

Stereochemistry and Stereocontrolled Reactions in Hydroazulene Chemistry: Functionalization in a 3,8a-Dihydroazulene *via* Singlet Oxygenation

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The racemic dihydroazulene (**1**) is resolved on triacetyl cellulose into its pure enantiomers; treatment of (**1**) with *N*-methyltriazolinedione and with singlet oxygen leads to the polycyclic compounds (**2**) and (**3**), respectively; (**3**) is converted to the dione (**5**), *via* (**4**), and to the diepoxide (**6**); all reactions are highly diastereoselective.

Hydroazulenes form the frame of many sesquiterpenes.¹⁻³ In this communication we describe new ways to stereocontrol the functionalization of hydroazulenes. Reaction of 8-methoxyheptafulvene with dimethyl acetylenedicarboxylate led *via* an (8 + 2)-cycloaddition to (**1**).² The stereochemistry of (**1**) was proved by shift measurements with Eu(fod)₃ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato).^{2,4†} The racemic mixture (±)-(**1**) was separated into the pure enantiomers by column chromatography on swollen triacetyl cellulose.⁵ The enantiomeric purities were deter-

mined by c.d. and by n.m.r. spectroscopy, using (+)-Eu(hfc)₃ [hfc = 3-(heptafluoropropylhydroxymethylene)camphorato] {(+)-(**1**), [α]_{D²⁰}²⁵ = +185.7 ° ml g⁻¹ dm⁻¹; (-)-(**1**), [α]_{D²⁰}²⁵ = -185.2 ° ml g⁻¹ dm⁻¹, *c* = 2.2 mg ml⁻¹, 95% EtOH} (Figure 1). Cycloaddition of (**1**) to *N*-methyltriazolinedione gave (**2**) (C₁₈H₁₉N₃O₇, m.p. 176–178 °C) as the single product. Likewise reaction of (**1**) with singlet oxygen gave (**3**). Treatment with base converted (**3**) into (**4**) which was then oxidized by MnO₂ to the homoquinone (**5**) (m.p. 114–115 °C). Thermolysis of (**3**) led to (**6**) (Scheme 1). All reactions were highly stereoselective, and occurred in good preparative yields.

The structures were established by spectroscopic methods (Table 1). The high-field shifted cyclopropane protons of (**2**) and (**3**) are characteristic of polycyclic structure. For (**4**)

† The ¹H n.m.r. shift measurements were quantitatively evaluated by computer simulation (ref. 4).

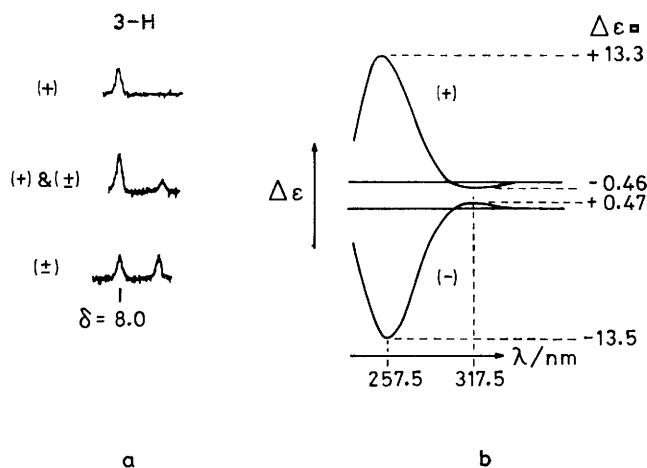
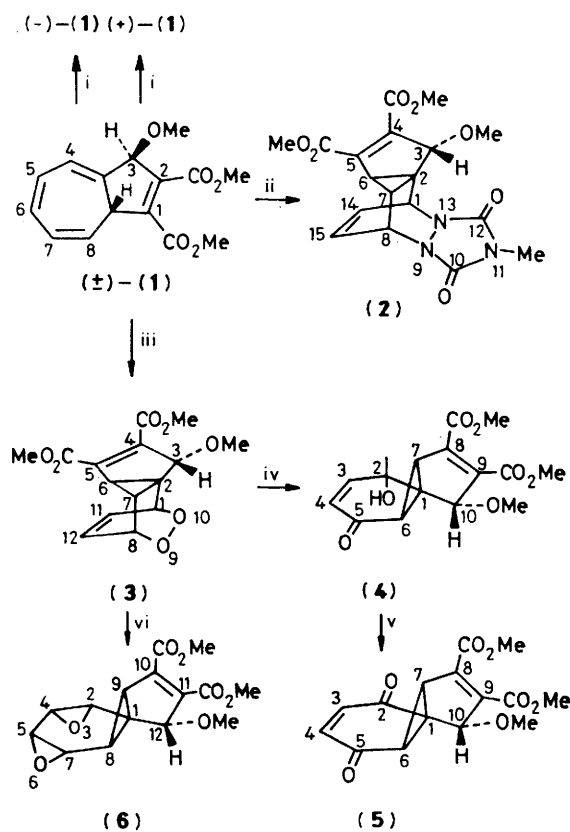


Figure 1. Chiroptic properties of (+)-(1) and (-)-(1): a, shift measurements with (+)-Eu(hfc)₃; b, c.d. curves in 95% EtOH.

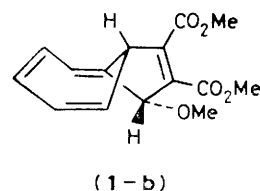


Scheme 1. If not otherwise indicated the compounds are racemic. Conditions and reagents: i, chromatography on swollen microcrystalline triacetyl cellulose; ii, *N*-methyltriazaolinedione, CH₂Cl₂, 25 °C; iii, O₂, hv, 0 °C, CCl₄, TPP (*meso*-tetraphenylporphine), 20 h; iv, NEt₃, CH₂Cl₂, 25 °C, 20 h; v, freshly precipitated MnO₂, CH₂Cl₂, 4 days; vi, toluene, 140 °C, 2 h in an evacuated tube.

the AB spectrum of the olefinic protons is significant. The stereochemistry of (5) and (6) follows from the known selectivities of the reactions of bicyclic peroxides.⁶ The preference for the stereospecific formation of (2) and (3) by

Table 1. Selected spectroscopic data.

Compound (2)	δ (¹ H N.m.r.)	ν (I.r.)/cm ⁻¹
(2)	1.53 (7-H), 2.10 (6-H), 3.03 (NMe), 3.60 (OMe), 3.81 (CO ₂ Me), 4.63 (3-H), 5.15 (8-H), 5.57 (1-H), 5.77–6.47 (14-H, 15-H)	3050, 3005, 2955, 2885, 2840, 1780, 1720, 1640, 1460, 1435, 1390, 1330, 1280, 1230, 1185, 785
(3)	1.58 (7-H), 1.84 (6-H), 3.52 (OMe), 3.80 (CO ₂ Me), 4.78 (3-H), 4.95 (8-H), 5.30 (1-H), 6.28–6.60 (11-H, 12-H)	3070, 3045, 3020, 2970, 2850, 1725, 1710, 1625, 1450, 1295, 1230, 1110, 940, 880
(4)	1.87 (6-H), 2.60 (7-H), 3.60 (OMe), 3.81 (CO ₂ Me), 4.84 (10-H), 4.94 (2-H), 6.02 (4-H), 6.80 (3-H)	3530, 3080, 3035, 3000, 2925, 2850, 1740, 1715, 1675, 1625, 1440, 1295, 1090
(5)	2.27 (6-H), 3.48 (7-H), 3.60 (OMe), 3.82 (CO ₂ Me), 4.92 (10-H), 6.39–6.68 (3-H, 4-H)	3055, 3010, 3000, 2980, 2940, 2870, 2845, 1735, 1725, 1690, 1670, 1655, 1440, 1325, 1275, 1235, 1090, 1045, 790
(6)	1.40 (8-H), 2.40 (9-H), 3.32–3.50 (2-H, 4-H), 5-H, 7-H), 3.62 (OMe), 3.79 (CO ₂ Me), 3.83 (CO ₂ Me), 4.50 (12-H)	3075, 3040, 3015, 2970, 2950, 2910, 2860, 2840, 1740, 1725, 1645, 1440, 1325, 1225, 1020, 940



the (4 + 2)-cycloaddition of (1) must be due to the presence of the boat form in (1), as indicated by (1-b).⁷

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