

Novel Rearrangement to a Pentacyclopentanoid (Polyquinane) System

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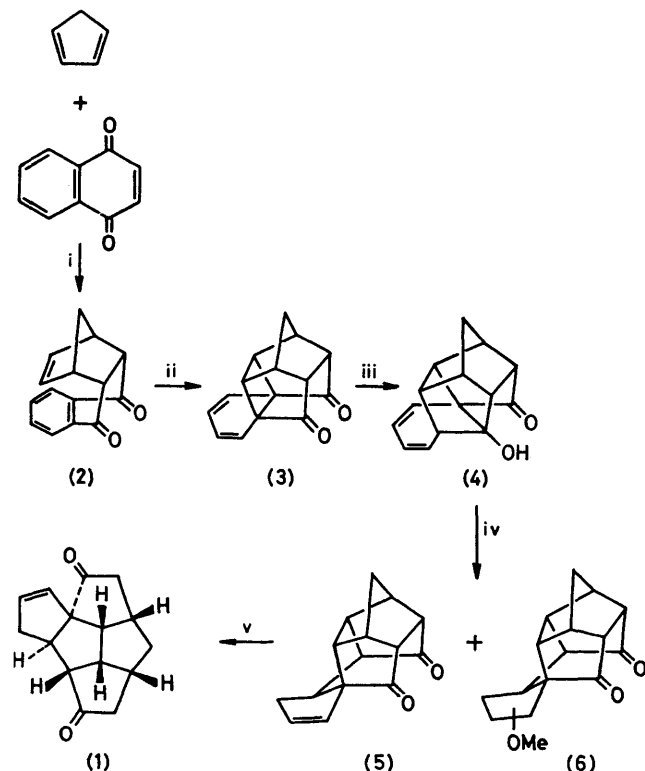
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Summary An efficient five-step synthesis of the pentacyclo-[10.2.1.0^{4,8}.0^{6,10}.0^{9,13}]pentadecane system from cyclopentadiene and 1,4-naphthoquinone is described.

CURRENT interest in fused cyclopentanoids (polyquinanes) has led to the development of many new strategies for their rapid synthesis.¹ In this report, we describe the efficient



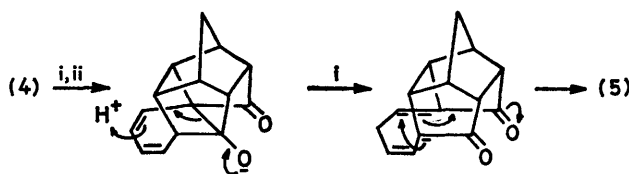
SCHEME 1. Reagents: i, Heat; ii, $h\nu$, C_6H_6 ; iii, $Zn-AcOH$, iv, $NaOMe-MeOH$, v, $Na-K$ alloy- Me_3SiCl .

† Spectral data: (4) ν (KBr) 3350 and 1770 cm^{-1} ; 1H n.m.r. δ ($CDCl_3$) 1.42(2 H, s), 2.2(2 H, s), 2.4—2.85(6 H, m), and 5.6—6.2 (4 H, m); ^{13}C n.m.r. δ ($CDCl_3$) 212.6(s), 130.9(d), 127.7(d), 125.8(d), 124.8(d), 76.3(s), 57.6(s), 57.5(d), 52.8(d, C-2), 50.3(d), 48.8(d), 46.0(d), 41.8(d), and 35.3(t) p.p.m. (5) ν (KBr) 1740 cm^{-1} ; 1H n.m.r. δ ($CDCl_3$) 1.9—3.6(12 H, m) and 5.5—5.8(2 H, m); ^{13}C n.m.r. δ ($CDCl_3$) 218.9(s), 218.0(s), 133.8(d), 131.2(d), 71.4(s), 67.1(d), 58.1(d), 55.4(d), 55.0(d), 54.7(d), 52.5(d), 45.4(d), 43.9(d), 41.2(t), and 36.3(t) p.p.m. (1) ν (KBr) 1735 cm^{-1} ; 1H n.m.r. δ ($CDCl_3$) 0.9(1 H, q, J 12 Hz), 2.0—3.0(11 H, m), 3.1—3.5 (2 H, m), 5.3—5.5(1 H, m), and 5.7—5.9 (1 H, m); ^{13}C n.m.r. δ ($CDCl_3$) 220.9(s), 219.3(s), 132.6(d), 131.7(d), 77.7(s), 63.0(d), 58.7(d), 54.1(d), 53.8(d), 45.2(t), 44.5(t), 41.2(d, C-2), 40.8(t), and 39.5(t) p.p.m.

synthesis of a novel pentacyclic C_{15} -quinane system, (1), whose molecular frame has potential for further exploitation. The most interesting aspect of our route to the polyquinane (1) is that the 15 carbon atoms are assembled from cyclopentadiene (C_5) and naphthoquinone (C_{10}) in only five steps *via* a hexacyclic-propellane intermediate (3).

The hexacyclic dione (3), obtained from the photocycloaddition of the cyclopentadiene-1,4-naphthoquinone Diels-Alder adduct (2) (Scheme 1),² on reduction with $Zn-AcOH$ furnished an annulated trishomocubane derivative (4), m.p. 108—116 °C (indistinct, 85% yield).†

Exposure of (4) to $NaOMe-MeOH$, under reflux, yielded a mixture of the annulated cages (5), m.p. 94 °C (45% yield),† and (6), m.p. 102—103 °C (30% yield). Reduction of the 1,4-dione system in (5), with $Na-K$ alloy- Me_3SiCl -dry toluene led to the expected uncaging to give compound (1), m.p. 150 °C (50% yield).† Although the pentacyclic structure of (1) was indicated by its spectral data and chemical transformations, it was unambiguously established from single crystal X -ray diffraction studies (*vide infra*). In the formation of (1), two interesting transformations, (3) \rightarrow (4) and (4) \rightarrow (5), were involved. While the mechanistic details of the facile (3) \rightarrow (4) rearrangement cannot be predicted with certainty at this stage, the (4) \rightarrow (5) transformation is quite straightforward and is shown in Scheme 2. Now that compound (1) and its derivatives are readily available in quantity, the chemistry of this novel C_{15} system can be investigated.



SCHEME 2. Reagents: i, $NaOMe$; ii, $MeOH$.

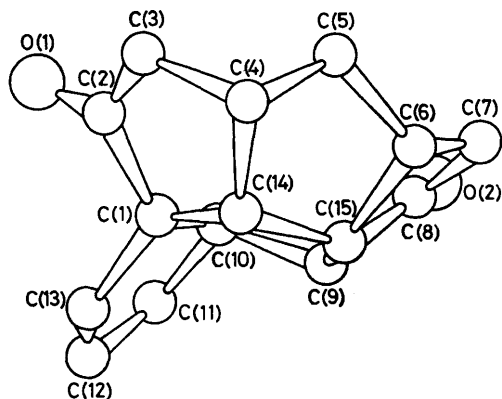


FIGURE. Perspective view of compound (1) along the *b* axis.

Crystal data: (1): $C_{15}H_{16}O_2$, $M^+ = 228$, monoclinic, space group $P2_1/n$, $a = 12.171(5)$, $b = 6.976(5)$, $c = 13.868(3)$ Å, $\beta = 102.56(3)^\circ$, $Z = 4$, $D_c = 1.318$ g cm $^{-3}$, $F(000) = 488$, $\mu(\text{Mo-K}\alpha)$, $\lambda = 0.92$ cm $^{-1}$. 1348 observed reflections [$|F| \geq 3\sigma(|F|)$, $2\theta \leq 45^\circ$] were measured on a CAD4 diffractometer and the structure was solved by MULTAN-78³ and refined by full-matrix least-squares methods to R 0.066. The Figure shows a perspective view of the molecule.†

The research was supported by grants from the University Grants Commission (GM) and the Council of Scientific and Industrial Research (KV), Government of India.

(Received, 3rd April 1981; Com. 389.)

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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