An Improved Synthesis of Triquinacene Derivatives. Two-step Regioselective Oxidation of *endo*-Dicyclopentadiene to Deslongchamps's Diketone

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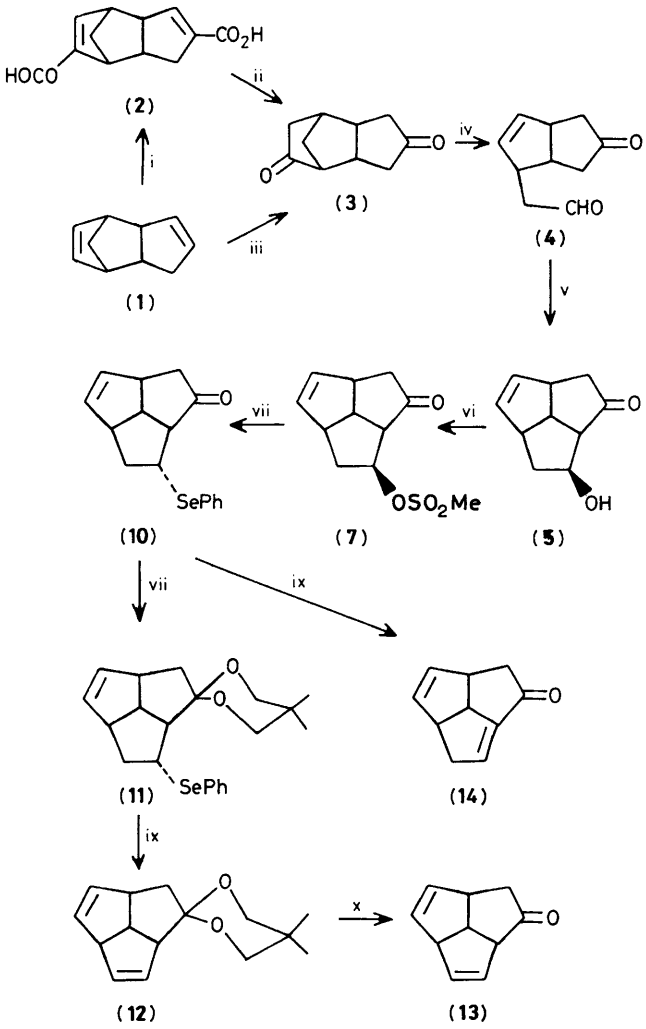
endo-Dicyclopentadiene can be *regioselectively* oxidised, in two steps, to Deslongchamps's diketone (**3**), from which either 2,3-dihydrotriquinacene-2-one (**13**) or the corresponding conjugated ketone (**14**) can be *selectively* prepared in excellent overall yields.

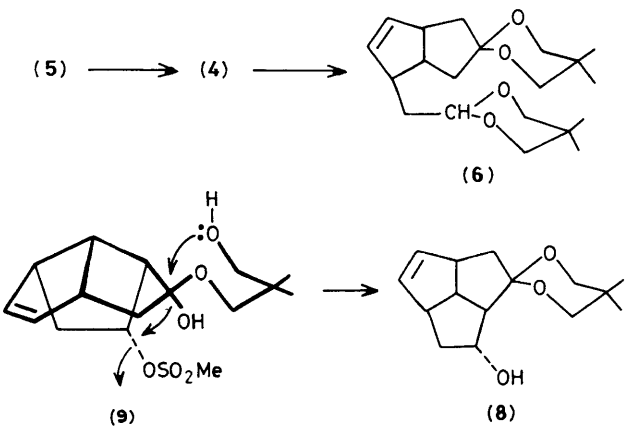
In the past few years, in connection with a more ambitious work,[1] we have been exploring some new synthetic approaches to polyquinanes, and one of our first objectives was developing highly efficient syntheses of triquinacene derivatives, namely those bearing one, two, or three carbonyl groups in 1,4-dissonant relationships.

Although several syntheses[2] of triquinacene have been reported since the pioneering work of Woodward in this field,[2a] the procedure described by Deslongchamps and his coworkers[3] is, by far, the most efficient and practical of all of them. The method, however, has some drawbacks, especially if monoketone (**13**) or its acetal (**12**) are the desired final products. In the first place, the preparation of the starting diketone (**3**) (Deslongchamp's diketone) is not only a tedious and low-yielding process (9—12%), but a redundant one as well. The *endo*-dicyclopentadiene skeleton (**1**) is first disrupted, then rebuilt through an energy and time consuming process [(**1**) heated → cyclopentadiene → cyclopentadienide anion → cyclopentadienylcarboxylic acid → Thiele's acid, (**2**) → Deslongchamps's diketone, (**3**)], the final transformation of the unsaturated carboxylic acid groups into carbonyl functional groups, which takes only place in moderate yields (*ca.* 30%), being particularly difficult and unsuitable for large scale preparations.[3,4]

In contrast, we have found that *endo*-dicyclopentadiene can be regioselectively dihydroxylated[5] under certain experimental conditions,†[6] and then oxidised to diketone (**3**) by pyridinium chlorochromate (PCC),[7] in 40% overall yield (Scheme 1). Photolysis of diketone (**3**) and the subsequent



Scheme 1. *Reagents:* i, Heat, EtMgBr–Et_2O (or NaH–tetrahydrofuran), CO_2; ii, NaN_3–H_2SO_4–trifluoroacetic acid; iii, $Hg(OAc)_2$–Na lauryl sulphate–H_2O, 3M NaOH–$NaBH_4$, PCC–CH_2Cl_2; iv, *hv*–MeOH; v, 2M HCl; vi, EtONa–EtOH, $MeSO_2Cl$–pyridine; vii, PhSeLi–C_6H_6; viii, 2,2,5,5-tetramethyl-1,3-dioxane–C_6H_6–*p*-$MeC_6H_4SO_2OH$; ix, *m*-chloroperbenzoic acid (MCPBA)–CH_2Cl_2; x, acetone–*p*-$MeC_6H_4SO_2OH$.



† *endo*-Dicyclopentadiene (0.03 mol) was treated with $Hg(OAc)_2$ (0.088 mol) in an aqueous solution of sodium lauryl sulphate (140 ml, 70 g/l) (ref. 6), and stirred at room temperature for 4—5 days. After reduction with $NaBH_4$, a crude product was obtained, the composition of which was determined by acetylation of an aliquot, followed by chromatographic separation on silica gel, to afford, in 15% yield, a mixture of unsaturated monoacetates, together with 67% of a mixture of two diastereoisomeric diacetates, in an approximately 7 : 3 relative ratio. Spectral data of these diacetates are as follows: *m/z* 253 (M^+ + 1, 0.5%), 209 (3), 192 (7), 132 (32); i.r. ($CHCl_3$), 1730, 1250 cm^{-1}; ^{13}C n.m.r. ($CDCl_3$), major isomer, 170.6 (s), 170.5 (s), 77.4 (d), 73.3 (d), 44.6 (d), 40.7 (d), 40.3 (t), 40.1 (d), 39.1 (d), 33.2 (t), 30.9 (t), 30.13 (t), 21.3 (q), 21.1 (q); minor isomer, 170.5 (s), 79.0 (d), 73.2 (d), 45.6 (d), 42.1 (d), 41.3 (d), 39.6 (d), 39.4 (t), 33.4 (t), 32.5 (t), 31.2 (t), 21.2 (q), 21.1 (q). The crude reaction mixture from oxymercuration–reduction was oxidised with PCC. Chromatographic purification on silica gel gave, after elution of the less polar unsaturated ketones, *only one* diketone in 40% overall yield (from *endo*-dicyclopentadiene), which was identical in all respects with Deslongchamps's diketone (**3**). The optimisation and scale-up of the procedure is presently being pursued.

aldol cyclisation proceeded in good yields as reported[3] [(**3**) → (**4**) → (**5**)]. However, attempts to protect the carbonyl group as a cyclic acetal, either by a direct acid catalysed acetalisation or by transacetalisation, induced a retroaldol reaction [(**5**) → (**4**)], the competitive bis-acetalisation of ketoaldehyde (**4**) being observed [(**4**) → (**6**)]. On the other hand, mesylation of the previously equilibrated *exo*-aldol [(**5**) → (**7**)], followed by acetalisation, leads to hydroxyacetal (**8**), probably by an intramolecular nucleophilic displacement of the leaving group in the intermediate hemiacetal (**9**).

The problem was solved by replacing the mesyloxy group by phenylselenide,[8] the new compound (**10**) being isolated in 77% overall yield from diketone (**3**). Since the phenylselenium group must be at the *endo* side of the molecule, it was expected that *syn*-elimination of the phenylselenoxide would lead directly to the unconjugated ketone (**13**). However, after oxidation with MCPBA almost quantitative yields (>95%) of the conjugated ketone (**14**) were obtained, which could be isolated by t.l.c. as described[3] and fully characterised by spectroscopy.‡ This result must be interpreted as an *anti*-elimination of the phenylselenoxide group rather than isomerization of the double bond.

Transacetalisation of the selenoderivative (**10**), followed by oxidation with MCPBA, afforded the desired acetal (**12**), in 95% yield, the overall yield from commercial *endo*-dicyclopentadiene being 29%. Acetal (**12**) could be hydrolysed to the free ketone (**13**) by acetone–*p*-$MeC_6H_4SO_2OH$.‡

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‡ All new compounds were completely characterised and gave satisfactory analytical and/or spectral data. The rather unstable conjugated ketone (**14**) was fully characterised by mass spectroscopy: *m/z* 146 (M^+, 73%), 117 (100); i.r. (film), 3040, 1715, 1620 cm^{-1}; ^{13}C n.m.r. ($CDCl_3$), 202.12 (s), 150.7 (s), 135.0 (d), 134.7 (d), 134.2 (d), 53.8 (d), 53.6 (d), 46.5 (t), 43.9 (d), 41.9 (t).