A Total Synthesis of $(\pm)$-$\Delta^{9(12)}$-Capnellene

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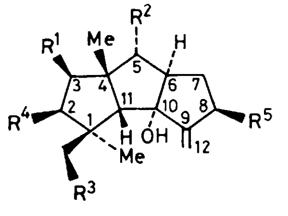
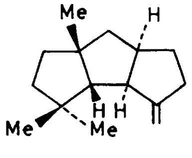
A novel synthesis of the linearly fused tricyclopentanoid marine natural product $(\pm)$-$\Delta^{9(12)}$-capnellene (**2**) from the readily available starting materials methylcyclopentadiene and *p*-benzoquinone is described.

The soft coral *Capnella imbricata* is an unusually rich source of polyhydroxylated sesquiterpenes (**1a**—**e**), known by the generic name capnellanes and possessing the novel tricyclo[6.3.0.0^{2,6}]undecane (triquinane) carbon framework.[1] The synthesis of the simplest member of the capnellane family and the presumed biogenetic precursor of the 'capnellanols' (**1a**—**e**), the tricyclic hydrocarbon $(\pm)$-$\Delta^{9(12)}$-capnellene (**2**)[1e] has aroused intense interest recently.[2,3] Here we report a short synthesis of the marine natural product (**2**) by a flexible strategy that can be adapted to make more complex members of the capnellane group.

Diels–Alder cycloaddition of methylcyclopentadiene isomers and *p*-benzoquinone gave a mixture of adducts from which the desired tricyclic *endo*-adduct (**3**), m.p. 71 °C [^{1}H n.m.r., δ 1.56 (3H, s); ^{13}C n.m.r. δ 57.7 p.p.m., (s)] could be isolated in 70% yield. Irradiation of (**3**) in ethyl acetate in a Pyrex vessel with a 450 W lamp furnished the pentacyclic dione (**4**), m.p. 176 °C (75%) (Scheme 1). Thermolysis of (**4**) under flash vacuum pyrolysis conditions gave the *cis,cisoid,cis*-triquinane bis-enone (**5**), m.p. 93—94 °C in 60% yield.[4] The structure of (**5**), which possesses 12 of the 15 carbon atoms of the capnellane framework, was elucidated from its ^{13}C n.m.r. spectrum [δ 207.2(s), 207.1(s), 170.3(d), 165.7(d), 132.8(d), 130.4(d), 59.9(d), 56.6(s), 52.7(d), 49.6(d), 38.3(t), and 26.8 p.p.m. (q)] and from other spectral data.

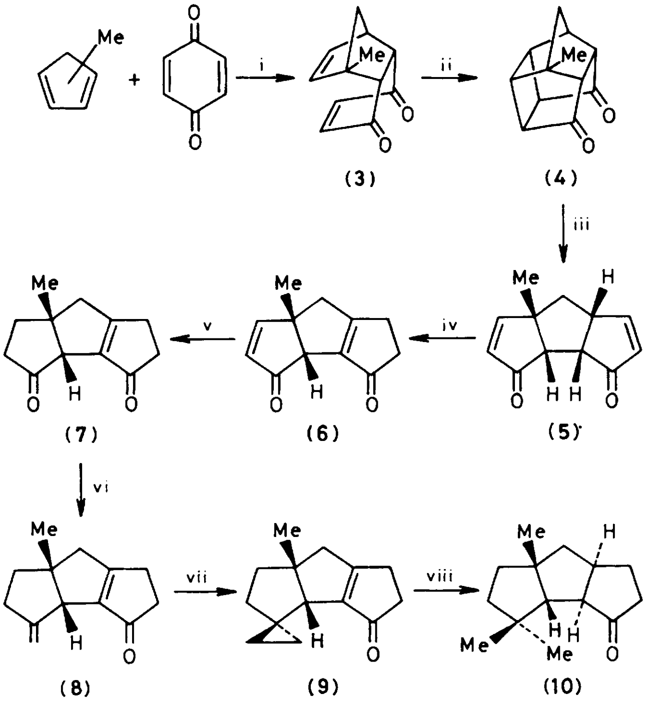


(**1**) a; $R^1 = R^2 = R^3 = H$, $R^4 = R^5 = OH$
b; $R^1 = R^3 = H$, $R^4 = R^2 = R^5 = OH$
c; $R^4 = R^2 = R^3 = H$, $R^1 = R^5 = OH$
d; $R^4 = R^2 = H$, $R^1 = R^5 = R^3 = OH$
e; $R^4 = R^1 = R^3 = H$, $R^2 = R^5 = OH$



(**2**)

Treatment of the *cis,cisoid,cis*-bis-enone (**5**) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) resulted in the relocation of the double bond to form a new bis-enone (**6**), m.p. 97—98 °C [^{13}C n.m.r. δ 204.6(s), 201.2(s), 183.8(s), 168.9(d), 147.6(s), 129.8(d), 57.5(s), 57.1(d), 42.6(t), 39.6(t), 25.3(t), and 25.0 p.p.m. (q)] in >90% yield. Catalytic hydrogenation of (**6**) gave (**7**) which was subjected to a selective Wittig reaction at



Scheme 1. i, Tetrahydrofuran, room temp., 70%; ii, *hν*, ethyl acetate, 75%; iii, 530 °C, column packed with quartz chips at 0.1 mmHg, 60%; iv, DBU–CH_2Cl_2, reflux, >90%; v, H_2–10% Pd/C in ethyl acetate, 80%; vi, Ph_3P^+–Me I^-–t-$C_5H_{11}O^-Na^+$, toluene, 30—40%; vii, CH_2I_2–Zn/Cu couple, 50%; viii, H_2–PtO_2 in $MeCO_2H$, 3 atm, 60%.

the saturated carbonyl group to yield (**8**) [^{1}H n.m.r. δ 5.2 (1H, t, J 1 Hz) and 4.96 (1H, t, J 1 Hz); ^{13}C n.m.r. δ 203.3, 183.3, 152.1, 148.6, 107.9, 56.6, 55.9, 46.4, 40.8, 40.4, 33.5, 27.3, and 25.7 p.p.m.]. Quaternization at C-1 was achieved through a cyclopropanation–hydrogenolysis sequence.[5] Simmons–Smith reaction of (**8**) proceeded satisfactorily to give the enone (**9**) with the desired spiro-fused cyclopropane ring. The *gem*-dimethyl group and the required *cis,transoid,cis*-stereochemistry of the capnellane system were now generated in one step through catalytic hydrogenation of (**9**) to give the known ketone nor-capnellanone (**10**).† Since (**10**) has been previously[2] converted into (**2**) through Wittig olefination, our synthesis of (**10**) completes the total synthesis of (**2**) in eight steps from the available starting materials methylcyclopentadiene and *p*-benzoquinone.

We thank Professor R. D. Little, University of California, Santa Barbara, for the comparison spectra of nor-capnellanone.

Received, 12th April 1983; Com. 460

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† The formation of *cis,transoid,cis*-stereochemistry by catalytic hydrogenation of (**9**) was not unexpected in view of the presence of 1,1′-substitution and has precedence (ref. 6). Another product, probably the *cis,cisoid,cis*-isomer of (**10**) was also formed during the reaction.

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