35 °C for 48 hr. Workup⁸ and recrystallization from hexane at -30 °C yielded 82% (6.0-g scale) of alcohol 5, homogeneous by gas chromatography: mp 84.0-85.0 °C (lit.^{5a} mp 80.0-81.5 °C); ¹H NMR (CDCl₃) δ 4.13 (d, J = 2 Hz, 1H, >CHOH), 0.67-2.57 (m, 15H, >CH- and >CH₂); IR (CCl₄) 899, 919, 1055, 1227, 1295, 2865, 2941, 3345, 3610 cm⁻¹; *p*-bromobenzenesulfon-

ate ester mp 112.0-113.5 °C (lit.^{5a} mp 112.5-113.8 °C).

Since numerous functional derivatives of 3 can be prepared by Diels-Alder synthesis, the pathway reported here should make conveniently available a variety of substituted representatives of system 1.¹¹



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