Tetrahedron Vol. 37, No. 25, pp. 4457 to 4463, 1981
Printed in Great Britain.

0040-4020/81/254457-07$02.00/0

PLANARIZATION OF TETRACOORDINATE CARBON. APPROACH TOWARD THE SYNTHESIS OF "TETRAQUINACANE"—II†

FUNCTIONALIZATION OF DICYCLOPENTADIENE

H. SCHORI,‡ B. B. PATIL§ and R. KEESE*
Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

(*Received in U.S.A.* 9 *March* 1981)

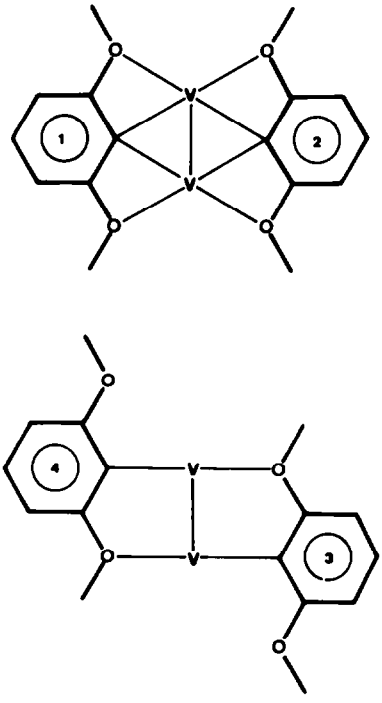
Abstract—Dicyclopentadiene is introduced as a useful starting material for the preparation of 2-*exo*-8-*endo*-disubstituted derivatives of bicyclo[3.3.0]octane.

It is a theoretical but particularly an experimental challenge to search for compounds containing tetrasubstituted carbon with completely *planar* rather than tetrahedral coordination. The specific bonding situation of planar, tetracoordinate carbon has been extensively studied by computational methods and many structures which contain carbon in this unusual ligand sphere and a corresponding nonclassical bonding situation have been suggested.[1] In most of them carbon is linked to one or more heteroatoms, but none of these structures have so far been prepared. Up to now the only *bona fide* case of carbon with four ligands in one plane is V_2(2,6-dimethoxyphenyl)$_4 \cdot 2$ THF.[2] The X-ray structure analysis of this complex shows a coplanar arrangement of one phenyl ring (1 or 2) and two vanadium ligands (Scheme 1).

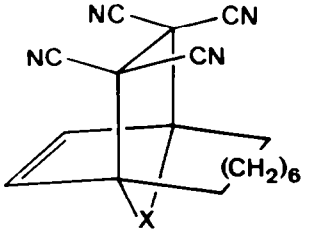
As an approximation to planar coordination one may search for structures containing carbon with a *planoid* arrangement of its four ligands. Particularly challenging are those compounds that consist exclusively of carbon and hydrogen. A variety of such hydrocarbons, paddlanes like **1a**[3] and tetracyclo[5.1.1.$0^{3,8}$.$0^{5,8}$] nonane ("fenestrane") **2** have been suggested and recently syntheses of **1b** and of potential precursors for **2** have been published.[4]

Hoffmann has used EHT-calculations to explore *inter alia* structures which consist of a central carbon σ-bonded to a peripheral annulene system.[5] Related compounds containing a spiro[4.4]nonatetraene moiety, with two bridging $(CH_2)_n$-chains (n = 6 or 7) **4** have been prepared by Prelog. Their X-ray structure shows planoid distortion at the central carbon.[6] Nature, as she often does, has anticipated compounds of this general structure; in the diterpene lauren-1-ene **6** the central carbon is connected to a bridgehead double bond which is part of a peripheral C_{14}-ring system.[7]

We reasoned that a carbon symmetrically bonded to a surrounding [12]annulene as in **3** might be a particularly attractive synthetic goal.[8] Subsequent MINDO-III[9] and

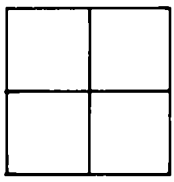


Scheme 1. The perpendicular planes of coordination in V_2 (2,6-dimethoxyphenyl)$_4$·2THF.[11]

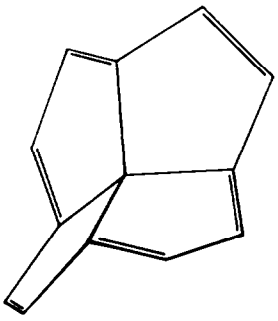


1a X = CH_2
1b X = 10

†For part I, see Ref. 8.
‡Part of the planned doctoral thesis of Hans Schori.
§Postdoctoral fellow 1975–1976.



2



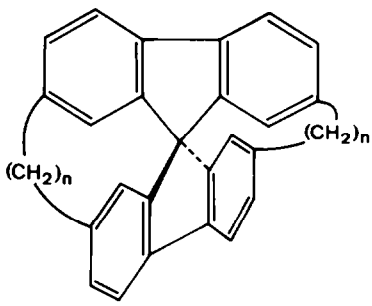
3

MNDO-calculations[10] have indeed indicated planoid deformation for this structure.

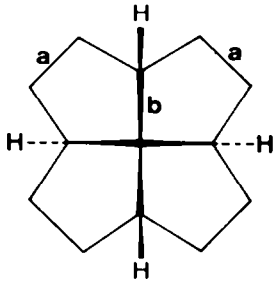
A possible precursor of **3**, might be the saturated cyclopentanoid ring structure **5**, which we have coined "tetraquinacane".[a] Cook and Weiss[11] as well as our group[8] have reported a synthesis of this ringsystem. Also, the preparation of benz-annulated precursors has recently been published.[12]

A synthesis of the skeleton of tetraquinacane could involve, as a last step, either formation of two peripheral bonds a (see **5**) or, alternatively, formation of the central bond b.[b] In case a the actual chemical reaction may involve an intramolecular alkylation or a type of Claisen condensation. This approach has been used by Cook and Weiss[11] in their synthesis of the tetraketone **8** from the keto acid **7**, for which they developed an elegant short synthesis using an appropriately substituted α-keto aldehyde and diethyl β-ketoglutarate. Our own attempts to use this approach for eventual formation of **3** were not persued further, because **7** could not be obtained on a preparatively useful scale.[13c]

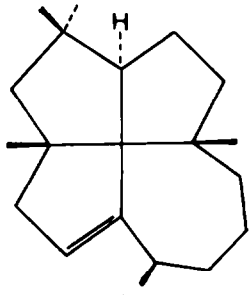
In case of path b the formation of the critical bond may be achieved by carbene insertion into the transannular bridgehead C–H–bond. This approach has been employed successfully in our hands: the pentacyclic lactone **11** is obtained by photolysis of the potassium salt of the tosylhydrazone **10**.[8] The corresponding keto lactone **9** itself has been obtained by a sequence involving double hydroxypropylation of a 2,8-disubstituted bicyclo[3.3.0]octane with subsequent oxidation and Dieckmann condensation.



4



5



6

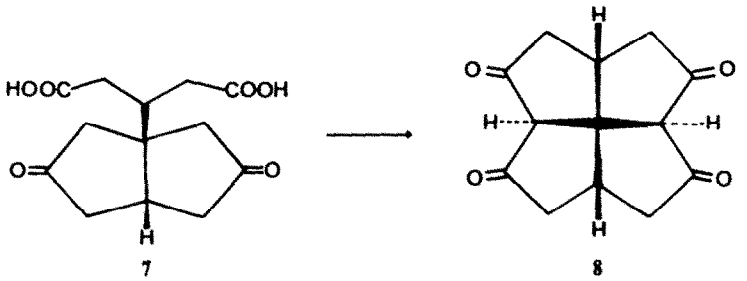
There are 6 stereoisomers of "tetraquinacane", which differ in the stereochemistry of the annulated cyclopentane subunits. The isomer **5**, containing only *cis*-fused cyclopentane subunits is certainly the most stable one. Our approach to the preparation of an isomer, which contains two *trans*-fused cyclopentane subunits intends to make use again of the transannular carbene insertion reaction. According to Dreiding models a carbonyl-containing ring attached exo–endo to the bicyclo[3.3.0]octane instead of exo–exo as in **9** should be flexible enough to allow this insertion. We report here our results of preparing derivatives of bicyclo[3.3.0]octane, utilizing dicyclopentadiene, an easily available "cyclopentanoid" starting material.

The plan is as follows: The enone **12**, readily available from dicyclopentadiene, should be well suited for preparing 2-exo-8-endo-disubstituted bicyclo[3.3.0]octanes; from these the ketone, needed as precursor for transannular insertion might be prepared. The 1,4-addition of a carbanion to the enone system in **12**, known to occur from the exo-side,[14] followed by oxidation of the remaining double bond should lead to a bicyclo[3.3.0]octane appropriately functionalized for our purposes. The carbonyl group then should provide selective blocking of the "undesired" carboxyl group by formation of a methoxy lactone and hence the construction of the 2,8-disubstituted bicyclooctane. After

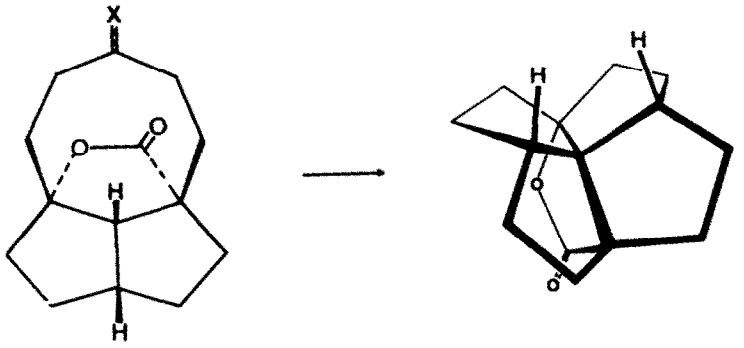
[a] In analogy to triquinacene, we proposed the name tetraquinacane for the saturated ringsystem tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecane **5**, to indicate that four 5-membered rings are connected by a common carbon atom. For the same structure Cook and Weiss proposed the name "staurane".[11]

[b] The possibility of preparing appropriate tricyclic structures as precursors of **5** by a multiple bond-forming step is under active investigation.

[c] We thank Dr. Weiss for helpful discussions, Dr. Cook for communicating experimental details and exchange of results prior to publication.



7 8

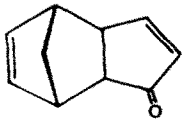


9 x = 10
10 x = N-HNTs

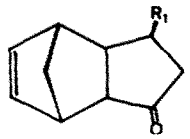
11

formation of the tetracyclic ringsystem, the additional functionalities might be used for introduction of double bonds (Scheme 2).

Along the lines of this synthetic concept, tricyclo[5.2.1.$0^{2,6}$]decan-3,8-dien-5-one **12** was hydroxypropylated according to the method of Eaton[15] and gave, after deprotection, the hydroxy propyl ketone **13** in 87% yield. Oxidation of the acetyl-derivative **14** with ruthenium trichloride and sodium metaperiodate[16] under neutral conditions gave the diacid **17** in 85% yield. Subsequent treatment with diazomethane in methanol lead to the keto ester **18**, containing only a trace of methoxy

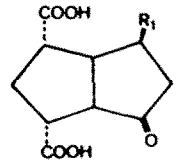


12



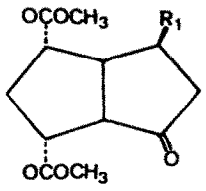
R_1

13 $(CH_2)_3OH$
14 $(CH_2)_3OCOCH_3$
15 $(CH_2)_3OCOC_6H_5$
16 $(CH_2)_3OCH_2C_6H_5$



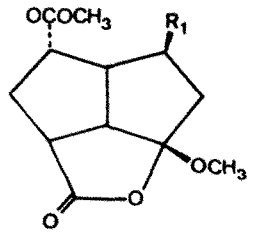
R_1

17 $(CH_2)_3OCOCH_3$



R_1

18 $(CH_2)_3OCOCH_3$
19 $(CH_2)_3OCOC_6H_5$



R_1

20 $(CH_2)_3OCOCH_3$
21 $(CH_2)_3OCOC_6H_5$

Scheme 2

lactone **20** whereas acid-catalyzed esterification with methanol gave, after benzoylation, a mixture of **19** and the methoxy lactone **21** in approximately a 1:1 ratio. This rather low proportion of **21** was disappointing, because we had planned, as mentioned above, to protect one carboxyl group as methoxy lactone, and to use the other one for introduction of the second side chain. Indeed, a pure sample of methoxy lactone **21** separated by chromatography, could be alkylated with 3-bromopropylethylacetaldehydeacetal, using lithium diisopropylamide as the base. However, the low proportion of **20** with respect to **18** in the esterification step, and the hydrolytic lability of the methoxy lactone made this approach preparatively unattractive.

After we found that the carbonyl group in either **17** or **19** had been reduced by sodium borohydride to provide mainly the exo alcohol, we altered our tactics and followed a route which finds analogy in the early steps of a synthesis of verbenalol.[17] The 1,4-addition of benzyloxypropyllithium to **12** in the presence of copper-(I)iodide lead to **16** in 76% yield. Subsequent reduction of the carbonyl group with sodium borohydride leads exclusively to **22** with an endo hydroxy group.[d] The acetylated derivative **23** was oxidized with potassium permanganate in the presence of sodium metaperiodate[e] and gave, after reaction with diazomethane, the triester **25**. Oxidation of **23** followed by treatment with base and diazomethane lead to the ester lactone **26**. Its structure is supported by infrared absorptions at 1750 and 1730 cm^{-1} and a ^1H NMR signal at $\delta = 4.8$–5.0 ppm, which is indicative of the alkoxy proton of a lactone contained in a molecule such as **26**.

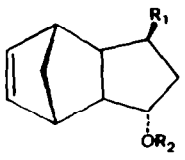
Thus, we have achieved our first goal, namely to prepare intermediate **26**, suitably functionalized for introduction of an additional side chain at the α-position of the carbomethoxy group and hence for the eventual formation of tetraquinacanes.

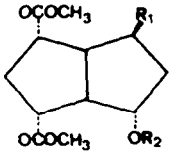
Another feature of this approach is the *exo–endo*-relationship between the side chain R_1 and the carbomethoxy group in **26**, because the latter group could be utilized in the future for chain extension to provide a tetraquinacane with two *trans*-fused cyclopentane subunits. For the subsequent steps of the planned synthesis, it would be more convenient to oxidize the olefinic bond to the stage of the dialdehyde rather than the diacid. Consequently, the hydroxy olefin **22** was treated with ethylvinylether to give **24** with a rather labile protecting group. Subsequent oxidation with potassium permanganate under phase transfer conditions[18] first at pH 7, later at pH 3, gave the hydroxydialdehyde **27** as a single isomer in 53% yield.

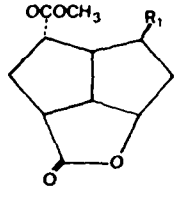
According to ^1H NMR-data, the formyl group adjacent to the alcohol exists entirely as lactol, probably with endo configuration of the hydroxy group. Reaction of **27** with triethylphosphono acetate gave a single isomer **28** as colourless oil. Inspection of the ^1H NMR-spectrum of crude product shows a double bond with (E) configuration and a lactol with the hydroxy group very likely still in endo position. The endo configuration of the acrylic side chain is based upon mechanistic considerations: during the Wittig–Horner chain extension endo–exo

[d] Reduction of **16** with sodium borohydride on alumina lead to a mixture of two diastereomeric alcohols.

[e] Oxidation of **23** with ruthenium tetroxide affected the benzylic group and gave, after esterification, 10% of **19**.





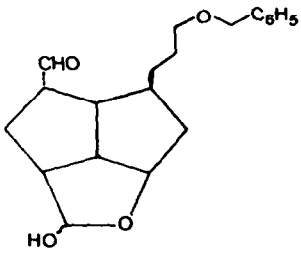


	R_1	R_2
22	$(CH_2)_3OCH_2C_6H_5$	H
23	$(CH_2)_3OCH_2C_6H_5$	$COCH_3$
24	$(CH_2)_3OCH_2C_6H_5$	$CH(CH_3)OC_2H_5$

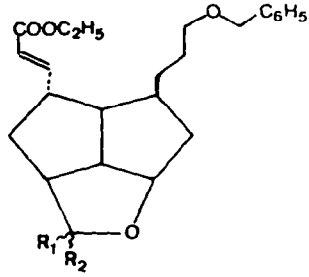
	R_1	R_2
25	$(CH_2)_3OCH_2C_6H_5$	$COCH_3$

	R_1
26	$(CH_2)_3OCH_2C_6H_5$

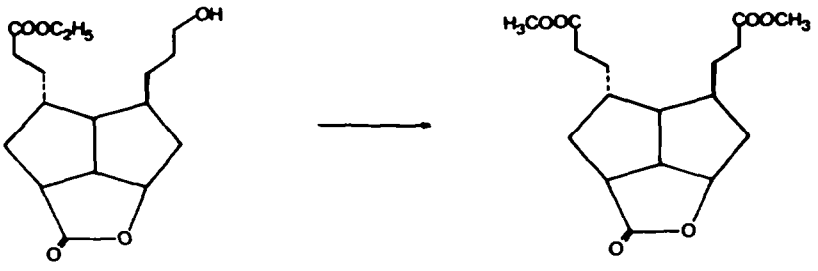
Scheme 3.



27



	R_1	R_2
28	H	OH
29	$R_1 + R_2 = 0$	



30 31

equilibration of the corresponding formyl group is very unlikely. Oxidation with pyridinium chlorochromate or with Jones reagent lead to the lactone **29**. Hydrogenation of both the double bond and the benzyl-oxygen bond gave **30** which after oxidation and esterification yielded the diester lactone **31**.

The scaled-up preparation of compounds like **31** should enable us to prepare tetraquinacanes in sufficient amounts to permit the investigation of this unusual cyclopentanoid structure.

EXPERIMENTAL

Melting points were taken in a Tottoli melting point apparatus in an open capillary tube and are uncorrected. Infrared spectra were measured in $CHCl_3$ on a Perkin–Elmer 457 instrument. Nuclear magnetic resonance spectra were obtained in $CDCl_3$ using Varian EM 360, Bruker WP 80 and Varian XL 100 (^1H and ^{13}C) instruments. Chemical shifts were recorded in ppm downfield from TMS as an internal standard (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or heavily overlapping signals), coupling constants are reported in Hz. Mass spectra were recorded on Varian MAT CH5-DF and CH-7A, signals are recorded as *m/z*. Elemental analysis were performed by M. Manser, Mikroanalytisches Labor, ETH, Zürich.

Silica gel used for preparative separations was Merck Silica gel 60; silica gel plates Merck 60F-254 were used for thin layer chromatography (R_f-values are ratio of fronts). Solvents, usually of purum quality (Fluka, Siegfried) were used as such. Reactions have not been optimized. If not stated otherwise, reactions were worked up by pouring the reaction mixture on ice-water and extracted three times with ether. If necessary base extractions were applied. The combined organic phases were dried over magnesium sulfate and concentrated *in vacuo* on a rotatory evaporator at temperatures <40°.

5 - exo - (3' - Hydroxypropyl)tricyclo[5.2.1.0^{2,6}]dec - 8 - en - 3 - one (**13**)

A cooled solution of 198 mmol ethyl 3-lithiopropyl acetaldehyde acetal[15] in 360 ml ether was added to 22.0 g (116 mmol) of anhydrous cuprous iodide and stirred at −40° until Gilman's test[19] was negative. Then, at −60°, a solution of 11.0 g (75.3 mmol) of tricyclo[5.2.1.0^{2,6}]dec-3,8-dien-5-one [20] in 100 ml ether was added dropwise. The solution was stirred overnight, allowed to warm up to −20° and carefully poured into a half-saturated solution of ammonium chloride. The crude product was stirred with a solution of 0.5 g dichloroacetic acid in 100 ml of water for 25 hr. After neutralization with potassium carbonate, the low boiling products were removed under reduced pressure and the product extracted with methylene chloride. The crude material was chromatographed on 250 g silica gel with hexane: methylene chloride = 1 : 1; and ether: methylene chloride = 1 : 1 eluted 13.5 g (65.5 mmol, 87%) of **13**. For analysis a sample was again chromatographed.[21] R_f (ether: methylene chloride = 1 : 1) 0.36. IR 3720–3320, 1720 cm^{-1}. NMR ^1H: 1.26–1.90 (m, 8H), 2.00–2.42 (m, 2H), 2.56–2.72 (m, 1H), 2.88–3.25 (m, 3H), 3.62–3.75 (m, 2H), 6.18 (t, 2H). ^{13}C: 219.5 s, 136.0 d, 135.1 d, 62.5 t, 54.8 d, 52.3 t, 48.7 d, 48.2 t, 47.1 d, 46.1 d, 36.7 d, 34.0 t, 30.7 t. MS 206 (M$^+$), **141**, 123, 95, 91, 81, 79, 67. Found: C 75.50; H 8.92. Calc. for $C_{13}H_{18}O_2$: C 75.69; H 8.80%. The acetyl derivative **14** was obtained from **13** by reaction with acetic anhydride-pyridine in methylene chloride. IR 1725 cm^{-1}. ^1H NMR 1.00–2.30 (m, 12H), 2.30–3.35 (m, 4H), 3.80–4.30 (~t, 2H), 6.00–6.25 (m, 2H). The benzoyl derivative **15** was prepared from **13** with benzoyl chloride–pyridine in methylene chloride, chromatographed on silica gel with methylene chloride: ethyl acetate = 94 : 6. R_f 0.44. IR 1715, 1600, 1275, 1115 cm^{-1}. NMR ^1H: 1.25–3.25 (m, 13H), 4.35 (t, J = 6, 2H), 6.15 (m, 2H), 7.25–7.60 (m, 3H), 7.90–8.20 (m, 2H). ^{13}C: 219.5 s, 166.8 s, 136.1 d, 134.9 d, 132.7 d, 132.6 d, 130.2 s, 129.3 d, 128.2 d, 64.7 t, 54.8 d, 52.3 t, 48.7 d, 48.1 t, 47.1 d, 46.0 d, 36.6 d, 34.1 t, 27.0 t.

5 - exo - (3' - Benzyloxypropyl)tricyclo[5.2.1.0^{2,6}]dec - 8 - en - 3 - one (**16**)

A solution of 12 ml of 0.6 N (7.2 mmol) 3-benzyloxy propyl lithium,[15] prepared from 3-benzyloxy propyl bromide,[22] was stirred with 1.10 g (5.8 mmol) cuprous iodide for 1 hr at −70°. At −70° a solution of 0.585 g (4.0 mmol) tricyclo[5.2.1.0^{2,6}]dec-3,8-dien-5-one[20] in 6 ml ether was added. The reaction mixture was stirred for 3 hr at −70°, and allowed to warm up to 20° for 14 hr. The crude material was chromatographed on 100 g silica gel and gave, after elution with methylene chloride: ether = 20 : 1 and Kugelrohr distillation at 160° (0.01 mm Hg) 0.9 g (3.0 mmol, 76%) of **16**. R_f (methylene chloride: ether = 10 : 1) 0.55. IR 3040, 2990, 2960, 2940, 1720, 1450, 1360, 1095 cm^{-1}. NMR ^1H: 1.22–2.71 (m, 11H), 2.80–3.23 (m, 2H), 3.45 (t, J = 6, 2H), 4.48 (s, 2H), 6.00–6.21 (m, 2H), 7.30 (s, 5H). ^{13}C: 219.9 s, 138.3 s, 135.9 d, 135.0 d, 128.1 d, 127.4 2d, 72.8 t, 70.0 t, 54.7 d, 52.2 t, 48.6 d, 48.2 t, 47.0 d, 46.0 d, 36.7 d, 34.3 t, 27.9 t. MS 296 (M$^+$), 231, 95, 92, **91**, 66, 65. Found: C 80.77; H 8.16. Calc. for $C_{20}H_{24}O_2$: C 81.04; H 8.16%.

Oxidation of keto-acetate **14**

To a solution of 2.0 g (8.0 mmol) **14** in 25 ml aqueous acetone (1:1) at 5° was added 50 mg ruthenium trichloride ($RuCl_3.xH_2O$), followed by dropwise addition of a solution of 10 g sodium periodate in 70 ml water.[16] After 6 hr, when the reaction mixture was dark green, excess ruthenium tetroxide was destroyed with isopropanol. After filtration through celite and work-up with ethyl acetate, the crude diacid **17** (2.0 g) was obtained. Esterification first with methanol and sulfuric acid and then with benzoyl chloride–pyridine gave a mixture of two compounds, which, according to NMR, consisted of a 1 : 1 mixture of **19** and **21**. Chromatographic separation first with methylene chloride, then with methylene chloride: ethyl acetate = 9 : 1 gave pure methoxy lactone **21**. Crystallisation from methylene chloride: hexane = 1 : 1 gave a pure sample m.p. 121–122°. IR 1765, 1715, 1600, 1275, 980, 960, 890 cm^{-1}. ^1H NMR 1.00–2.20 (m, 6H), 2.20–3.30 (m, 7H), 3.35 (s, 3H), 3.55 (s, 3H), 4.21 (t, J = 6, 2H), 7.20–7.55 (m, 3H), 7.85–8.05 (m, 2H). MS 402 (M$^+$), 239, 207, 195, 150, 122, 110, **105**. Found: C 65.63; H 6.50. Calc. for $C_{22}H_{26}O_7$: C 65.66; H 6.51%. Esterification of the crude acid **17** with ethereal diazomethane in methanol gave methoxy lactone **20** and keto ester **18** in a ratio of 1:3.4. ^1H NMR 0.60–3.30 (m, ~16H), 3.35 (s, 30% of 1 CH_3), 3.70 (s, 3H), 3.77 (s, 3H), 4.10 (t, 2H).

6,8 - endo - Dicarbomethoxy - 4 - exo - (3' - benzoyloxypropyl)bicyclo[3.3.0]octan - 2 - one (**19**)

A solution of 0.593 g (2 mmol) **16** in 10 ml acetone was added slowly at 4° to a mixture of 2.13 g (10 mmol) sodium periodate,

50 mg ruthenium trichloride ($RuCl_3 \cdot xH_2O$), 80 mg sodium hydroxide in water : acetone = 3 : 1. The crude product was treated with ethereal diazomethane and gave, after chromatography with ether 80 mg (0.2 mmol, 10%) cristalline **21**. A pure sample was obtained from crystallisation in ether m.p. 80–81°. R_f(ether) 0.34, IR 2955, 1735, 1435, 1365, 1315, 1280, 1165 cm^{-1}. ^1H NMR 1.06–3.19 (m, 13H), 3.67 (s, 3H), 3.71 (s, 3H), 4.31 (t, J = 6, 2H), 7.29–7.64 (m, 3H), 7.99–8.20 (m, 2H). MS 402 (M^+), 352, 316, 262, 239, 220, 207, **105**, 91, 77. Found: C 65.52; H 6.48. Calc. for $C_{22}H_{26}O_7$: C 65.66: H 6.51%.

3 - *endo* - *Hydroxy* - 5 - *exo* - (3' - *benzyloxypropyl*)*tricyclo*[5.2.1.$0^{2,6}$]*dec* - 8 - *ene* (**22**)

A solution of 0.236 g (0.8 mmol) **16** in 2 ml methanol was added to 0.3 g (8 mmol) sodium borohydride in 5 ml methanol at 4°. The crude product was chromatographed and ether eluted 0.219 g (0.73 mmol, 92%) **22** as colourless liquid. R_f (ether) 0.55. IR 3005, 2940, 2870, 1450, 1095, 695 cm^{-1}. ^1H NMR 1.10–1.95 (m, 10H), 2.14–2.50 (m, 1H), 2.61–2.98 (m, 3H), 3.44 (t, J = 6, 2H), 4.03–4.43 (m, 1H), 4.48 (s, 2H), 6.07 (dxd, J_{AB} = 6, J = 3, 1H), 6.35 (dxd, J_{AB} = 6, J = 3, 1H), 7.30 (s, 5H). MS 298 (M^+), 197, 123, 107, 92, **91**, 79, 67, 66. Found: C 80.42; H 8.67. Calc. for $C_{20}H_{26}O_2$: C 80.50; H 8.78%.

3 - *endo* - *Acetoxy* - 5 - *exo* - (3' - *benzyloxypropyl*)*tricyclo*[5.2.1.$0^{2,6}$]*dec* - 8 - *ene* (**23**)

A solution of 0.598 g (2 mmol) **22** was heated in 5 ml acetic anhydride containing 60 mg sodium acetate and gave after work-up 0.614 g (1.8 mmol, 90%) **23** as slightly yellow oil. A pure, colourless sample was obtained by chromatography with methylene chloride. R_f (methylene chloride) 0.33. IR 3000, 2940, 1725, 1260 cm^{-1}. ^1H NMR 1.11–1.86 (m, 9H), 2.03 (s, 3H), 2.19–2.46 (m, 1H), 2.61–3.14 (m, 3H), 3.45 (t, J = 6, 2H), 4.49 (s, 2H), 5.09 (q, J = 8, 1H), 5.94–6.24 (m, 2H), 7.31 (s, 5H). MS 340 (M^+), 215, 197, 189, 123, 107, **91**, 79, 66. Found: C 77.49; H 8.31. Calc. for $C_{22}H_{28}O_3$: C 77.61, H 8.29%.

3 - *endo* - (2' - *Methyl* - 3' - *oxa* - *butyloxy*)5 - *exo* - (3' - *benzyloxypropyl*)*tricyclo*[5.2.1.$0^{2,6}$]*dec* - 8 - *ene* (**24**)

A mixture of 0.3 g (1.0 mmol) alcohol **22** and 0.2 ml (2.0 mmol) ethyl vinyl ether was stirred with 0.01 ml dichloroacetic acid for 16 hr at room temperature. After treatment with cold 2N sodium hydroxide and work-up with methylene chloride, the crude product was chromatographed with pentane : ether = 2 : 1 and gave 0.24 g (0.65 mmol, 64%) **24** as colourless oil. R_f (pentane : ether = 2 : 1) 0.67. IR 3010, 2980, 2940, 2880, 1455, 1100, 1060 cm^{-1}. ^1H NMR 0.97–1.93 (m, 12H), 1.19 (t, J = 7, 3H), 2.10–2.45 (m, 1H), 2.55–3.03 (m, 3H), 3.27–3.93 (m, 2H), 3.47 (t, J = 7, 2H), 4.03–4.38 (m, 1H), 4.52 (s, 2H), 4.68 (q, J = 5, 1H), 5.88–6.35 (m, 2H), 7.37 (s, 5H). MS 370 (M^+), 215, 123, 103, 99, 91, 80, 75, 73, 66.

2 - *endo* - *Acetoxy* - 4 - *exo* - (3' - *benzyloxypropyl*)6,8 - *endo* - *dicarbomethoxybicyclo*[3.3.0]*octane* (**25**)

A solution of 0.80 g (2.3 mmol) **23** in 160 ml dioxane was oxidized by dropwise addition of a mixture of 3.0 g (14 mmol) sodium metaperiodate, 0.2 g (1.3 mmol) potassium permanganate and 100 mg sodium carbonate in 120 ml water.[17] After stirring at 20° for 16 hr, a small amount of 30% hydrogen peroxide was added. After filtration through Celite and work-up the crude product (0.42 g) was treated with ethereal diazomethane. After chromatography of crude **25** with ether 0.258 g (0.58 mmol, 25%) **25** was obtained as colourless oil. A pure sample was prepared by another chromatography. R_f (ether) 0.55. IR 2950, 1730, 1435, 1375, 1170, 1150, 1100, 1025 cm^{-1}. ^1H NMR 0.98–3.14 (m, 13H), 1.95 (s, 3H), 3.39 (t, J = 6, 2H), 3.60 (s, 6H), 4.45 (s, 2H), 5.21–5.40 ("d"x"d", 1H), 7.30 (s, 5H). MS 432 (M^+), 372, 359, 340, 281, 266, 249, 234, 206, 92, **91**. Found: C 66.94; H 7.66. Calc. for $C_{24}H_{32}O_7$: C 66.65; H 7.46%.

3 - *endo* - *Carbomethoxy* - 5 - *exo* - (3' - *benzyloxypropyl*)8 - *oxa* - *tricyclo*[5.2.1.$0^{4,10}$]*decan* - 9 - *one* (**26**)

The tricyclic lactone **26** was prepared from **23** following for oxidation the procedure of **25**. The crude diacid obtained from 0.40 g (1.2 mmol) **23**, was treated with 180 mg (3.2 mmol) potassium hydroxide in 6 ml aqueous dioxane (1 : 1) at room temp for 16 hr. After work-up the reaction mixture was treated with ethereal diazomethane. Subsequent chromatography with ether gave 0.068 g (0.2 mmol, 16%) **26** as colourless crystals of m.p. 75–76° (from pentane). For analysis a sample was again chromatographed. R_f (ether) 0.30. IR 2950, 1750, 1730, 1355, 1170, 1100, 1000 cm^{-1}. ^1H NMR 0.91–2.10 (m, 6H), 2.20–2.63 (m, 4H), 2.85–3.53 (m, 5H), 3.58 (s, 3H), 4.45 (s, 2H), 4.80–5.01 (m, 1H), 7.29 (s, 5H). MS 358 (M^+), 252, 235, 234, 220, 206, 149, 120, 92, **91**. Found: C 70.32; H 7.34. Calc. for $C_{21}H_{26}O_5$: C 70.37; H 7.31%.

3 - *endo* - (2' - *E* - *Carbethoxyethenyl*)5 - *exo* - (3' - *benzyloxypropyl*)8 - *oxa* - *tricyclo*[5.2.1.$0^{4,10}$]*decan* - 9 - *ol* (**28**)

A solution of 1.64 g (4.4 mmol) **24** in 30 ml methylene chloride was oxidized by slow addition of a mixture of 1.05 g (6.6 mmol) potassium permanganate and 1.51 g (6.6 mmol) benzyltriethylammonium chloride in 30 ml methylene chloride at 20°. After 2 hr, 30 ml of a buffer, prepared from sodium acetate and acetic acid, was added and after stirring for 2 hr, the reaction mixture was filtrated through Celite and worked-up by extraction with 2N sodium hydroxide. The crude hydroxy dialdehyde **27**, dissolved in 10 ml ether, was added at 0° to a solution, prepared from 2.81 g (12.5 mmol) triethylphosphono acetate in 10 ml ether and 8.4 ml 1.5N (12.6 mmol) n-butyllithium in hexane. The reaction mixture was worked-up after 3 hr at room temperature and the crude product was chromatographed with ether to give 0.81 g (2.0 mmol, 45%) **28** as colourless oil. R_f (ether) 0.36. IR 3000, 2935, 2860, 1710, 1650, 1450, 1370, 1310, 1270, 1200, 1125, 1095, 1075 cm^{-1}. ^1H NMR 0.98–2.33 (m, 10H), 1.24 (t, J = 7, 3H), 2.41–2.90 (m, 2H), 3.05–3.59 (m, 4H), 4.15 (q, J = 7, 2H), 4.46 (s, 2H), 4.56–4.78 (m, 1H), 5.25 (d, J = 3, 1H), 5.80 (d, J_{AB} = 16, 1H), 6.99 (dxd, J_{AB} = 16, J_{AX} = 7, 1H), 7.31 (s, 5H). MS 400 (M^+), 382, 276, 245, 230, 217, 202, 131, 92, **91**, 79. Found: C 71.86; H 8.10. Calc. for $C_{24}H_{32}O_5$: C 71.97; H 8.05%.

3 - *endo* - (2' - *E* - *Carbethoxyethenyl*) - 5 - *exo* - (3' - *benzyloxypropyl*)8 - *oxa* - *tricyclo*[5.2.1.$0^{4,10}$]*decan* - 9 - *one* (**29**)

To a solution of 0.260 g (0.65 mmol) **28** in methylene chloride was added 1.3 g (6.0 mmol) pyridinium chlorochromate in small portions. After 6 hr, the reaction mixture was worked-up; from the chromatography of the crude product with ether 0.130 g (0.32 mmol, 50%) **29** was obtained. R_f (ether) 0.33. IR 3000, 2960, 2940, 2860, 1760, 1715, 1655, 1455, 1370, 1360, 1310, 1275, 1180, 1100 cm^{-1}. ^1H NMR 1.08–3.65 (m, 15H), 1.30 (t, J = 7, 3H), 4.22 (q, J = 7, 2H), 4.50 (s, 2H), 4.84–5.12 (m, 1H), 5.82 (d, J_{AB} = 16, 1H), 6.88 (dxd, J_{AB} = 16, J_{AX} = 7, 1H), 7.37 (s, 5H). MS 398 (M^+), 366, 352, 262, 246, 123, 105, **91**.

3 - *endo* - (2' - *Carbomethoxyethyl*)5 - *exo* - (2' - *carbomethoxyethyl*)8 - *oxa* - *tricyclo*[5.2.1.$0^{4,10}$]*decan* - 9 - *one* (**31**)

A solution of 0.035 g (0.09 mmol) **29** in 10 ml aqueous ethanol was hydrogenated with 10% palladium on charcoal to give **30**. After filtration through Celite, the reaction mixture was evaporated and dissolved in acetone. Oxidation of **30** with Jones reagent gave after work-up and acid catalyzed esterification with methanol 0.025 g (0.08 mmol, 88%) diester lactone **31**. R_f (ether) 0.24. IR 2960, 2930, 1735 (shoulder at 1765), 1435, 1360, 1305, 1295, 1180, 1000 cm^{-1}. ^1H NMR 1.09–3.48 (m, 17H), 3.68 (s, 6H), 4.80–5.01 (m, 1H). MS 324 (M^+), 293, 275, **251**, 233, 219, 207, 206, 191, 173, 145, 131. Found: C 62.97; H 7.57. Calc. for $C_{17}H_{24}O_6$: C 62.95; H 7.46%.

Acknowledgement—This work was supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung, project no. 2.103-0.74, 2.560-0.76, 2.046-0.78 and 2.690-0.80. We acknowledge the competent technical assistance of Roland Ulrich.

REFERENCES

[1]J. B. Collins, J. D. Dill, E. D. Jemmis, P. v. R. Schleyer, R. Seeger and J. A. Pople, *J. Am. Chem. Soc.* **98**, 5419 (1976).
[2]F. A. Cotton and M. Millar, *Ibid.* **99**, 7886 (1977).

[3]H. Wynberg and L. A. Hulshof, *Tetrahedron* **30**, 1775 (1974); see also: E.-U. Würthwein, J. Chandrasekhar, E. D. Jemmis and P. v. R. Schleyer, *Tetrahedron Letters* **22**, 843 (1981).
[4]K. B. Wiberg, L. K. Olli, N. Golembeski and R. D. Adams, *J. Am. Chem. Soc.* **102**, 7467 (1980).
[5]R. Hoffmann, R. W. Alder and C. F. Wilcox, *Ibid.* **92**, 4992 (1970).
[6]G. Haas and V. Prelog, *Helv. Chim. Acta* **52**, 1202 (1969); we thank Prof. Prelog for communication of these results prior to publication.
[7]R. E. Corbett, D. R. Lauren and R. T. Weavers, *J. Chem. Soc. Perkin I*, 1774 (1979).
[8]R. Keese, A. Pfenninger and A. Roesle, *Helv. Chim. Acta* **62**, 326 (1979).
[9]M. C. Böhm, R. Gleiter and P. Schang, *Tetrahedron Letters* 2575 (1979).
[10]J. Chandrasekhar, E.-U. Würthwein and P. v. R. Schleyer, *Tetrahedon* **37**, 921 (1981).
[11]R. Mitschka, J. M. Cook and U. Weiss, *J. Am. Chem. Soc.* **100**, 3974 (1978).
[12]W. ten Hoeve and H. Wynberg, *J. Org. Chem.* **45**, 2930 (1980).
[13]P. Pradhan and R. Keese, unpublished results; N. Oesch, Diploma thesis, University of Bern, 1980.
[14]G. Stork, G. L. Nelson, F. Rouersac and O. Gringore, *J. Am. Chem. Soc.* **93**, 3092 (1971).
[15]P. E. Eaton, G. F. Cooper, R. C. Johnson and R. H. Mueller, *J. Org. Chem.* **37**, 1947 (1972).
[16]H. Nakata, *Tetrahedron* **19**, 1959 (1963).
[17]T. Sakan and K. Abe, *Tetrahedron Letters* 2471 (1968).
[18]T. Ogino and K. Mochizuki, *Chemistry Letters* 443 (1979).
[19]H. Gilman and F. Schulze, *J. Am. Chem. Soc.* **47**, 2002 (1925).
[20a]K. Alder and F. H. Flock, *Chem. Ber.* **87**, 1916 (1954); [b]M. Rosenblum, *J. Am. Chem. Soc.* **79**, 3179 (1957).
[21]I. Winkler, Diploma thesis, University of Bern, 1978.
[22a]L. I. Smith and J. A. Sprung, *J. Am. Chem. Soc.* **65**, 1276 (1943); [b]F. Delay and G. Ohloff, *Helv. Chim. Acta* **62**, 369 (1979).