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SYNTHESIS OF [4.4.5.5]FENESTRANE

V. BHASKAR RAO, STEVEN WOLFF and WILLIAM C. AGOSTA*
Laboratories of The Rockefeller University, New York, NY 10021-6399, U.S.A.

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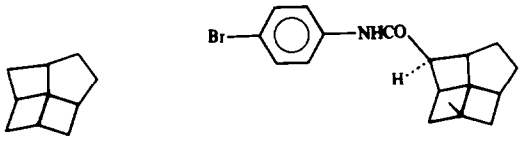
Abstract—Intramolecular photochemical [2+2] cyclization of **3b** gives **4b** regio- and stereospecifically, along with fragmentation product **12b**. The Cl atom of **4b** was removed by ketalization, Li–NH_3 reduction, and reoxidation with RuO_4 to furnish **17b**. The derived diazoketone **17d** on treatment with rhodium(II) acetate underwent cyclization to the [4.4.5.5]fenestrane keto ketal **15**. Subsequent reductions gave monoketone **23** and ultimately the parent hydrocarbon **6**.

Fenestranes have attracted considerable synthetic and theoretical interest in recent years, primarily because of the strain and distortion expected at the central quaternary carbon atom. We have recently reported the synthesis of derivatives of [4.4.4.5]fenestrane (**1**), the smallest and most strained of the tetracyclic fenestranes prepared to date.[1] The X-ray structure of **2** reveals that



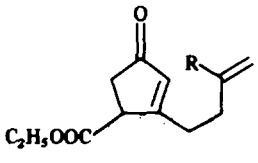
1 **2**

flattening at the central carbon atom has increased the two relevant bond angles to 129°.[1] A key step in the preparation of **2** was photochemical cyclization of dienone ester **3a**, which leads to a 2:1 mixture of the epimeric tricyclic esters **4a** and **5a**; the major, more stable ester **4a** was then elaborated into **2** and related [4.4.4.5]fenestranes. The methyl group in **3a** is present in order to control the regiochemistry of the [2+2] cyclization; without it, a mixture of crossed and straight closure products from the diene system is expected, since this behavior appears to be general in the photocyclization of 1-acyl-1,5-hexadienes.[2] In the present work we have explored the possibility of utilizing a chlorine atom rather than a methyl group to provide the desired regiochemical control in the cycloaddition step[3] and then later removing this substituent reductively. We report below the results of this exploration including the synthesis of the parent hydrocarbon [4.4.5.5]fenestrane (**6**) that it has permitted.

Starting dienone **3b** was available by way of base-catalyzed condensation between the two acetoacetic esters **7** and **8** to yield **9**. Selective cleavage of the methyl ester and decarboxylation then gave **3b**. The sequence is closely patterned after our earlier preparation of **3a**.[1,4] As with **3a**, irradiation of **3b** led only to 1,6 cyclization products derivable from biradicals **10** and **11**.[2] In the chloro series, however, these products were **4b** (48%) and **12b** (22%); there was no evidence for formation of **5b**. Ester **4b** reverted to **3b** on thermolysis in benzene at 170°. The stereochemistry of **4b** was assignable through comparison of its ^{1}H-NMR spectrum with those of **4a** and **5a**.[1] Cyclopentenone **12b** arises from fragmentation of **10b** and/or **11b**, followed by a shift of the exocyclic β,γ double bond into conjugation; such products are typically quite minor or absent in related systems studied previously.[2] Formation of **12b** and this difference in photoproducts from **3a** and **3b** suggest that in both series the major biradical **10** collapses to **4**, but that the minor biradical **11** behaves differently in the two cases, with **11a** closing to **5a**, but **11b** fragmenting to **12b**. Such divergent behavior can be attributed to steric and dipolar interactions between chlorine and carboethoxy that disfavor collapse of **11b** to **5b**, but that are less significant in **11a** where the interacting groups are methyl and carboethoxy.

Our initial plan for **4b** was first to elaborate the fourth ring and then remove the chlorine atom. Ketone **4b** was converted to the ketal **13a** and then to acid **13b**. Surprisingly, direct saponification of **13a** gave only a poor yield of acid, so that it was advantageous to reduce **13a** first with lithium aluminum hydride and then reoxidize alcohol **13c** to **13b** with ruthenium tetroxide in the presence of acetonitrile.[5] Treatment of **13b** with oxalyl chloride and then diazomethane and triethylamine gave the desired diazoketone **13d**. This underwent rapid decomposition on exposure to rhodium(II) acetate[6] in dichloromethane, but from the IR spectrum of the crude reaction mixture it appeared that the expected[1] tetracyclic product **14** was formed in less than 5% yield. We comment on this result below, but for the moment we note simply that this approach to tetracyclic fenestranes appeared impractical.

We turned then to removal of the chloro substituent of **4b** prior to ring closure and found this to be a more successful route. Of various methods explored the most useful was reduction of hydroxy ketal **13c** with excess lithium in liquid ammonia, followed by quenching of the reaction with sodium benzoate.[7] This furnished **17c** in an overall yield of 67% from **13a**. In contrast, lithium aluminum hydride–nickel chloride[8] failed to remove the halogen of **13a** and gave only **13c**. Reaction of **13a** with tributyltin hydride,[9] on the other hand, yielded only a small amount of unreacted starting material and no recognizable products on work up. Reoxidation of **17c** with ruthenium trichloride–sodium periodate[5] then gave the crystalline ketal acid **17b**. The derived diazoketone **17d** was decomposed as before to yield **15** in 25% yield. In the methyl-substituted series the parallel reaction to form **16** proceeds in 64% yield.[1] Carbene insertions to form **14**, **15**, and **16** under identical conditions thus give yields of < 5, 25, and



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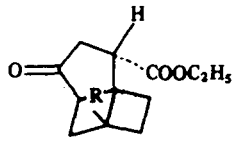

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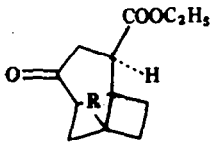

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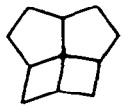

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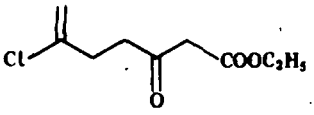

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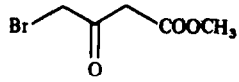

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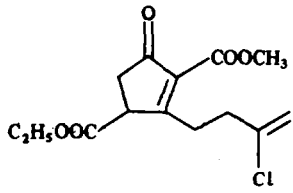

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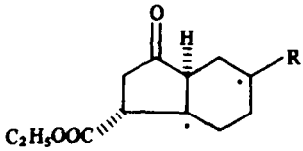

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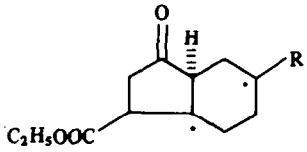

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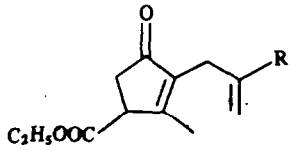


12

a R = CH_3; b R = Cl

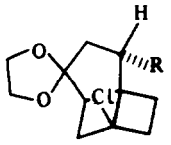
64%, respectively.† Our previous studies in the methyl-substituted series[1] revealed a sensitivity in this insertion reaction also to changes of substitution at the carbon bearing the ethylene ketal grouping.‡ There are many earlier examples of the effects of structural and conformational change on the success of intramolecular carbene insertion reactions,[10] and our variable results probably reflect conformational changes in the five-membered ring and therefore in the effective position of the diazoketone side chain as a function of specific molecular structure.

We also investigated the effect on the insertion reaction of replacing the ketal of **17d** by a trialkylsilyloxy function. Keto ester **4b** was reduced to **18** with sodium borohydride, and this alcohol was converted to t-butyldimethylsilyl ether **19**.[11] The stereochemistry shown for **18** and **19** is that expected from approach of hydride to **4b** from the less hindered side of the carbonyl group. Reaction of **19** with lithium aluminum hydride and then lithium in liquid ammonia gave **20** which was directly treated with ruthenium trichloride–sodium periodate as above to furnish acid **21**. Decomposition of the diazoketone formed from **21** gave (32%) a single monomeric product assigned structure **22** on the basis of its spectroscopic properties (IR, 1745 cm^{-1};[12] no carbinyl proton in ^{1}H-NMR spectrum). Insertion then occurs preferentially into the tertiary carbinyl C—H bond in this system, leading to the novel ring system of **22** rather than the [4.4.5.5]fenestrane system. In models formation of **22** appears to involve a greater increase in strain than closure to a [4.4.5.5]fenestrane. The observed specificity probably originates in a conformational effect, as mentioned above, in combination with the known[13] preference for carbene insertion into tertiary rather than secondary C—H bonds.

Finally, we examined stepwise reduction of **15**.

† All yields are based on the overall conversion of carboxylic acid to keto ketal. Formation of acyl chloride and diazoketone proceeded in comparable yields in all three cases.

‡ Changes at the ketal carbon atom also influence the insertion reaction in the unsubstituted series. Replacement of the ethylene ketal of **17d** by a 2,2-dimethyl-1,3-trimethylene ketal grouping causes the yield in the cyclization to drop from 25 to 8%. V. B. Rao, unpublished results in these laboratories.



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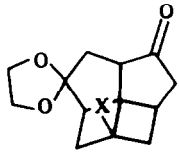
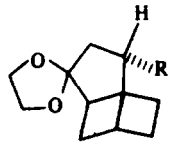


14 X = Cl
15 X = H
16 X = CH_3



17

a R = $COOC_2H_5$; b R = COOH; c R = CH_2OH; d R = $COCHN_2$

Hydride reduction, tosylation of the hydroxy ketal, a second hydride reduction, and deketalization provided the simple [4.4.5.5]fenestrane ketone **23**. Repetition of these steps on **23** then gave the parent hydrocarbon, [4.4.5.5]fenestrane (**6**), the ^{13}C-NMR spectrum of which contains only seven signals as required by symmetry. Parallel reactions had been employed previously to convert **16** into the corresponding methyl derivative of **6**;[1] spectroscopic properties of the two hydrocarbons were quite similar, as expected.

From these experiments we conclude that, despite the reduced yield in the carbene insertion step, this sequence provides a workable route to fenestranes free of alkyl substituents.

EXPERIMENTAL†

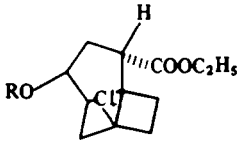
Preparation of ethyl 3-oxo-6-chlorohept-6-enoate (**7**). The dianion of ethyl acetoacetate (19.5 g, 0.15 mol) was reacted with 2,3-dichloropropene (15.4 g, 0.14 mol) following a known procedure.[14] The mixture was stirred at 0° for 16 h; workup and distillation (90–92°, 0.1 mm Hg) yielded pure **7** (80%): IR 2970 (s), 2920 (m), 1740 (s), 1725 (s), 1660 (s), 1410 (m), 1310 (m), 1255 (s) and 1030 (m) cm^{-1}; NMR δ 5.19 (dd, J = 1.33, 6.13 Hz, 2H), 4.21 (q, J = 7.13 Hz, 2H, OCH_2), 3.46 (s, 2H, $COCH_2CO$), 2.85 (t, J = 7.30 Hz, 2H, CH_2), 2.65 (t, J = 7.29 Hz, 2H, CH_2), 1.29 (t, J = 7.13 Hz, 3H, $CH_2\underline{CH_3}$). Anal. ($C_9H_{13}ClO_3$), C, H.

4-Carboethoxy-2-carbomethoxy-3-(3-chloro-3-butenyl)-2-cyclopenten-1-one (**9**). The anion generated from **7** (22.9 g, 0.112 mol) and NaH (2.7 g, 0.112 mol) was reacted with methyl 4-bromoacetoacetate (11.0 g, 0.056 mol) according to the earlier described procedure.[1] Workup yielded unreacted **7** (11.0 g, 96%) and product **9** as a low melting solid in virtually quantitative yield (16.1 g, 99%): IR 1725 cm^{-1} (s); NMR (60 MHz, CCl_4) δ 5.2 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H, OCH_2), 3.82 (s, 3H, OCH_3), 3.15–4.10 (m, 5H), 2.45–2.80 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H, $CH_2\underline{CH_3}$). This was used without further purification.

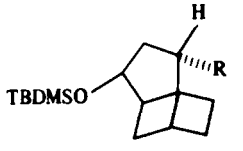
Ethyl 2-(3-chloro-3-butenyl)-4-oxo-2-cyclopentene-1-carboxylate (**3b**). Ketodiester **9** (2.8 g, 9.3 mmol) in diglyme (10 ml) was heated at reflux with AcOH (1 ml) and NaI (6.0 g, 40 mmol) for ~ 15 min. Workup and distillation yielded pure **3b** (1.1 g, 49%, b.p. 125°, 0.1 mm Hg): IR 2985 (w), 2945 (w), 1725 (s), 1625 (m), 1325 (m), 1245 (w) and 1175 (w) cm^{-1}; NMR δ 6.06 (d, J = 1.24 Hz, 1H), 5.21 (dd, J = 1.38, 7.85 Hz, 2H, $C{=}CH_2$), 4.225 and 4.22 (two q, J = 7.1 Hz, 2H, OCH_2), 3.72–3.77 (m, 1H), 2.57–2.79 (m, 6H), 1.31 (t, J = 7.1 Hz, 3H, $CH_2\underline{CH_3}$). Anal. ($C_{12}H_{15}ClO_3$) C, H.

Photolysis of **3b** *to yield* **4b** *and* **12b**. A soln of **3b** (2 g) in hexane (200 ml) was degassed by bubbling N_2 and irradiated at

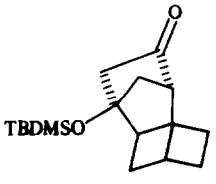
† General procedures have been described earlier.[1]



18 R = H
19 R = TBDMS



20 R = CH_2OH
21 R = COOH



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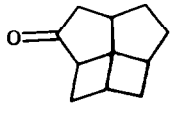

23

TBDMS = t-Bu$(CH_3)_2$Si

25°, using a uranium glass filter with 450 W Hanovia lamp for 24 h. Hexane was removed and crude photolysate was purified by flash chromatography[15] using 33% ether in hexane as eluent to obtain pure **4b** (0.9 g, 45%), **12b** (0.4 g, 20%), and unreacted **3b** (0.14 g, 7%). For **4b**: IR ($CDCl_3$) 2990 (m), 2950 (m), 1740 (s), 1370 (w), 1330 (m), 1260 (m), 1230 (m) and 1180 (m) cm^{-1}; NMR δ 4.11 (q, J = 7.13 Hz, 2H, OCH_2), 3.25 (dd, J = 0.85, 8.26 Hz, 1H), 3.06 (dd, J = 8.50, 13.5 Hz, 1H), 2.93 (dd, J = 8.31, 18.21 Hz, 1H), 2.81 (ddd, J = 1.9, 4.64, 8.42 Hz, 1H), 2.53–2.72 (m, 3H), 2.50 (dd, J = 7.41, 12.00 Hz, 1H), 2.40 (ddd, J = 1.72, 4.60, 13.37 Hz, 1H), 2.10–2.18 (m, 1H) and 1.21 (t, J = 7.14 Hz, 3H, $CH_2C\underline{H}_3$). Anal. ($C_{12}H_{15}ClO_3$) C, H. For **12b**: IR 2990 (m), 2950 (m), 1740 (s), 1715 (s), 1380 (m), 1370 (w), 1180 (m), 1155 (m) cm^{-1}; NMR δ 5.15 (br s, 1H), 5.125 (t, J = 1.3 Hz, 1H), 4.18 (q, J = 7.14 Hz, 2H, OCH_2), 3.62–3.63 (m, 1H), 3.23 (s, 2H, CH_2), 2.59–2.65 (m, 2H), 2.10 (s, 3H) and 1.255 (t, J = 7.14 Hz, 3H, $CH_2C\underline{H}_3$); mass spectrum *m/z* 242.0700 (M^+, calc for $C_{12}H_{15}ClO_3$, 242.0709).

Ketalization of **4b**. A soln of **4b** (0.24 g, 1 mmol) in benzene (40 ml) with pyridinium tosylate (25 mg) and ethylene glycol (0.4 ml) was heated at reflux for 8 h with azeotropic removal of water. Extractive workup with ether yielded **13a** (0.27 g, 96%): IR 2980 (m), 2948 (m), 2880 (m), 1730 (s), 1445 (w), 1330 (m), 1240 (w), 1175 (m) and 1115 (w) cm^{-1}; NMR δ 4.06–4.22 (m, 2H, OCH_2), 3.72–3.95 (m, 4H, OCH_2OH_2O), 2.94 (dd, J = 1.2, 8.29 Hz, 1H), 2.25–2.75 (m, 9H), 1.25 (t, J = 7.13 Hz, 3H, $CH_2C\underline{H}_3$). This product was used without further purification.

Ethylene ketal of 4 - *chloro* - 7 - *oxo* - *tricyclo* - [4.3.0.0^{1,4}]*octane* - 9 - *carboxylic acid* (4β,6α,9α) (**13b**). A soln of **13a** (0.35 g, 1.2 mmol) in 10% aq MeOH (15 ml) was stirred with KOH (0.3 g) for 24 h at room temp. MeOH was removed under vacuum and the residue was taken up in water (25 ml). This soln was extracted with ether (2 × 20 ml) followed by acidifying to pH 4 with 3 M HCl and extraction with CH_2Cl_2 (2 × 100 ml). Standard workup and removal of solvent yielded crude acid which was purified by flash chromatography[15] using 60% ether in hexane to obtain pure acid as a colorless crystalline solid, m.p. 101–102° (0.1 g, 32%): IR ($CDCl_3$) 3500–2500 (br, COOH), 2985 (s), 2950 (s), 2980 (s), 1715 (s), 1410 (m), 1330 (m) and 1230 (m) cm^{-1}; NMR δ 10.5 (br, 1H, COOH), 3.91–4.01 (m, 4H, OCH_2CH_2O), 3.82 (t, J = 7.28 Hz, 1H), 3.05 (d, J = 8.25 Hz, 1H) and 2.18–2.75 (m, 8H); mass spectrum *m/z* 258.0645 (M^+, calc for $C_{12}H_{15}ClO_4$, 258.0658).

Alternatively, **13b** was prepared by way of **13c**. Ketal ester **13a** (0.80 g, 2.8 mmol) was reduced with $LiAlH_4$ (0.15 g) in ether (50 ml). Extractive workup after destroying excess $LiAlH_4$ yielded **13c** (0.66 g, 96%, IR hydroxyl absorption). This (0.41 g, 1.7 mmol) was taken up in a mixture of acetonitrile (3.5 ml), CCl_4 (3 ml), water (5 ml), and sodium periodate (1.4 g, 6.5 mmol). To this was added $RuCl_3 \cdot 3H_2O$ (10 mg), and the mixture was stirred at 25° for 2 h.[5] Extractive workup with CH_2Cl_2 and flash chromatography[15] of the crude residue yielded acid **13b** (0.21 g, 48%).

Preparation and decomposition of diazoketone **13d**. To a well-stirred soln of **13b** (0.12 g, 0.46 mmol) in dry benzene (5 ml) was added oxalyl chloride (0.126 g, 1 mmol) dropwise under N_2. The mixture was stirred at 25° for 2 h and solvent removed to obtain acid chloride (IR, 1798 cm^{-1}). This was taken up in ether (10 ml) and added dropwise to a soln of excess CH_2N_2 and Et_3N (50 mg, 0.5 mmol) in ether at 0°. The mixture was left stirring for 16 h at room temp, and solvent was then removed on a steam bath. The residue was dissolved in pentane (40 ml) and dried over $MgSO_4$. The pentane soln was filtered and solvent removed to yield **13d** as a pale yellow oil (0.12 g, IR 2100 cm^{-1}).

To a soln of the above **13d** in dry CH_2Cl_2 (15 ml) under N_2 was added rhodium(II) acetate (10 mg). Reaction started immediately and vigorous gas evolution was observed. Stirring was continued for 1 h and the mixture was diluted with 3% HCl aq (10 ml). Pentane extraction (2 × 30 ml) and standard workup yielded crude product (0.11 g). This was found to be a mixture of many compounds by TLC and showed weak absorption due to C=O around 1740 cm^{-1}. No further purification was attempted.

Ethylene ketal of 7 - *oxo* - *tricyclo*[4.3.0.0^{1,4}]*octane* - 9 - methanol (4β,6α,9α) (**17c**). Chloro alcohol **13c** (2.1 g, 8.6 mmol) in ether (20 ml) was added dropwise to a blue suspension of Li (0.21 g, 30 mmol) in freshly distilled liquid NH_3 (50 ml). The resulting mixture was stirred at −33° for 30 min followed by quenching of the reaction with excess of sodium benzoate. Ammonia was allowed to evaporate and residue was taken up in water (100 ml) and extracted with ether (2 × 100 ml). Standard workup yielded the crude product, which was purified by flash chromatography[15] using 66% ether in hexane as eluent to obtain pure **17c** (1.15 g, 64%): IR 3640 (m), 3500 (br), 2970 (s), 2940 (s), 2880 (m), 1335 (m), 1125 (m), 1020 (m) and 985 (w) cm^{-1}; NMR δ 3.74–4.03 (m, 4H, —OCH_2O—), 3.58 (d, J = 3.95 Hz, 2H, OCH_2), 2.61–1.87 (m, 12H). Anal. ($C_{12}H_{18}O_3$) C, H.

Ethylene ketal of 7 - *oxo* - *tricyclo*[4.3.0.0^{1,4}]*octane* - 9 - *carboxylic acid* (1*S**,4β,6α,9α) (**17b**). To a well-stirred mixture of **17c** (0.61 g, 2.9 mmol) in CCl_4 (6 ml), acetonitrile (6 ml) and water (9 ml) containing $NaIO_4$ (2.63 g, 12 mmol) was added $RuCl_3 \cdot 3H_2O$ (15 mg).[5] Stirring continued at room temp under N_2 for 1 h, and mixture was extracted with CH_2Cl_2 (2 × 20 ml) after diluting with water (3 ml). The organic layer was dried over $MgSO_4$ and residue obtained after removal of the solvent was subjected to flash chromatography.[15] Elution with 75% ether in hexane gave pure acid **17b** as a colorless solid, m.p. 82–84° (0.38 g, 58%): IR 3500–2500 (br, COOH), 2965 (s), 2945 (s), 1710 (s), 1400 (w), 1326 (w), 1120 (w) cm^{-1}; NMR δ 10.45 (br, 1H, COOH), 3.94–4.02 (m, 4H, —OCH_2CH_2O—), 3.81–3.85 (m, 1H), 2.75 (ddd, J = 1.71, 5.93, 7.89 Hz, 1H), 2.89 (d, J = 7.95 Hz, 1H), 2.25–2.56 (m, 6H) and 1.92–2.04 (m, 2H). Anal. ($C_{12}H_{16}O_4$) C, H.

4 - *Ethylene ketal of tetracyclo*[4.4.1.0^{3,11}.0^{9,11}]*undecane* - 4,7 - *dione* (1α,3β,6α,9β) (**15**). Ketal acid **17b** (0.4 g, 1.78 mmol) was converted to **17d** by reacting the corresponding acid chloride with diazomethane as described above for **13d**. This **17d** (IR, 2100 cm^{-1}) was taken up in anhyd CH_2Cl_2 (25 ml) under N_2. To this well-stirred soln was added rhodium(II) acetate (15 mg). Vigorous gas evolution was observed immediately and the soln turned emerald green. Stirring was continued for 30 min and the mixture was diluted with pentane (100 ml) followed by washing with 3% HCl aq (10 ml). The organic layer was washed with sat $NaHCO_3$ aq (20 ml) and brine. Standard workup yielded a residue which was further purified by flash chromatography[15] (50% ether in hexane) to obtain pure **15** (98 mg, 25%) which solidified overnight in the cold room (4°), m.p. 54–5°: IR ($CDCl_3$) 2955 (m), 2935 (m), 2880 (m), 1740 (s), 1435 (w), 1310 (w), 1250 (w) and 1140 (m) cm^{-1}; NMR 3.86–4.02 (m, 4H, —OCH_2CH_2O—), 2.43–2.77 (m, 8H), 2.24–2.32 (m, 1H), 2.12 (ddd, J = 3.0, 7.45, 12.78 Hz, 1H), 2.02 (dd, J = 8.38, 13.05 Hz, 1H) and 1.57–1.63 (m, 1H); mass spectrum *m/z* 220.1094 (M^+, calc for $C_{13}H_{16}O_3$ 220.1099).

Ethyl 4 - *chloro* - 7 - *hydroxytricyclo*[4.3.0.0^{1,4}]*octane* - 9 - *carboxylate* (4β,6α,7β,9α) (**18**). To a soln of **4b** (0.19 g, 0.78 mmol) in anhyd MeOH (6 ml) at 0° was added $NaBH_4$ (30 mg) in three separate portions under N_2. The mixture was stirred for 2 h at 25°. This was acidified with 5% HCl aq and diluted with water (40 ml). Extractive workup with ether yielded **18** (0.18 g, 95%) as a colorless oil: NMR (60 MHz, CCl_4) δ 4.3–4.75 (m, 1H), 4.04 (q, J = 7.2 Hz, 2H, OCH_2), 3.4–4.0 (m, 1H), 1.6–3.0 (m, 10H), 1.3 (t, J = 7.2 Hz, 3H, $CH_2C\underline{H}_3$). This was used in the next step without further purification.

Ethyl 4 - *chloro* - 7 - (t - *butyldimethylsilyloxy*) - *tricyclo*[4.3.0.0^{1,4}]*octane* - 9 - *carboxylate* (4β,6α,7β,9α) (**19**). A mixture of **18** (0.17 g, 0.7 mmol), imidazole (0.24 g, 3.5 mmol), and t-butyldimethylsilyl chloride (0.135 g, 0.9 mmol) in DMF (4 ml) was stirred under N_2 at room temp for 20 h. The mixture was diluted with water (30 ml) and extracted with ether (2 × 50 ml). Standard workup yielded **19** in quantitative yield: IR 2955 (s), 2940 (s), 2895 (m), 1728 (s), 1465 (m), 1360 (m), 1255 (s) and 1180 (s); NMR (60 MHz, CCl_4) δ 4.4–4.8 (m, 1H), 4.1 (q, J = 7.1 Hz, 2H, OCH_2), 1.6–3.0 (m,

10H), 1.24 (t, J = 7.1 Hz, 3H, CH_2CH_3), 0.96 (s, 9H, $C(CH_3)_3$), 0.1 (s, 6H, $2CH_3$). This was used directly in the reaction described below.

7 - (t - *Butyldimethylsilyloxy)tricyclo*[4.3.0.0^{1,4}]*octane* - 9 - *methanol* (4β,6α,7β,9α) (**20**). Chloro ester **19** (0.25 g, 0.7 mmol) was reduced to the chloro alcohol (0.21 g, 95%, m.p. 79–81°) using $LiAlH_4$ following the procedure described for preparing **13c** from **13a**. This chloro alcohol was added as an ethereal soln to a blue suspension of Li (30 mg) in liquid ammonia (25 ml). This mixture was stirred at −33° for 1 h followed by quenching with excess sodium benzoate. Extractive workup with ether yielded **20** (0.16 g, 85%): IR 3625 (br), 2960 (s), 2940 (s), 2855 (m), 1250 (m) and 1120 (s). This was directly used in the next reaction.

7 - (t - *Butyldimethylsilyloxy)tricyclo*[4.3.0.0^{1,4}]*octane* - 9 - *carboxylic acid* (1*S**,4β,6α,7β,9α) (**21**). A soln of **20** (0.16 g, 0.57 mmol) in CCl_4 (1.5 ml), acetonitrile (1.5 ml), and water (2 ml) was treated with $NaIO_4$ (0.5 g) and $RuCl_3 \cdot 3H_2O$ (5 mg) following the procedure described earlier.[5] Workup and flash chromatography[15] using 25% ether in hexane as eluent yielded pure acid **21** (0.1 g, 59%) as a colorless crystalline solid, m.p. 89–91°: IR 3300–2500 (br), 2955 (s), 2940 (s), 2900 (s), 1705 (s), 1250 (m), 1110 (s) and 1050 (m) cm^{-1}; NMR δ 4.58 (dt, J = 7.46, 9.43 Hz, 1H), 2.81 (dt, J = 4.89, 7.86 Hz, 1H), 2.68 (d, J = 6.97 Hz, 1H), 1.93–2.45 (m, 8H), 1.62–1.68 (m, 1H), 0.88 (s, 9H, $C(CH_3)_3$), 0.042 (s, 3H, CH_3), 0.016 (s, 3H, CH_3). Anal. ($C_{16}H_{28}O_3Si$) C, H.

Preparation of **22**. Carboxylic acid **21** (80 mg, 0.27 mmol) was converted to the corresponding diazomethylketone (IR, 2105 cm^{-1}) as above. This was dissolved in CH_2Cl_2 (15 ml) under N_2 and reacted with rhodium(II) acetate dimer (3 mg). Reaction started immediately and vigorous evolution of gas was observed. The mixture was stirred at 20° for 30 min. Standard workup as above yielded the product, which was purified by flash chromatography[15] (10% ether in hexane) to obtain pure **22** as a solid, m.p. 78–79° (25 mg, 32% from **21**): IR 2960 (s), 2940 (s), 2860 (m), 1745 (s), 1315 (m) and 1270 (s) cm^{-1}; NMR δ 1.85–2.72 (m, 12H), 1.65–1.75 (m, 1H), 0.873 (s, 9H, $C(CH_3)_3$), 0.079 (s, 3H, CH_3), 0.063 (s, 3H, CH_3); mass spectrum *m/z* 292.1907 (M^+, calc for $C_{17}H_{28}O_2Si$, 292.1858).

Tetracyclo[4.4.1.0^{3,11}.0^{9,11}]*undecan* - 4 - *one* (1α,3β,6α,9β) (**23**). Ketone ketal **15** (90 mg, 0.41 mmol) was reduced to the hydroxy ketal using $LiAlH_4$ (40 mg) in ether (10 ml). Workup yielded crude alcohol which was converted to its tosylate by reacting with *p*-toluenesulfonyl chloride in pyridine in the usual fashion. This crude tosylate was further reduced with $LiAlH_4$ in refluxing THF and treated with *p*-toluenesulfonic acid as described earlier for preparing the corresponding methyl derivative.[1] Flash chromatography[15] (10% ether in pentane) yielded pure **23** (35 mg, 53%): IR 2950 (s), 2920 (s), 2840 (w), 1740 (s), 1440 (w) and 1245 (m) cm^{-1}; NMR δ 2.80 (dd, J = 4.88, 8.23 Hz, 1H), 2.40–2.58 (m, 3H), 2.06–2.47 (m, 8H), 0.70–1.37 (m, 2H); mass spectrum *m/z* 162.1046 (M^+, calc for $C_{11}H_{14}O$, 162.1045).

Tetracyclo[4.4.1.0^{3,11}.0^{9,11}]*undecane* (1α,3β,6α,9β) (**6**). This hydrocarbon was prepared in three steps from the ketone **23** (25 mg, 0.15 mmol) following the earlier described procedure[1] (9 mg, 40% overall yield): IR ($CDCl_3$) 2940 (s), 2915 (s), 2850 (m), 1450 (m) cm^{-1}; NMR δ 2.16–2.37 (m, 7H), 2.13 (dd, J = 3.05, 6.5 Hz, 1H), 2.09 (dd, J = 3.05, 6.5 Hz, 1H), 1.87–2.00 (m, 3H), 1.56–1.67 (m, 2H), 0.88–1.01 (m, 2H); ^{13}C-NMR 66.482, 49.547, 40.525, 40.115, 35.405, 33.621, 32.295; mass spectrum *m/z* 148.1242 (M^+, calc for $C_{11}H_{16}$, 148.1252).

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