Tetrahedron Vol. 42, No. 6, pp. 1831 to 1839, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

SYNTHESIS OF TRIQUINACENE DERIVATIVES

NEW APPROACH TOWARDS THE SYNTHESIS OF DODECAHEDRANE

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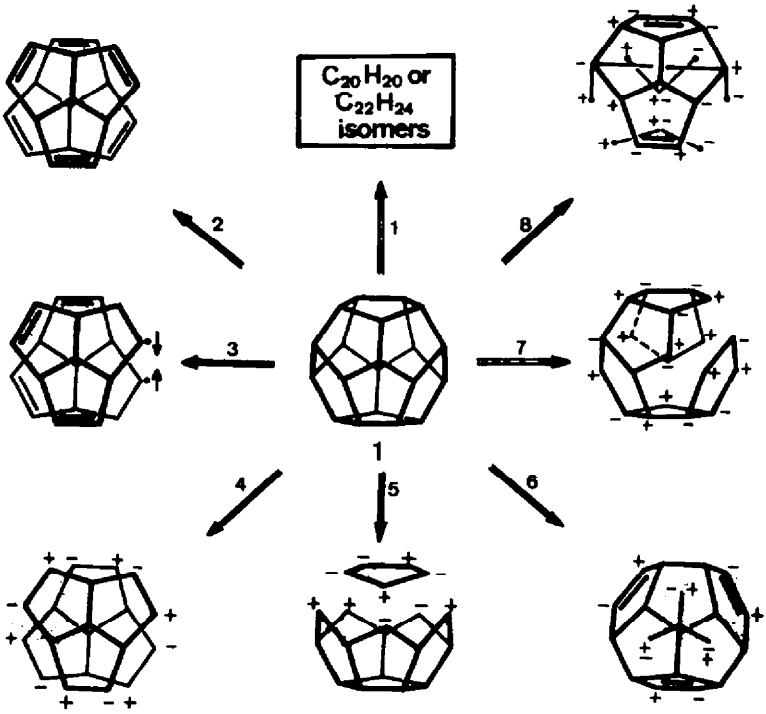
(*Received in USA 25 April 1985*)

Abstract—Different synthetic approaches to tricyclo(5.2.1.$0^{4,10}$)decane-2,5,8-trione (2)—a triquinacene derivative especially designed for a convergent and reflexive synthesis of dodecahedrane (1)—have been explored, the acetylenic approach through a Pauson–Khand bis-annulation being the method of choice.

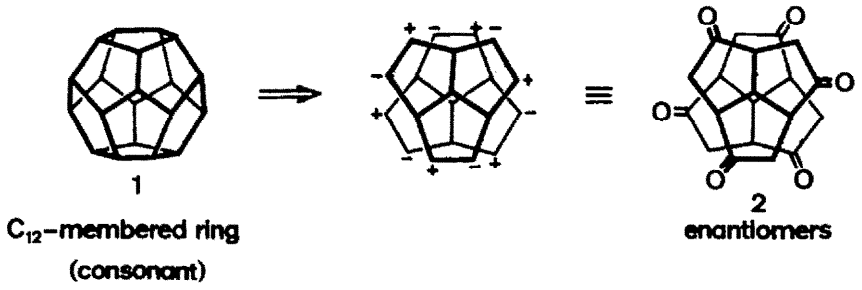
Dodecahedrane (1), which exhibits the highest symmetry (I_h) ever imagined for any organic compound, has been one of the target molecules more actively pursued in the last decade[1–7] by organic synthetic chemists.

Scheme 1 summarizes, in a very dramatic manner, the strategies used by different groups of workers all over the world in their attempts to synthesize dodecahedrane. Up to now, only Paquette *et al.*,[2] at Ohio State University, have succeeded in synthesizing dodecahedrane by a 25-step linear synthetic sequence, starting from cyclopentadiene and proceeding through the so-called "Domino Diels–Alder" adduct (strategy 8).

Strategy 1 involves the isomerization of either some $C_{20}H_{20}$ or $C_{22}H_{24}$ polycyclic hydrocarbons to dodecahedrane or its dimethyl derivative.[3] Very recently, Prinzbach and co-workers[4] have found that dodecahedrane is in fact one of the minor components of the complex mixture resulting from isomerization of "pagodane". Strategy 2 involves the pericyclic disconnection of dodecahedrane to two identical, non-chiral moieties of triquinacene. This was the original idea proposed idependently, in the early 1960s, by Müller, Jacobson, and Woodward.[5] Strategy 3 implies the homolytic disconnection of *at least one of the bonds* and leads to two moieties of identical chirality, in which case the synthesis would require the optical resolution of the starting material (or some other equivalent procedure, as the separation of the *d,l*- and *meso*-dimers).[6] Strategies 5–8 all involve heterolytic disconnections through dissonant pathways or rings.[2,7] Strategy 4, on the other hand, involves a disconnection through a consonant 12-membered ring and leads to two moieties of opposite chirality and, in contrast with strategies 5–8, defines a "seam" in the



Scheme 1. Strategies for the synthesis of dodecahedrane.



Scheme 2. Disconnection of dodecahedrane molecule through a consonant 12-membered ring.

molecule of dodecahedrane which may be constructed using aldol-type reactions, which are essentially reversible. The three main advantages of such an approach would be:

(1) the synthesis would be a convergent and reflexive one, as the original proposed by Müller, Jacobson, and Woodward (strategy 2);

(2) in contrast with strategy 3, it does not require optical resolution of the starting material;

(3) it opens the possibility of falling into the "energetic well" of the dodecahedrane structure by working under equilibrating conditions.

Scheme 2 shows this strategy in more detail: actualization of the formal charges, conferred by the heterolytic disconnection along the secondary consonant 12-membered ring, by the pertinent functional groups, leads to the dissymmetric triketone **2**, the two moieties being of opposite ("enantio") chirality. The "narcissistic coupling"[8] of the two enantiomeric triketones might lead, through a series of aldol-type condensations, in which all the steps, except the last one, are reversible, to the relatively stable structure of dodecahedrane (Scheme 3). Transformation of the resulting hexahydroxydodecahedrane (**3**) — which is an achiral molecule belonging to the D_{3d} symmetry group — to the hydrocarbon is in principle a feasible, almost trivial, synthetic operation.[9]

In Fig. 1 a comparison of our projected synthesis with Paquette's synthesis, as well as with the "ideal" (a one-step synthesis) and the original one via triquinacene, is made in terms of the complexity index η vs the number of steps k, as proposed by Bertz.[10] Such representations are very useful to evaluate alternative synthetic routes to the same target molecule. The most effective and economical synthesis would be the one in which the area under function F is minimized

$$F = \int_0^{k_r} C(k)\,\mathrm{d}k.$$

From Fig. 1, we can see how Paquette (curve 4), in very few steps, constructs intermediates with similar or even higher complexity than dodecahedrane itself. In contrast, in the convergent and reflexive syntheses (curves 2 and 3) the intermediates are kept at a much lower order of complexity and only in the last steps is dodecahedrane's complexity reached.

The challenge

Triketone **2** *as the target molecule.* Apart from its potential use as a dodecahedrane precursor, triketone **2**, which belongs to the rarely encountered C_3 symmetry point group, represents an interesting synthetic objective in its own right. In this context, the study of the interactions and reactivity of the carbonyl groups located on the perimeter of the rigid hemispherical framework displayed by this molecule requires the development of a synthetic protocol which allows the access to substantial amounts of **2**.

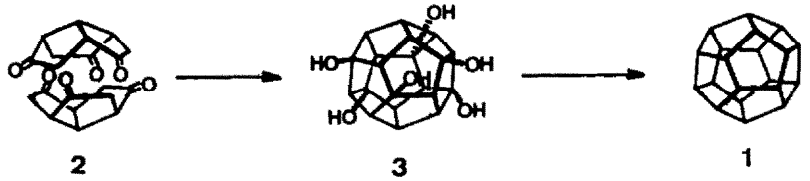
Owing to the presence of multidissonant relationships, the synthesis of triketone **2** is not a trivial objective, and no less than three *Umpolungs* or "reactivity inversion operations" can be foreseen in designing the synthesis of this molecule.

For the synthesis of triketone **2** we have devised two general strategies:

(1) one, involving the pertinent functionalization of the triquinacene skeleton (**5**), requires *regioselective control* in order to create the three 1,4-dissonant bifunctional relationships between the three carbonyl groups present in the molecule;

(2) the other one, based on the use of some intermediates previously functionalized, requires, by contrast, *stereoselective control* in order to create the all-*cis*-all-*syn* configuration characteristic of polyquinanes.[11]

The pertinent retrosynthetic manipulations involving either FGIs (functional group interchange) or 1-, 2- or 3-bond disconnections lead to the simple synthetic precursors shown in Scheme 4. Obviously, the simplest synthesis would be the one in which the C_3 axis of symmetry present in the target molecule is conserved all along the synthetic sequence.[12] This approach (route 3, **4**, X = Cl) was attempted in 1975 in connection with



Scheme 3. Narcissistic coupling of two enantiomeric moieties leading to a dodecahedrane structure.

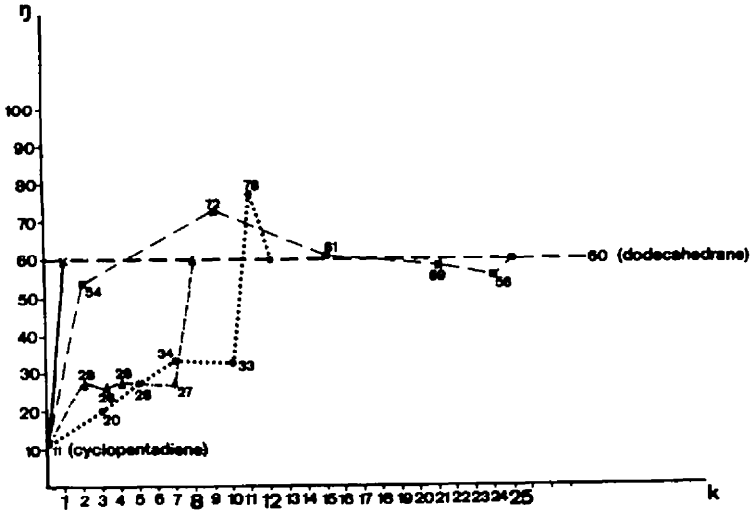


Fig. 1. Complexity index η vs number of steps k.[10] Syntheses of dodecahedrane from cyclopentadiene: (1)——x, "ideal synthesis" (1 step); (2)– – – –▲, via triquinacene **5** (8 steps); (3)·····•, via triketone **2** (12 steps); (4) – – – ■, via "Domino Diels–Alder" (25 steps).

our own work on the synthesis of bullvalene.[13] However, rather than the expected triketone **2** a triasterane structure was formed.[14]

Disconnection of two non-adjacent bonds of triketone **2** (route 2) leads to a unsaturated bicyclic diketone **6** and a two-carbon fragment with "carbonyl inverted reactivity". The synthesis of the bicyclic diketone **6**, from the readily accessible *cis*-bicyclo(3.3.0)octan-3,7-dione, has been already reported[15] and the reaction with different "nucleophilic carbonyl equivalents" (**6** → **2**) is being studied at present.

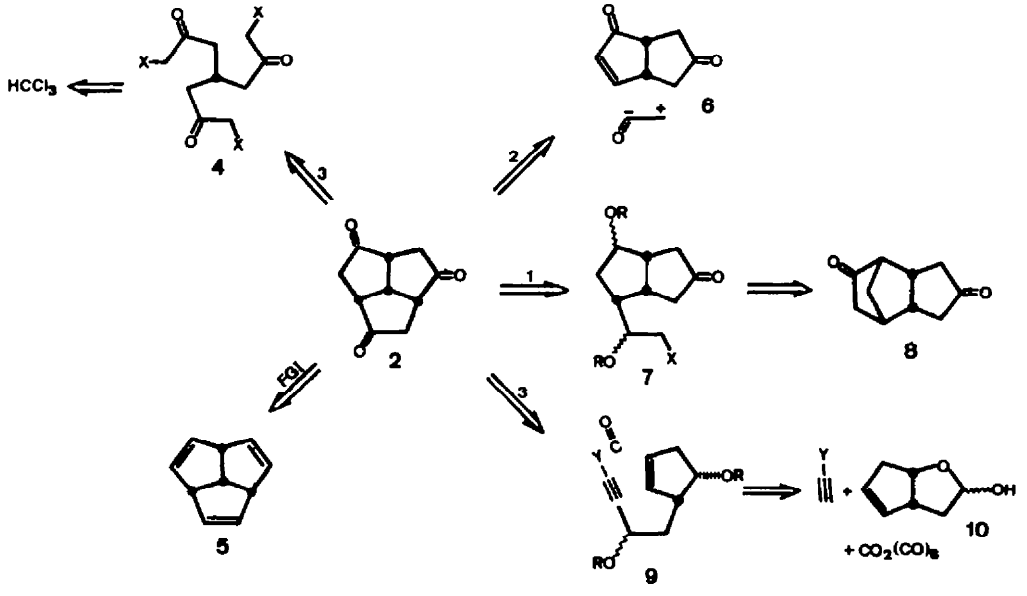
On the other hand, the "one-bond disconnection" strategy, which starts from the so-called Deslongchamp's diketone (**8**)[16] and requires rigorous stereoselective control, will be discussed in full in a forthcoming paper. In this paper we deal exclusively with the FGI and the "three-bond disconnection" strategies, which are the most straightforward entries to triketone **2** we have so far developed.

RESULTS

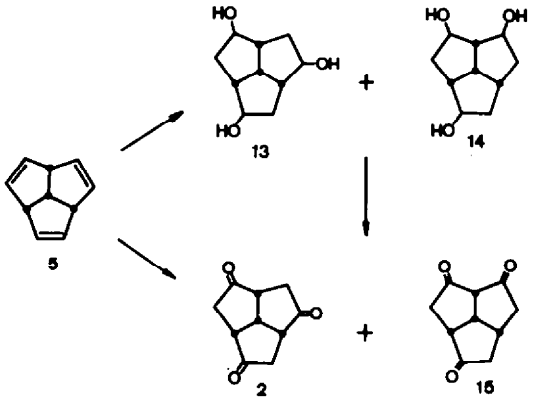
FGI strategy

According to the strategies outlined in Scheme 4, our second approach to triketone **2** starts from triquinacene itself or some of its simple derivative.

Triquinacene (**5**) was prepared from *endo*-dicyclopentadiene by the procedure described by Deslongchamps *et al.*[16] The method has, however, some drawbacks if the monoketone **11** or the

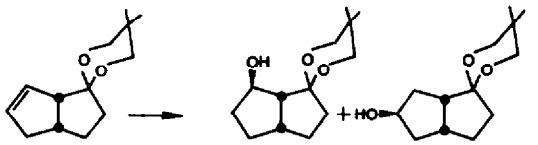


Scheme 4. General strategies for the synthesis of triketone **2**.



Scheme 5. Hydroboration of triquinacene (5).

Table 1. Hydroboration–oxidation and oxymercuration–demercuration of bicyclo(3.3.0)oct-7-en-2-one, 2,2-dimethyltrimethylene acetal



BH_3.THF	62:38
BH_3.SMe_2	61:39
$TxBH_2$	62:38
9-BBN	64:36
$(Sia)_2BH$	85:15
$Hg(OAc)_2$	30:70

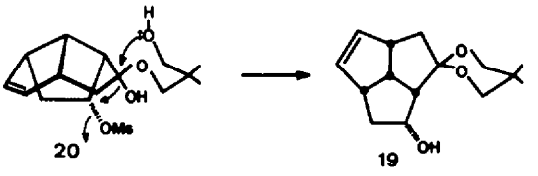
corresponding acetal **12** are the desired final product (see below).

As shown in Scheme 5, hydroboration of triquinacene, followed by oxidation, could afford either one of the two possible isomeric triketones **2** or **15**, or more probably a mixture of both in which the unwanted regioisomer would be the predominant one since it is statistically favoured in a 3:1 ratio. Although we found[17] experimental conditions in which the ratio of the symmetrical triketone **2** was higher than that, the method—which implies three transformations in each one of the three double bonds present in the molecule—is neither a gratifying one nor painless. Paquette and co-workers,[18] also reported the synthesis of this triketone by the same procedure, had to use a highly sophisticated HPLC system, with four 6 ft × 0.75 in silica gel columns connected in series, in order to separate the intermediate isomeric triols **13** and **14**. As Paquette and co-workers stated in their article: "their separation required conditions somewhat out of the ordinary".

Since we did not have access to such sophisticated equipment, and the oxidation of the triols presented serious technical difficulties, we looked for more attractive routes to the triketone **2**. The regioselective functionalization of acetal **12** was envisaged as one of the alternative routes to it.

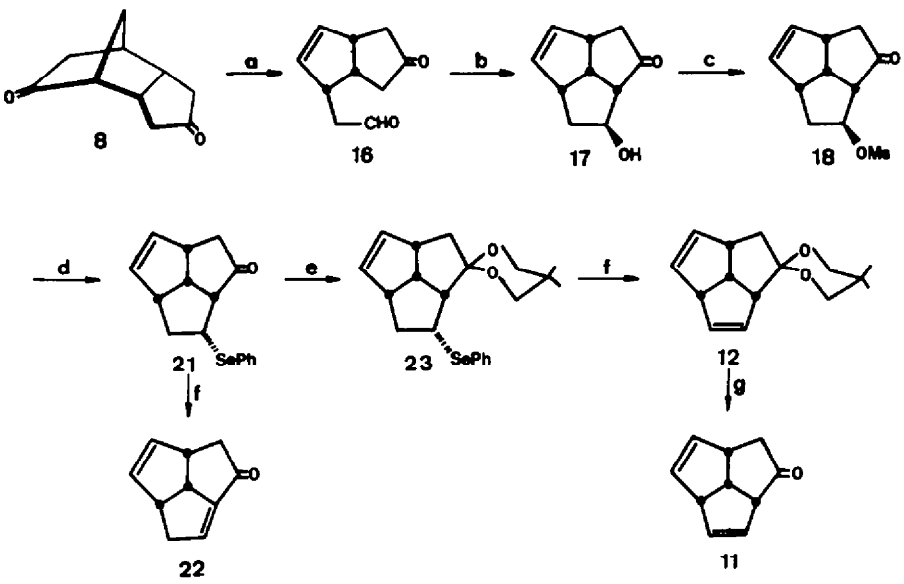
Previously reported studies[19] on the related cyclic acetal of the bicyclo(3.3.0)oct-7-en-2-one showed that the effect of an acetal group on hydroboration is electronic rather than steric. The observed regioselectivity leading to 1,3-bifunctional relationships must be ascribed to inductive effects like those observed in allylic and homoallylic derivatives bearing electron-withdrawing functional groups (see Table 1).[20] On the other hand, although the alternative Markovnikov oxymercuration of the bicyclic model afforded the desired 1,4-bifunctional derivative[19] as the major component of a 70:30 mixture of the two regioisomers, the method may not show the same regioselectivity in the case of acetal **12** since the two olefinic carbon atoms here are almost equivalent owing to the presence of the third ring.

For the preparation of acetal **12** we used an improved procedure of the synthesis previously reported by Deslongchamps *et al.*[16] (Scheme 6). The starting point is "Deslongchamp's diketone" (**8**), which we prepared by direct regiofunctionalization of *endo*-dicyclopentadiene by an improved procedure of the method previously developed by our group.[21] Photolysis of diketone **8** and subsequent aldol cyclization of the resulting aldehyde proceeded in good yields as reported (**8** → **16** → **17**).[16] Since attempts to protect the carbonyl group of **17** as a cyclic acetal induced a retro-aldol reaction (**17** → **16**). Under these conditions, the competitive bis-acetalization of ketoaldehyde **16** was also observed. On the other hand, mesylation of the previously equilibrated *exo*-aldol (**17** → **18**), followed by acetalization, led to hydroxy-acetal **19**, probably by an intramolecular nucleophilic displacement of the leaving group in the intermediate hemiacetal **20**. The mesyloxy group was replaced by phenylselenide,[22] the new compound **21** was then isolated in 77% overall yield from diketone **8**.

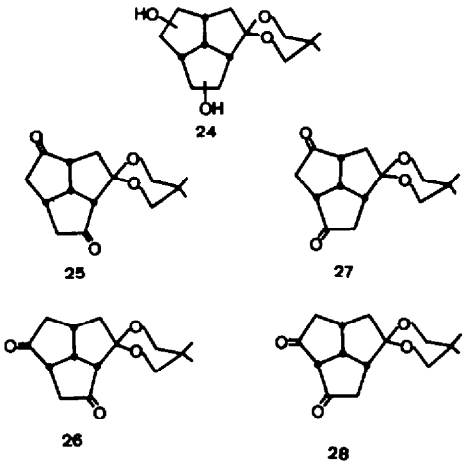


Since the phenylselenium group must be on the *endo* face of the molecule, it was expected that *syn*-elimination of the phenylselenoxide would lead directly to the monoketone **11**. However, after oxidation with MCPBA or, better, with sodium metaperiodate in methanol–water,[23] almost quantitative yields of the conjugated monoketone **22** were obtained.[16] It was isolated by preparative TLC and fully characterized by spectroscopic techniques. On the other hand, transacetalization of the phenylseleno derivative **21**, followed by oxidation with MCPBA, afforded the desired acetal **12** in 95% yield (**21** → **23** → **12**); the overall yield from commercial *endo*-dicyclopentadiene was *ca* 30%.

Oxymercuration–demercuration of acetal **12** (Scheme 7) led to a mixture of diols **24** which, after oxidation with pyridinium chlorochromate (PCC) and chromatographic separation, afforded in 43% yield a



Scheme 6. Synthesis of triquinacene derivatives: (a) MeOH/*hv*; (b) acetone/3 N HCl; EtONa/EtOH; (c) MsCl/pyr; (d) PhSeLi; (e) $Me_2C(CH_2OH)_2$/*p*-TsOH/benzene; (f) MCPBA or $NaIO_4$; (g) *p*-TsOH/acetone.



Scheme 7. Hydroboration and oxymercuration of triquinacene derivative **12**.

1 : 7 mixture of diketone acetals **27** and **28**; the latter was easily identified by its IR absorptions at 1770 (s) and 1715 (w) cm^{-1}, characteristic of a 1,3-dicarbonyl system.[16] The structure of diketone **27** was confirmed by isolation of a sample by preparative TLC and hydrolysis to the symmetrical triketone **2**. It is worth noting that only two (**27** and **28**) of the four possible regioisomers (**25**–**28**) were detected in the reaction mixture, the ratio of diketone **28** being higher than the statistical one. Eventually, from the crude regioisomeric mixture of diols **24**, the predominant one crystallized out, the oxidation of which, with PCC, led exclusively to diketone **28**.

On the other hand, hydroboration of acetal **12** with the borane–dimethyl sulfide complex, followed by oxidation—first with alkaline hydrogen peroxide and then with PCC—led in 66% yield to a mixture of three diketones in which **27** was practically present in the statistical ratio (24%) and **28** was absent. The results are summarized in Table 2.

Three-bond disconnection strategy

The success of the strategies so far discussed for the synthesis of triketone **2** relies on a strict regio- and/or stereoselective control of the reactions in order to attain the 1,4-dissonant relationships and the all-*cis*-all-*syn* configuration of the polyquinane skeleton.

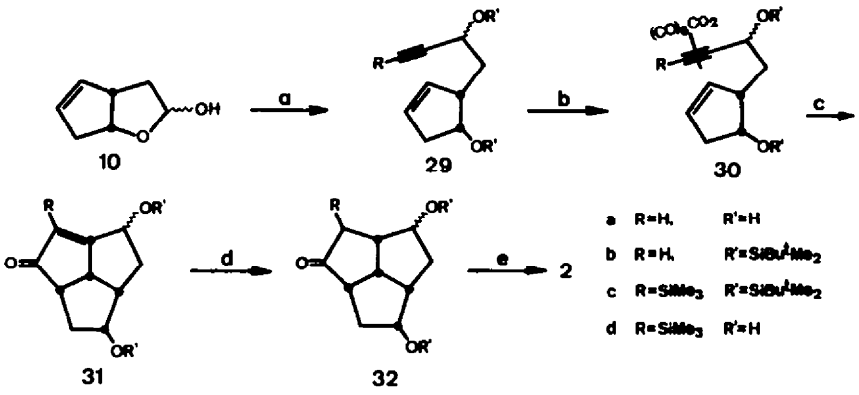
In our last approach[24] to the synthesis of triketone **2** we decided to explore the use of an intramolecular version of the Pauson–Khand annulation.[25] In the present context, this method of cyclopentenone synthesis could present the following advantages.

First, it is well known that intramolecular annulations of this kind proceed with good yields; the Pauson–Khand reaction has been successfully used in the synthesis of diquinanes[26] and of angularly fused triquinanes.[27]

Second, if the precursor is properly designed, in the sense that the multiannulation process can only lead to

Table 2. Functionalization of acetal **12**: relative ratio of regioisomeric tricyclic diketones

Procedure	Overall yield	25	26	27	28
$Hg(OAc)_2/NaBH_4$/PCC	43%	0	0	20%	80%
BH_3/H_2O_2/PCC	66%	76% (1 : 4)		24%	0



Scheme 8. Pauson–Khand bis-annulation leading to triketone **2**: (a) ethynylmagnesium bromide; Bu^tMe_2SiCl/imidazole; BuLi/Me_3SiCl; (b) $Co_2(CO)_8$; (c) isooctane, 160°, 3 days; (d) 10% Pd–C/H_2/EtOH; (e) HF/H_2O/acetonitrile; pyridine; PCC/celite.

the desired polycyclic structure, the problems of regio- and stereochemical control are automatically obviated, provided that cyclization actually takes place.

Finally, the synthesis of the key intermediate **9** (see Scheme 4) should be easily achieved starting from the known lactol **10**.[28]

As shown in Scheme 8, when lactol **10** was added to a solution of ethylmagnesium bromide in THF a 3.8:1 diastereomeric mixture of diols **29a** was obtained in 95% yield. After protection of the hydroxyl groups as t-butyldimethylsilyl ethers (88% yield), the diastereomeric mixture of enynes **29b** was converted into the corresponding hexacarbonyl dicobalt complex **30b**. When an isooctane solution of this complex was heated in a sealed tube, under a carbon monoxide atmosphere, at 160° for 5 days only low yields of the desired enone **31b** were obtained. However, when the terminal acetylenic carbon of **29b** was silylated (87% yield) and the resulting protected enyne **29c** was converted into the corresponding dicobalt complex **30c**, which was either isolated (82% yield) or directly subjected to cyclization by the same conditions as above for 3 days, the silylenone **31c** was obtained in yields ranging from 76% (starting from pure **30c**) to 51% (when the intermediate complex was not isolated). It is interesting to observe that silylenone **31c** was isolated as a single stereoisomer, most probably the *exo*-5-*endo*-8 isomer, as shown by its ^{1}H- and ^{13}C-NMR spectra. This suggests that, though only one of the two diastereomers present in the diastereomeric mixture **29c** can be successfully cyclized, it is fortunately the predominant isomer, the one suitable for undergoing the expected cyclization

It is worth noting that the addition of lithium trimethylsilylacetylide to lactol **10** takes place in a rather low yield (20%), so that the more direct route to **29c** through intermediate **29d** suffers the important drawback of a considerably lower overall yield. On the other hand, attempts to induce cyclization of the hexacarbonyl dicobalt complex **30d** of the unprotected intermediate **29d** failed, no traces of cyclization product **31d** were detected.

Hydrogenation of **31c** in ethanol solution with 10% palladium on carbon usually consumed between one and two equivalents of hydrogen. Although yields as high as 78% have been observed for cyclopentanone **32b**, the hydrogenation process was usually accompanied by cleavage of the O—Si bonds. Thus, in one experiment the tricyclic ketone **32b** was obtained in 18% yield along with a mixture of the monoprotected derivatives (51% yield) and the dihydroxyketone **32a** (21% yield).

In any case, although the observed deprotection during the hydrogenation step is a complicating experimental factor,† it does not substantially affect the overall yield of the synthetic sequence since any of the by-products can be easily converted into triketone **2** by the same process as for the tricyclic ketone **32b**.

In fact, pure tricyclic ketone **32b** was converted in triketone **2** in 85% overall yield by desilylation with hydrofluoric acid in acetonitrile–water, followed by neutralization with pyridine and oxidation with pyridinium chlorochromate in celite in dichloromethane solution. On the other hand, when the three main fractions, obtained from the hydrogenation experiment in which substantial deprotection had occurred (see above), were separately converted by the same procedure into triketone **2**, the overall yield was 66% from enone **31c**.

Considering the limited number of steps, the cobalt mediated bis-annulation procedure is probably the method of choice for the preparation of triketone **2** in quantities large enough to allow a systematic study of its reactivity and, ultimately, incorporation into a dodecahedrane synthesis.

EXPERIMENTAL

M.ps were determined in a m.p. Büchi 510 apparatus and are uncorrected. UV, IR and ^{1}H-NMR (60 MHz) spectra were recorded on Perkin–Elmer instruments, models Lambda 5, 681 and R-24, respectively, and ^{1}H-NMR (200 MHz) and ^{13}C-NMR with a Varian XL-200 (eventually, in the spectrum of isomeric mixtures only unambiguously assigned peaks for the minor components are reported). Mass spectra were run in a Hewlett–Packard 5930A spectrometer and high resolution MS with an updated AIE instrument, model 902 S. Evaporative distillations were performed with a Büchi Kugelrohrofen GKR-50 and, unless otherwise stated, all chromatographic purifications were performed on silica gel, using hexane–EtOAc mixtures of increasing polarity as eluent. All solvents were dried and distilled before use, and reactions were usually run under an atmosphere of dry N_2.

† *Note added in proof*: we have found that desilylation is completely inhibited if hydrogenation is performed in the presence of triethylamine.

endo-9-*Phenylselenotricyclo*(5.2.1.0^{4,10})*dec*-5-*en*-2-*one*, **21**

(a) Methanesulfonyl chloride (6 ml, 76 mmol) was added to a stirred soln of *exo*-aldol **17** (3.50 g, 21 mmol)[16] in CH_2Cl_2 (250 ml) and pyridine (96 ml) and stirred at room temp for 24 h. The mixture was diluted with CH_2Cl_2 and washed with 2 M HCl, sat $NaHCO_3$ aq and NH_4Cl aq and water, and then dried. The solvent was evaporated off under reduced pressure, and the resulting crude *exo*-mesylate **18** (5.35 g) was used for the next operation without further purification. IR (film): 3020, 2940, 1740, 1350, 1170 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$): 1.8–3.0 (complex m, 5H), 3.1 (s, 3H), 3.2–3.8 (m, 3H), 4.9 (m, 1H), 5.5 (m, 2H).

(b) To a soln of diphenyl diselenide (0.967 g, 3.10 mmol) in THF (20 ml), 50% aq hypophosphorous acid (1.64 ml, 31.0 mmol) was added and the mixture refluxed for 20 min.[22] After cooling at room temp, benzene (125 ml) was added to the mixture and then dried over $MgSO_4$. The benzene soln was filtered through a pad of $MgSO_4$ and transferred to a dry reaction vessel fitted with septum, condenser and N_2 inlet. Lithium phenylselenolate was generated via addition of 1.6 M n-BuLi in hexane (4.3 ml, 6.88 mmol). After 10 min at room temp the reaction vessel was charged with crude *exo*-mesylate **18** (1.55 g, 6.40 mmol), dissolved in a few ml THF and kept at room temp for 3 h, until no more starting material was detected by TLC. The mixture was washed with sat NH_4Cl aq, dried and the solvents evaporated off under reduced pressure, to afford the *endo*-phenylseleno derivative **21** (1.50 g, 4.97 mmol) as a yellow liquid (78% yield). The analytical sample was prepared by evaporative distillation at 230°/0.45 Torr. IR (film): 3045, 2945, 2915, 1740, 1570, 1470, 1440, 1300, 1260, 1155, 1025, 740, 690, 670 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$): 1.6–2.65 (complex m, 5H), 3.25 (m, 3H), 3.55 (q, J = 7 Hz, 1H), 5.45 (br.s, 2H), 7–7.5 (complex m, 5H). (Found: C, 63.29; H, 5.58. Calc for $C_{16}H_{16}OSe$: C, 63.39; H, 5.20%.)

Tricyclo(5.2.1.0^{4,10})*deca*-5,9-*dien*-2-*one*, **22**

To a soln of $NaIO_4$ (0.15 g, 0.7 mmol)[23] in water (1 ml) was added a soln of *endo*-**21** (0.105 g, 0.35 mmol) in MeOH (5 ml). The resulting yellow turbid mixture was stirred for 1 h at room temp. After the addition of sat $NaHCO_3$ aq (10 ml), the mixture was extracted with $CHCl_3$ (10 ml × 3) and dried. Elimination of solvents under reduced pressure gave the crude conjugated **22** in almost quantitative yields (53 mg, 0.35 mmol), which was purified by preparative TLC. UV (cyclohexane), λ_{max}: 241.2 nm (ε 6028); IR (film): 3040, 2920, 1715, 1620 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$): 2.1–3.8 (complex m, 7H), 5.45 (br. s, 2H), 6.2 (m, 1H); ^{13}C-NMR ($CDCl_3$): 41.9 (t), 43.9 (d), 46.5 (t), 53.6 (d), 53.8 (d), 134.2 (d), 134.7 (d), 135.0 (d), 150.7 (s), 202.1 (s); MS, *m/e* calc for $C_{10}H_{11}O$: 146.0729 (M^+); obs 146.0747.

endo-9-*Phenylselenotricyclo*(5.2.1.0^{4,10})*dec*-5-*en*-2-*one*, 2,2-*dimethyltrimethylene acetal*, **23**

To a mixture of *endo*-**21** (0.520 g, 1.72 mmol), 2-ethyl-2,5,5-trimethyl-1,3-dioxane (1.627 g, 10.30 mmol) and 2,2-dimethyl-1,3-propanediol (0.045 g, 0.43 mmol) a few crystals of *p*-toluenesulfonic acid were added and then stirred for 18 h. The mixture was diluted with benzene, neutralized with Et_3N and dried. The solvents were evaporated under reduced pressure to give a residue (0.750 g), which was purified by chromatography, pure **23** (0.619 g) being isolated in 93% yield. The analytical sample was prepared by evaporative distillation at 240°/0.40 Torr. IR (film): 3040, 2960, 2880, 1580, 1470, 1440, 1110, 1095, 1000, 790, 690 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 0.96 (s, 3H), 0.97 (s, 3H), 1.56–3.4 (complex m, 9H), 3.4 (half AB pattern, J_{AB} = 11.2 Hz, 1H), 3.5 (s, 2H), 3.70 (half AB pattern, J_{AB} = 11.2 Hz, 1H), 5.42 (d of t, J_1 = 6 Hz, $J_2 = J_3$ = 1.7 Hz, 1H), 5.64 (d of t, J_1 = 6 Hz, $J_2 = J_3$ = 1.7 Hz, 1H), 7.28 (m, 3H), 7.6 (m, 2H); MS, *m/e*: 390/388 (M^+), 304/302, 233, 157/155, 147, 119, 117, 105. (Found: C, 64.74; H, 6.60. Calc for $C_{21}H_{26}O_2Se$: C, 64.81; H, 6.68%.)

Tricyclo(5.2.1.0^{4,10})*deca*-5,8-*dien*-2-*one*, 2,2-*dimethyltrimethylene acetal*, **11**

To a soln of **23** (2.41 g, 6.21 mmol) in CH_2Cl_2 (25 ml), cooled at −78°, 85% MCPBA (1.34 g, 6.60 mmol) in CH_2Cl_2 (10 ml) was added and the mixture stirred at low temp for 1 h. The mixture was then added into refluxing CCl_4 (200 ml) containing diisopropylamine (2 ml). After cooling at room temp, it was washed with 2 M HCl and sat $NaHCO_3$ aq, and dried. The solvents were evaporated off under reduced pressure and the residue purified by flash chromatography to give **11** (1.39 g, 6.02 mmol) in 93% yield. The analytical sample was prepared by evaporative distillation at 120°/0.5 Torr. IR (film): 3050, 2960, 2870, 1420, 1310, 1170, 1120, 1110, 850, 730 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$): 0.97 (s, 6H), 1.2–3.2 (complex m, 4H), 3.5 (m, 6H), 5.6 (m, 4H). (Found: C, 77.53; H, 8.89. Calc for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.)

Hydroboration–oxidation of tricyclo(5.2.1.0^{4,10})*deca*-5,8-*dien*-2-*one*, 2,2-*dimethyltrimethylene acetal*, **11**

(a) To a soln of **11** (0.217 g, 0.935 mmol) in THF (2.5 ml), cooled at 0°, 12.6 M BH_3–SMe_2 complex (94 μl, 1.18 mmol) was added via syringe. After 4 h at room temp, water (2 ml), 3 M NaOH (0.5 ml) and 30% H_2O_2 (0.5 ml) were added and the mixture stirred at 50° for 1 h. The aq layer was saturated with $NaHCO_3$ and thoroughly extracted with ether. The combined ether extracts were dried and solvents evaporated off under reduced pressure to give a mixture of diol acetals **24** (0.264 g).

(b) The crude mixture of diols (0.264 g, 1.0 mmol) was dissolved in CH_2Cl_2 (5 ml) and NaOAc (50 mg), celite (0.90 g) and PCC (0.63 g, 2.5 mmol) were added. After stirring at room temp for 5 h, the mixture was diluted with ether (30 ml) and filtered through a column of silica gel under pressure. The resulting clear soln was evaporated and the residue (0.20 g) purified by flash chromatography to give, in 66% overall yield, pure diketone acetal **27** (38 mg, 24% relative yield) and a 61 : 15 mixture (122 mg, 76% relative yield) of **25** and **26**.

Oxymercuration–demercuration of tricyclo(5.2.1.0^{4,10})*deca*-5,8-*dien*-2-*one*, 2,2-*dimethyltrimethylene acetal*, **11**

(a) To a stirred soln of $Hg(OAc)_2$ (1.39 g, 4.36 mmol) in a 1 : 1 mixture of THF–H_2O (12 ml) a soln of **11** (0.506 g, 2.18 mmol) in THF (2 ml) was added dropwise and the mixture stirred at room temp for 24 h. 3 M NaOH (5 ml) and 0.5 M soln of $NaBH_4$ in 5 M NaOH (5 ml) were then added and the reduced precipitated Hg filtered off. The aq layer was saturated with NaCl and thoroughly extracted with EtOAc, the combined organic extracts dried and solvents evaporated off under reduced pressure to give a crude mixture of diols **24** (0.60 g), from which the predominant regioisomer crystallized out as colourless crystals (79 mg), m.p. 180–184°. IR (KBr): 3300, 2950, 2880, 1120, 1070, 1040, 1000 cm^{-1}; ^{1}H-NMR (60 MHz, MeOD): 0.5 (s, 3H), 0.6 (s, 3H), 0.9–2.8 (complex m, 10H), 3.0 (m, 4H), 3.2 (m, 2H).

(b) Oxidation of the remaining oily mixture of diols (0.515 g, 1.95 mmol) with PCC (1.24 g, 5.8 mmol) in CH_2Cl_2 soln gave, after stirring at room temp for 5 h and the usual working up, a crude mixture of diketone acetals (0.36 g) which was purified by column chromatography to give: (i) a small fraction (73 mg) of olefinic material, (ii) a 1 : 1 mixture of **27** and **28** (81 mg) from which pure **27** was isolated by preparative TLC. IR (film): 2960, 2870, 1730, 1135, 1105, 1010 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 0.69 (s, 3H), 1.11 (s, 3H), 1.6–3.5 (complex m, 14H); ^{13}C-NMR ($CDCl_3$): 21.8 (q), 23.0 (q), 29.6 (s), 33.7 (t), 38.3 (t), 40.6 (t), 42.6 (d), 44.0 (d), 47.4 (d), 48.7 (d), 69.9 (t), 73.1 (t), 106.1 (s), 218.4 (s), 218.8 (s); MS, *m/e*: 264 (M^+).

Hydrolysis of **27** (20 mg) in acetone soln, containing pyridinium *p*-toluenesulfonate gave pure **2** (6 mg) identical in all respects with an authentic sample[18] (see below).

(c) Oxidation of the crystalline diol (79 mg) with PCC gave **28** (66 mg). IR ($CHCl_3$): 2960, 2870, 1770, 1715, 1120, 1040 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 0.75 (s, 3H), 1.1 (s, 3H), 1.5–3.1 (complex m, 9H), 3.4 (m, 5H).

cis-2-(2-*Hydroxybut*-3-*ynyl*)*cyclopent*-3-*en*-1-*ol*, **29a**

A stream of dry acetylene was passed through 75 ml of THF, while a soln of EtMgBr in THF [prepared from Mg (2.1 g, 86.4 mmol) and EtBr (9.09 g, 86.4 mmol) in THF (100 ml) under an atmosphere of purified N_2] was added dropwise and to the

stirred resulting clear soln of HC≡CMgBr, cooled with an ice bath, a soln of **10**[27] (3.08 g, 24.46 mmol) in THF (20 ml) was then slowly added. The mixture was stirred at room temp for 5 h, sat NH_4Cl aq (50 ml) was then added, the layers separated and the aq layer extracted with ether (25 ml × 3). The combined organic extracts were dried and solvents evaporated off under reduced pressure to give the crude mixture of diols **29a** (3.53 g, 95% yield). The analytical sample was purified by column chromatography, followed by evaporative distillation at 170°/0.5 Torr, to yield a colourless oily material. IR ($CHCl_3$): 3610, 3360, 3300, 3030, 2930, 1435, 1315, 1080, 1010, 660, 635 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$): 1.80–2.87 (m, 6H), 4.10–4.63 (m, 4H), 5.43–5.73 (m, 2H); ^{13}C-NMR ($CDCl_3$): major isomer, 35.92 (t), 41.71 (t), 48.70 (d), 61.77 (d), 72.19 (d), 72.65 (s), 85.25 (d), 128.24 (d), 132.82 (d); minor isomer, 34.48 (t), 41.61 (t), 46.68 (d), 60.72 (d), 73.46 (s), 84.45 (d), 128.35 (d), 132.74 (d). (Found: C, 70.71; H, 8.04. Calc for $C_9H_{12}O_2$: C, 71.03; H, 7.95%.)

cis - (2 - *Hydroxy* - 4 - *trimethylsilylbut* - 3 - *ynyl*)*cyclopent* - 3 - *en*-1-*ol*, **29d**

A 1.6 M soln of n-BuLi in hexane (10.5 ml, 1.62×10^{-2} mol) in THF (10 ml) and a soln of trimethylsilylacetylene (1.75 g, 1.62×10^{-2} mol) in the same solvent (10 ml) were introduced via syringe to a reaction flask cooled at −30°. The mixture was stirred for 15 min and a soln of **10** (1.0 g, 7.93×10^{-3} mol) in THF (10 ml) was added dropwise. The mixture was stirred at room temp for 4 h, sat NH_4Cl aq (30 ml) was then added and, after the usual work up, a crude product was obtained (0.99 g) which was purified by column chromatography to give the starting **10** (0.295 g) and the diastereomeric mixture of diols **29d** (0.445 g) in 25% yield. IR ($CHCl_3$): 3600, 3400, 3010, 2940, 2170, 1250, 1040, 980, 845 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$): 0.23 (s, 9H), 1.73–3.03 (m, 7H), 4.37–4.73 (m, 2H), 5.47–5.87 (m, 2H).

cis - 1 - t - *Butyldimethylsiloxy* - 2 - (2 - t - *butyldimethylsiloxybut* - 3 - *ynyl*)*cyclopent* - 3 - *ene*, **29b**

To a soln of **29a** (0.50 g, 3.28 mmol) in DMF (5 ml), t-butyldimethylsilyl chloride (1.48 g, 9.84 mmol) and imidazole (0.914 g, 19.68 mmol) were added and the mixture stirred at room temp for 30 h. It was then poured into water (100 ml) and extracted with hexane (25 ml × 3). The dried soln was evaporated to dryness under reduced pressure, first at room temp and then at 60°, to give the crude product (1.02 g, 82% yield). The analytical sample was prepared by evaporative distillation at 145°/0.7 Torr. IR (CCl_4): 3310, 3060, 2950, 2920, 2850, 1470, 1460, 1360, 1250, 1085, 830, 655, 630 cm^{-1}; ^{1}H-NMR (60 MHz, CCl_4): 0.03–0.13 (m, 12H), 0.80 (s, 18H), 1.53–1.97 (m, 2H), 2.10–2.87 (m, 4H), 4.10–4.47 (m, 2H), 5.30–5.70 (m, 2H); ^{13}C-NMR ($CDCl_3$): major isomer, −4.37 (q), −4.28 (q), −4.22 (q), −4.01 (q), 18.80 (s), 18.89 (s), 26.43 (q), 26.59 (q), 38.05 (t), 41.42 (t), 45.77 (d), 62.46 (d), 72.82 (s), 74.84 (d), 86.73 (d), 128.47 (d), 134.18 (d); minor isomer, 38.14 (t), 41.75 (t), 46.14 (d), 62.92 (d), 72.88 (s), 74.41 (d), 128.47 (d), 134.09 (d); MS, *m/e*: 380 (M^+), 365, 323, 243, 191, 189, 157, 147, 133, 117, 115. (Found: C, 66.23; H, 10.89. Calc for $C_{21}H_{40}O_2Si_2$: C, 66.23; H, 10.59%.)

cis - 1 - t - *Butyldimethylsiloxy* - 2 - (2 - t - *butyldimethylsiloxy* - 4 - *trimethylsilylbut* - 3 - *ynyl*)*cyclopent* - 3 - *ene*, **29c**

To a reaction flask, cooled at −20°, THF (5 ml), n-BuLi in hexane (0.3 ml of a 1.6 M soln, 0.48 mmol) and a soln of **29b** (0.125 g, 0.328 mmol) in THF (5 ml) were introduced via syringe. After 15 min, a soln of trimethylsilyl chloride (0.040 g, 0.368 mmol) in THF (5 ml) was added dropwise. The mixture was stirred at room temp for 2 h, and water (50 ml) and hexane (50 ml) were then added. The layers were separated, the aq layer extracted with hexane (15 ml × 2) and the combined hexane solns dried. Evaporation of solvents under reduced pressure gave crude **29c** (0.138 g, 93% yield), which was purified by evaporative distillation at 165°/0.7 Torr, to give the pure product (0.130 g) in 87% yield. IR (CCl_4): 2960, 2930, 2860, 2180, 1470, 1460, 1360, 1250, 1085, 840 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$): 0.03–0.10 (m, 12H), 0.12 (s, 9H), 0.87 (s, 18H), 1.5–2.5 (m, 5H), 4.2–4.5 (m, 2H), 5.6–5.8 (m, 2H); ^{13}C-NMR ($CDCl_3$): major isomer, −4.86 (q), −4.63 (q), −4.24 (q), −0.17 (q), 18.22 (s), 18.28 (s), 25.84 (q), 25.97 (q), 37.42 (t), 40.74 (t), 45.18 (d), 62.47 (d), 74.25 (d), 77.20 (s), 108.35 (s), 127.69 (d), 133.73 (d); minor isomer, 37.53 (t), 41.05 (t), 45.56 (d), 62.91 (d), 73.79 (d), 127.69 (d), 133.80 (d); MS, *m/e*: 452 (M^+), 437, 395, 315, 263, 241, 223, 189, 147, 133, 117, 115. (Found: C, 64.07; H, 10.66. Calc for $C_{24}H_{48}O_2Si_3$: C, 63.65; H, 10.68%.)

5,8 - *Di* - t - *butyldimethylsiloxy* - 3 - *trimethylsilyl* - *tricyclo*(5.2.1.0^{4,10})*dec* - 3 - *en* - 2 - *one*, **31c**

(a) *Hexacarbonyl dicobalt complex* **30c**. To a soln of $Co_2(CO)_8$ (76 mg, 0.22 mmol) in isooctane (2 ml), a soln of **29c** (0.10 g, 0.22 mmol) in the same solvent (5 ml) was added dropwise and the mixture stirred at room temp for 16 h. Filtration through a column of alumina and evaporation to dryness gave **30c** (0.133 g) in 82% yield. IR (CCl_4): 2960, 2940, 2900, 2860, 2090, 2060, 2030, 2020, 1255, 1090, 1075, 840 cm^{-1}; MS, *m/e*: 626 ($M^+ - 4CO$), 598, 570, 511, 438, 395, 315, 263, 247, 223, 189, 147, 133, 117, 115, 75, 73 (100%), 59, 57, 41.

(b) *Cyclization to enone* **31c**. A soln of **30c** (0.492 g, 0.666 mmol) in isooctane (20 ml), was saturated with a stream of CO and heated in a sealed tube at 160° for 3 days. The mixture was then filtered through celite, evaporated to dryness and chromatographed to give **31c** (0.244 g, 76%), as colourless crystals, m.p. 49–50°. IR ($CHCl_3$): 2960, 2860, 1705, 1610, 1475, 1465, 1365, 1250, 1160, 1075, 885, 835, 780 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): −0.04 (s, 3H), −0.02 (S, 3H), 0.02 (s, 3H), 0.09 (s, 3H), 0.16 (s, 9H), 0.81 (s, 9H), 0.84 (s, 9H), 1.22–1.37 (m, 1H), 1.74–1.90 (m, 2H), 1.98–2.11 (m, 1H), 2.60–2.79 (m, 2H), 3.46 (dd, J = 9.2 Hz, J' = 7.8 Hz), 4.22–4.33 (m, 1H), 4.93 (d, J = 2.6 Hz); ^{13}C-NMR ($CDCl_3$): −4.89 (q), −4.81 (q), −4.38 (q), −4.34 (q), −1.04 (q), 17.95 (s), 18.14 (s), 25.67 (q), 25.83 (q), 36.72 (t), 37.45 (t), [illegible], 72.52 (d), 75.85 (d), 129.41 (s), 132.83 (s), 192.56 (s); MS, *m/e*: 480 (M^+), 465, 423, 293, 277, 221, 219, 149, 147, 133, 115. (Found: C, 62.30; H, 10.13. Calc for $C_{23}H_{48}O_3Si_3$: C, 62.44; H, 10.06%.)

(c) *Direct conversion of* **29c** *into* **31c**. To a soln of **29c** (0.500 g, 1.10 mmol) in isooctane (15 ml), disposed in a thick wall glass tube, $Co_2(CO)_8$ (0.415 g, 1.21 mmol) was added under N_2. The mixture was stirred at room temp for 4h, the N_2 was then evacuated and the tube sealed after saturation with CO. After heating at 170° for 60 h, the mixture was filtered through a pad of celite, evaporated to dryness and the crude product chromatographed to afford the pure crystalline **31c** (0.268 g) in 51% overall yield.

5,8 - *Di* - t - *butyldimethylsiloxytricyclo*(5.2.1.0^{4,10})*decan* - 2 - *one*, **32b**

(a) A soln of the unsaturated **31c** (0.131 g, 0.272 mmol) in anhyd EtOH (20 ml) was hydrogenated in the presence of 10% Pd–C (80 mg) until *ca* 16 ml of H_2 were consumed. The alcoholic soln was filtered through celite and evaporated to dryness to give a crude product (0.107 g), which was purified by flash chromatography to give pure **32b** (87 mg, 78°, yield) as colourless crystals, m.p. 62° (from pentane at −78°). IR ($CHCl_3$): 2960, 2860, 1740, 1480, 1460, 1370, 1260, 1080, 850 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 0.00–0.01 (m, 12H), 0.85 (s, 18H), 1.55–1.70 (m, 1H), 1.88–2.30 (m, 4H), 2.40–2.60 (m, 3H), 2.62–2.80 (m, 1H), 3.24 (q, J = 9.7 Hz, 1H), 4.07–4.14 (m, 2H); ^{13}C-NMR ($CDCl_3$): −4.95 (q), −4.61 (q), 17.94 (s), 19.09 (s), 25.82 (q), 25.88 (q), 35.24 (t), 40.56 (t), 42.51 (t), 46.89 (d), 48.43 (d), 49.24 (d), 49.38 (d), 75.09 (d), 82.69 (d), 221.70 (s); MS, *m/e*: calc for $C_{32}H_{42}O_3Si_2$ 410.2661; obs 410.2614.

(b) *Hydrogenation with concomitant deprotection*. A soln of the unsaturated **31c** (0.432 g, 0.898 mmol) in anhyd EtOH (50 ml) was hydrogenated in the presence of 10% Pd–C (260 mg) as above, until 1.6 equiv of H_2 were consumed. After filtration through celite and evaporation of the solvent under reduced pressure, a crude oily residue (0.266 g) was obtained, from which an insoluble material (35 mg) was separated by treatment with a 9:1 mixture of hexane–EtOAc that was identified as 5,8-dihydroxytricyclo(5.2.1.0^{4,10})decan-2-one

(**32a**) on the basis of its IR spectrum, as well as by its high yield oxidation into triketone **2** (see below).

The soluble part of the hydrogenated product was chromatographed, two main fractions being separated: (i) with a 98 : 2 mixture of hexane–EtOAc, pure saturated tricyclic ketone **32b** (68 mg) was obtained, and (ii) washing the column out with pure EtOAc a colourless oily material was isolated, which probably is a mixture of t-butyldimethylsiloxy monoethers of dihydroxyketone **32a** on the basis of its IR spectrum and the high yield conversion into **2** (see below).

Compound **32a**, IR (film): 3350, 2940, 1735, 1090, 1065 cm^{-1}.

"*Monosilylated* **32a**", IR (film): 3400, 2960, 2930, 2860, 1740, 1475, 1465, 1260, 1110, 1080, 1035, 840, 780 cm^{-1}.

Tricyclo(5.2.1.$0^{4,10}$)*decan* - 2,5,8 - *trione*, **2**

(a) To a stirred soln of pure **32b** (68 mg, 0.18 mmol) in acetonitrile (10 ml), 45% aq HF was added (0.1 ml) and the mixture left overnight at room temp. The soln was then neutralized with pyridine and evaporated to dryness under reduced pressure. To the resulting residue CH_2Cl_2 (20 ml), pyridinium chlorochromate (0.50 g, 2.34 mmol) and celite (0.50 g) were successively added and the mixture stirred overnight; ether was then added in order to insolubilize the Cr salts, filtered through a pad of celite and evaporated under reduced pressure. Purification of the residue by column chromatography afforded pure **2** (25 mg) in 85% yield, which was recrystallized from acetone to give colourless crystals, m.p. 170–171° (lit.[18] 170–170.5°). IR ($CHCl_3$): 2965, 2930, 1745, 1410, 1310, 1180, 1155 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 2.43–2.54 (m, J_{gem} = 19 Hz, J_{vic} = 4.2 Hz, $3H_{endo}$), 2.67–2.83 (m, J_{gem} = 19 Hz, J_{vic} = 13.4 Hz, J'_{vic} = 1.8 Hz, $3H_{exo}$), 3.07–3.21 (m, 3H), 3.88 (q, J = 10.4 Hz, 1H); ^{13}C-NMR (CD_3COCD_3): 39.34 (t) 42.10 (d), 45.54 (d), 216.58 (s); MS, *m/e*: 178 (M^+), 150, 122, 94, 79, 55. (Found: C, 67.61; H, 5.51. Calc for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66%.)

(b) The monoprotected **32a** (0.136 g) (see above) was desilylated and oxidized as described in the preceding paragraph to afford pure chromatographed **2** (54 mg) in 66% overall yield.

(c) The dihydroxyketone **32a** (35 mg) (see above) was oxidized with PCC as described, to give pure **2** (27 mg) in 79% yield.

Acknowledgements—The authors wish to acknowledge their indebtedness to the graduate student Víctor Centellas for his technical assistance in the last part of this work; to Dr J. Rivera and Miss M. Guerra, from the "Instituto de Química Bio-Orgánica de Barcelona (CSIC)" for the reported high resolution mass spectra and microanalyses, respectively; and finally to "Comisión Asesora de Investigación Científica y Técnica" for financial support (Proyecto No. 3218/83).

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[8] "*Narcissistic*, from *Narkissos*, youth who fell in love with his reflection in water", *The Oxford English Dictionary*; cf. L. A. Salem, J. Durup, G. Bergeron, D. Cazes, X. Chapuisat and H. Kagan, *J. Am. Chem. Soc.* **92**, 4472 (1970), "a reaction is defined as narcissistic if reactant(s) and product(s) are mirror images with respect to a fixed plane and if the image of the reactant(s) undergoes the reverse 'reaction' to the image of the product(s)".

[9] Cf. L. H. Sommer, K. W. Michael and W. D. Korte, *J. Am. Chem. Soc.* **89**, 868 (1967); M. G. Adlington, M. Orfanopoulos and J. L. Fry, *Tetrahedron Lett.* 2955 (1976).

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