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Carbon-Carbon Bond Cleavage via Carbon Centred Radical in Strained Tricyclo[5.2.1.$0^{2,6}$]decenes. A Facile Route to Bridged Eight Membered Rings Related to Taxanes

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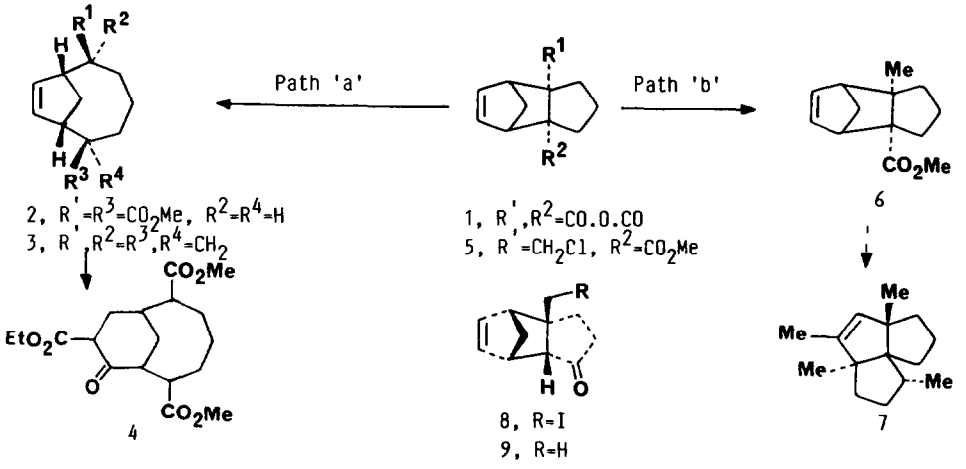
Abstract : Tributyltin hydride reaction of the tricyclo[5.2.1.$0^{2,6}$]decenes **5**, **16** and **23** bearing a halo-carbonyl moiety has been shown to involve C-C bond cleavage as the major reaction path leading to bridged eight-membered rings **12**, **17** and **24**. In contrast the halo-carbonyl derivatives **8**, **33** and **36** undergo only reduction of the carbon-halogen bond. The ring cleavage observed has been attributed to the release of strain arising from nonbonded interaction as well as strain associated with norbornene.

Tricyclo[5.2.1.$0^{2,6}$]decenes are valuable intermediates[1] in the synthesis of natural products. Recently we have reported[2] the transformations of **1** to the bicyclo[5.2.1]decenes **2** and **3** through cleavage of the C_2-C_6 bond (Scheme-1). The latter have further been transformed[2] to bicyclo[5.3.1]undecane **4** present in taxanes. In order to increase the synthetic potential of tricyclo[5.2.1.$0^{2,6}$]decenes, we envisaged that these could also serve as intermediates to angular triquinanes. For example, the anhydride **1** could be an intermediate to isocomene **7**[3] through the ester **6** provided **1** could be transformed efficiently to **6**. Recent investigation by Sarkar et al.[4] demonstrated that the tricyclo[5.2.1.$0^{2,6}$]decene **9**, structurally analogous to **6**,



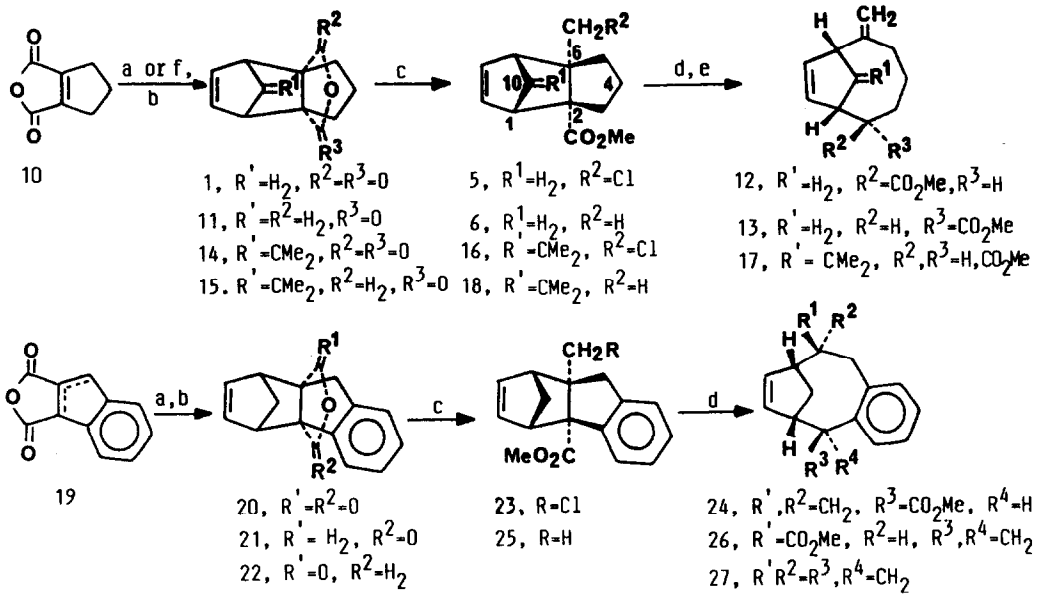
Scheme-1

could be prepared through reduction of the iodo-ketone 8 with tributyltin hydride (TBTH). Based on this observation we anticipated that transformation of the chloro-ester 5, derivable in principle from the anhydride 1, should proceed cleanly to afford the desired ester 6. We now report[5] that reaction of the chloro-esters embodied in tricyclo[5.2.1.$0^{2,6}$]decenes with TBTH may be made to follow either a C_2-C_6 bond fragmentation path (path 'a') or a reduction path (path 'b') by altering the ring strain through structural modification. Such C-C bond fragmentation[6] results in an easy access to bridged eight-membered rings present in taxanes,[7] a family of highly biologically active diterpenes.

Results and Discussions

Tricyclo[5.2.1.$0^{2,6}$]decenes bearing a syn-1,4-chloro ester moiety required for this investigation was prepared according to the sequence portrayed in Scheme-2. A Diels-Alder cycloaddition between cyclopentadiene with appropriate dienophiles was sought for rapid access to the tricyclic skeletons. For example, reaction[8] of the anhydride 10 with cyclopentadiene afforded the adduct 1 in excellent yield. For transformation of the anhydride moiety to the chloro ester moiety, the adduct 1 was first reduced[9] with $NaBH_4$ in THF to afford the lactone 11 in 81% yield. Refluxing[10] a methanolic solution of the lactone 11 with $SOCl_2$ afforded the chloro-ester 5. When a benzene solution of the chloro-ester 5 was refluxed with 1.6 equivalent of TBTH in presence of AIBN, the diene 12 with a trace of the reduced product 6 was obtained. The pure diene 12 was isolated in 87% yield after chromatography of this mixture. That the C_2-C_6 bond in the chloro-ester 5 had been cleaved to produce 12 was indicated by the presence of a two proton multiplet at δ 4.62 assigned to C_6-methylene protons in addition to a two proton olefinic singlet at δ 5.76 (8,9-protons) in ^{1}H NMR spectrum of the product 12. This structural assignment was corroborated by the ability of 12 to undergo epimerisation to form 13 on treatment with NaOMe-MeOH. The stereochemical assignment of the ring cleaved product 12 was made by comparison of ^{1}H NMR spectroscopic data for the C_9-proton of 12 with that of the epimerised product 13. Of the two diastereoisomers, the C_9-proton in the isomer with the CO_2Me and the olefinic bridge syn to each other is expected to be deshielded. Thus, the isomer with the C_9-proton appearing at δ 5.96 was assigned the structure 13 while the isomer with the C_9-proton appearing at δ 5.76 was assigned the structure 12. The formation of a trace amount of the reduced product 6 was indicated by the presence of a Me singlet at δ 0.93 and a CO_2Me (s) at 3.53 in ^{1}H NMR spectrum of the product mixture.

Ring cleavage via carbon centred radical has so far been successful[11] only in strained rings like cyclopropanes and cyclobutanes. Thus, the ring cleavage observed during TBTH reaction of the chloro-ester 5 appears to be the result of release of the strain associated with norbornene. However, the contrasting behaviour of the structurally analogous iodo-ketone 8 to undergo reduction instead of ring cleavage

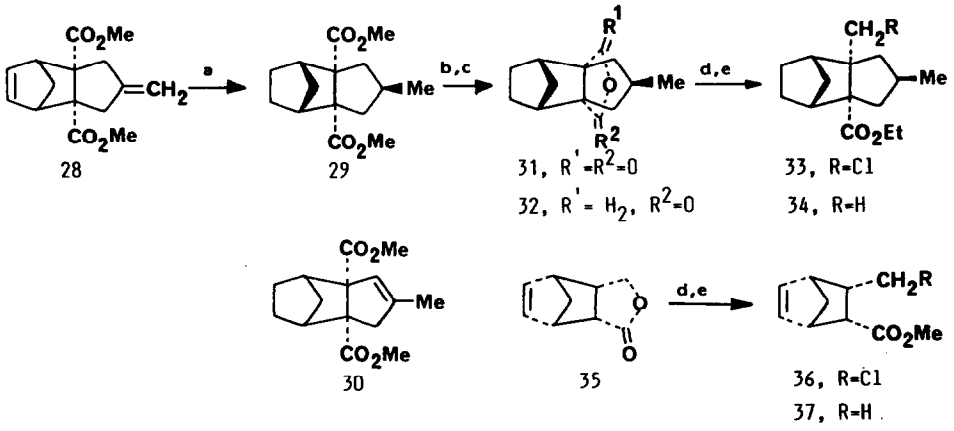


Scheme 2. Reagents : a, cyclopentadiene, THF, $AlCl_3$, 0°C. b, $NaBH_4$, THF, 0°C to rt. c, $SOCl_2$, MeOH, reflux. d, TBTH, AIBN, C_6H_6, reflux. e, NaOMe, MeOH, reflux. f, 6,6-dimethyl fulvene, xylene, reflux.

suggests that it is possibly the strain arising through nonbonded interaction between hydrogens at C_{10} and those at C_3, C_4 and C_5, which makes the chloro-ester 5 undergo facile C-C bond cleavage when CH_2 is generated on reaction with TBTH. To determine the importance of nonbonded interaction on the reaction course we first chose the chloro-ester **16** in which nonbonded interaction is expected to be less due to lack of C_{10}-hydrogens. The chloro-ester **16** was prepared from the lactone **15**. The lactone **15** was obtained from $NaBH_4$ reduction of the anhydride **14**[12] prepared from Diels-Alder reaction of the anhydride **10** with 6,6-dimethyl fulvene. Reaction of the chloro-ester **16** with TBTH afforded in 65% yield an inseparable mixture of the ring cleaved product **17** and the reduced product **18** in ca. 4:1 ratio (from ^1H NMR). The shielding of the 8,9-protons ($\Delta\delta$ 0.32-0.70) in going from **16** to **17** comparable to that ($\Delta\delta$ 0.50) observed for 8,9-protons in the transformation of **5** to **12** and the presence of a two proton multiplet at δ 4.56-4.88 (C_6 methylene protons) clearly dictated that C_2-C_6 bond in **16** had been cleaved to produce the diene **17**. Further the presence of two CO_2Me singlets at δ 3.66 and 3.68 showed that **17** was obtained as a diastereoisomeric mixture. The formation of the reduced product **18** was indicated from ^1H NMR [δ 1.26 (s, Me), 3.72 (s, CO_2Me) and 6.38 (m, 8,9 protons)] of the mixture of **17** and **18**.

We next chose the chloro-ester 23 in which nonbonded interaction has been reduced by removing the hydrogens at C_3 and C_4. The synthesis of the chloro-ester 23 started with reaction[13] of the anhydride 19 with cyclopentadiene to form the endo-adduct 20. Reduction of the anhydride 20 with $NaBH_4$ afforded a mixture of the lactones 21 and 22 in ca. 4:1 ratio as evidenced from integration of the lactone CH_2 singlets at δ 4.20 and 4.30 respectively. The major lactone was isolated through crystallisation in 51% yield. Of the two regioisomers, the isomer with lactone CH_2 proximal to the aromatic ring experiences a greater degree of diamagnetic anisotropy of the aromatic ring and is thus expected to be deshielded over the isomer with the lactone CH_2 distal to the aromatic ring. Thus, the major isomer with lactone CH_2 appearing at 4.20 was assigned the structure 21. This assignment was confirmed by its subsequent transformation to the diene 24. The lactone 21 was then transformed to the chloro-ester 23 in the usual way. Reaction of the chloro-ester 23 with TBTH gave as expected a mixture of the ring cleaved product 24 and the reduced product 25 with slight preponderance of the latter. From this mixture, the products 24 and 25 were isolated in 25% and 31% yields respectively. The assignment of structure to the ring cleaved product is based on shielding of the C_8-proton ($\Delta\delta$ 1.15) and C_9-proton (δ0.73) in going from 23 to 24 and the appearance of a two proton doublet of doublet at 4.84. The stereochemical assignment is based on analogy to the formation of the diene 12 from the chloro-ester 5. That the structure of the ring cleaved product is 24 and not the regioisomer 26 which would arise from the lactone 22 was established from comparison of the chemical shift of its methylene protons (δ 4.84) with those for the triene 27[14] where both aromatic conjugated methylene (δ 5.05 and 5.15) and non-conjugated methylene protons (δ 4.70 and 4.80) were present. With the establishement of the structure of the ring cleaved product as 24, the structure of the starting lactone was established as 21.

To determine whether strain associated with norbornene or the strain arising from nonbonding interaction is sufficient for the observed ring cleavage, the chloro-ester 33 and 36 were prepared as follows (Scheme-3). Hydrogenation of the diester 28 gave the saturated diester 29 with ca. 15-20% of the unsaturated diester 30. Addition of hydrogen from the side[15] of the carbomethoxy groups ensured a syn oreientation of the C_4-Me group with one carbon bridge in the diester 29. Hydrolysis of this mixture of diesters to the corresponding acids and their subsequent reaction with CH_3COCl gave a mixture of the anhydrides from which the anhydride 31 was isolated in 45% yield through fractional crystallisation. The anhydride 31 was then reduced with $NaBH_4$ to give the lactone 32 which gave the chloro-ester 33 with $SOCl_2$-EtOH. The chloro-ester 36 was obtained from the known lactone 35. In the chloro-ester 33 nonbonded interaction involving C_{10}-H and C_4-Me is slightly more compared to that in 5 while strain[16] due to norbornene structure has been reduced significantly. On the



Scheme 3, Reagents : a, H_2, EtOAc, 10% Pd-C. b, i) KOH, H_2O, $(CH_2OH)_2$, reflux; ii) HCl, iii) CH_3COCl, reflux. c, $NaBH_4$, THF. d, $SOCl_2$, EtOH or MeOH, reflux. e, TBTH, AIBN, C_6H_6, reflux.

other hand, the chloro-ester **36** does not have nonbonded interaction like the one present in **5**. Reaction of both these chloro-esters **33** and **36** with TBTH gave exclusively the reduced products **34** and **37** in 83% and 79% yields respectively demonstrating that the strain arising from nonbonding interaction as well as the strain associated with norbornene is essential for C_2-C_6 bond cleavage in tricyclo [5.2.1.$0^{2,6}$]decenes.

The investigation has developed a facile route for the synthesis of bi- and tricyclic network possessing bridged eight-membered rings with suitable functional groups for further elaboration. This route may be useful for entry into the family of taxanes.

EXPERIMENTAL SECTION

The compounds described are all racemates. Melting points are uncorrected and were taken in open capillary in sulphuric acid bath. Petroleum refers to the fraction of b.p. 60-80°C. Drying of organic layers was done with sodium sulphate. Column chromatography was done with silica gel (60-120 mesh). ^{1}H NMR spectra were determined at 60 MHz on Varian EM-360L, at 100 MHZ on a Jeol FX-100 and at 200 MHz on a Varian XL-200 spectrometers. Peak positions are indicated in ppm downfield from internal TMS in units. NMR spectra were taken in carbon tetrachloride for EM-360L and in $CDCl_3$ for FX-100 and XL-200 spectrometers. IR spectra were recorded on a Perkin Elmer 298 infrared spectrometer and were taken in chloroform.

cis-endo-6-(Hydroxymethyl)tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2-carboxylic Acid Lactone (11). A solution of the anhydride **1** (2 g, 10 mmol) in THF (15ml) was added dropwise to a

magnetically stirred ice cooled suspension of $NaBH_4$ (560mg, 15mmol) in THF (10ml). After complete addition, the cooling bath was removed and stirring was continued for additional 1.5h. The reaction mixture was again cooled in ice and to it 6N HCl was added dropwise to make it acidic. THF was then removed under reduced pressure. The organic material was extracted with ether (3x30ml). The ether extract was washed with aqueous $NaHCO_3$ (5%), brine and dried. Solvent was removed and the residual mass was chromatographed with ether-petroleum (1:9) as eluent to afford the lactone **11** (1.5g, 81%), m.p. 179°C; ν_{max} 1750 cm^{-1}; δ (200MHz) 1.44-2.44 (8H, m), 2.86 (1H, narrow t), 3.0 (1H, narrow t), 3.80 (H_A, AB_q, J=8 Hz), 3.97 (H_B, AB_q, J=8 Hz) and 6.4 (2H, m). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found : C, 75.73; H, 7.68.

10-Isopropylidene-cis-endo-6-(Hydroxymethyl)tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2-carboxylic Acid Lactone (15). Following the above procedure the anhydride **14** (0.98g, 4mmol) was reduced with $NaBH_4$ (0.25g, 12mmol) to afford the lactone **15** (0.71g, 85%), m.p. 118-120°C; ν_{max} 1750 cm^{-1}; δ (60MHz), 1.03-2.43 (12H, m, merged with a br s at 1.63 for Me), 3.20 (1H, br s), 3.33 (1H, br s), 3.75 (H_A, AB_q, J=10 Hz), 3.91 (H_B, AB_q, J=10 Hz) and 6.38 (2H, t, J= 2 Hz). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found : C, 77.88; H, 8.16.

cis-endo-6-(Hydroxymethyl)-3,4-Benzotricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2-carboxylic Acid Lactone (21). Following the above procedure the anhydride **20** (2.50g, 10mmol) was reduced with $NaBH_4$ (530 mg, 14 mmol) to afford a mixture of the lactones **21** and **22** (1.90 g, 80%) m.p. 105°C in ca. 4:1 ratio. Fractional crystallisation from ether-petroleum afforded the major lactone **21** (1.2 g, 51%); m.p. 120°C; ν_{max} 1755, 1600 cm^{-1}; δ (100 MHz), 1.63 (2H, q, J=9 Hz), 3.0 (1H, br s), 3.07 (H_A, AB_q, J=16 Hz), 3.24 (H_B, AB_q, J=16 Hz), 3.28 (1H, br s), 4.20 (2H, s), 6.44 (2H, m), 7.26 (3H, m) and 7.6 (1H, m). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92; Found : C, 80.28; H, 5.94.

4-exo-Methyl tricyclo[5.2.1.$0^{2,6}$]decane-endo-2,6-dicarboxylic anhydride (31). A solution of the diester **28** (3.9 g, 15 mmol) in ethylacetate (50ml) was stirred under H_2 atmosphere in presence of 10% Pd-C (250mg) for 3h. The catalyst was filtered off. The solvent was removed to afford 3.9g (98%) of an inseparable mixture of the saturated diester **29**; δ (60 MHz) (from ^1H NMR of the mxiture) 1.0 (3H, d, J=6 Hz), 1.16-2.63 (13H, m), 3.63 (6H, s) and the unsaturated diester **30** in ca. 80:20 ratio.

This mixture of the diesters (3.5g, 13 mmol) was added to a solution prepared from KOH (15g, 0.3 mol), H_2O (10ml) and ethyleneglycol (60ml) and refluxed for 6h. After cooling to room temperature, the reaction mixture was diluted with H_2O (150ml) and extracted with ethyl acetate to remove unhydrolysed material. The aqueous part was then acidified with 6N HCl, and extracted with ethyl acetate (3x70ml). The

organic extract was washed with brine, dried and concentrated to afford a viscous mass (2.9gm).

The viscous mass was then refluxed with acetyl chloride (30ml) for 8h. Excess acetyl chloride was removed under vacuum and the residual mass was rapidly chromatographed through SiO_2 using ethyl acetate–petroleum (1:9) as eluent to provide a white solid (2.4g), m.p. 70-71°C. Repeated crystallisation from ether–petroleum afforded the anhydride 31 (1.3g, 45%), m.p. 79°C; ν_{max} 1850, 1775 cm^{-1}; δ (60 MHz), 0.95 (3H, d, J=7 Hz), 1.20-2.63 (13H, m). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89 : H, 7.32. Found : C, 70.64; H, 7.58.

4-exo-Methyl-cis-endo-6-(Hydroxymethyl)tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2-carboxylic Acid Lactone (32). Following the procedure described for preparation of the lactone 11 the anhydride 31 (1.1g, 5mmol) was reduced to the lactone 32 (0.9g, 87%), m.p. 105°C, ν_{max} 1750 cm^{-1}; δ (60 MHz), 1.00 (3H, d, J=7 Hz), 1.21-2.75 (13H, m), 3.87 (H_A, AB_q, J=11 Hz) and 4.30 (H_B, AB_q, J=11 Hz). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80 Found : C, 75.45; H, 8.65.

Methyl-cis-endo-6-(Chloromethyl)tricyclo[5.2.1.$0^{2,6}$]decane-2-carboxylate (5). To a refluxing solution prepared by dropwise addition of freshly distilled $SOCl_2$ (2ml, 25 mmol) to ice cold anhydrous MeOH (7ml) was added a solution of the lactone 11 (950mg, 5 mmol) in MeOH (3ml). Refluxing was continued for 1h. The reaction mixturte was cooled to room temperature and a second aliquot of the above solution of $SOCl_2$ (2ml) in MeOH (7ml) was added to it. The resulting solution was refluxed for 1.5h. Most of MeOH was then removed under vacuum and the residual liquid was poured on to ice. The organic material in it was extracted with ether (4x20 ml). The ether extract was washed with aqueous $NaHCO_3$ (5%), brine, dried and concentrated and the residual liquid on column chromatography[ether–petroleum (1:19)] to afford the chloro-ester 5 (0.48g, 63% based on consumed lactone) as a liquid; ν_{max} 1725 cm^{-1}; δ (60 MHz), 1.13-2.46 (8H, m), 2.73-3.20 (2H, m), 3.50-3.86 (5H, m, merged with a s at 3.63) and 6.26 (2H, m) and the starting lactone 11 (0.35g). Attempted preparation of analytical samples of the chloro-esters led rapid decomposition.

Methyl-10 -isopropylidene-cis-endo-6(chloromethyl)tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2-Carboxylate (16). The lactone 15 (500 mg, 2.2 mmol) on reaction with $SOCl_2$ in MeOH afforded the chloro-ester 16 (150 mg, 60% based on consumed lactone) as a liquid; ν_{max} 1725 cm^{-1}; δ (60 MHz), 1.20-2.33 (12H, m, merged with a singlet at 1.66 for vinylic Me), 3.26 (2H, t, J= 2 Hz), 3.60 (3H, s), 3.63 (2H, s) and 6.36 (2H, br s) and the starting lactone 15 (300 mg).

Methyl-cis-endo-6-(chloromethyl)-3,4-Benzotricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2-carboxylate (23). The lactone 21 (950 mg, 5 mmol) on reaction with $SOCl_2$ in MeOH under the above condition gave the chloro-ester 23 (0.7 g, 67% based on consumed lactone) as a liquid; ν_{max} 1730 cm^{-1}; δ (60 MHz) 1.28 (2H, m), 2.73-4.08 (9H, m, merged with a s at 3.60), 6.35 (2H, m) and 6.9-7.28 (4H, m) and the starting lactone 23 (0.3 g).

Ethyl-4-exo-methyl-cis-endo-6-(chloromethyl)tricyclo[5.2.1.$0^{2,6}$]decane-2-carboxylate (33). The lactone 32 (0.5 g, 2.5 mmol) on reaction with $SOCl_2$ in ethanol under the above condition gave the chloro-ester 33 (0.25 g, 61% based on consumed lactone) as a liquid; ν_{max} 1725 cm^{-1}; δ (60 MHz) 1.06 (3H, t, J = 7 Hz), 1.16-2.5 (16H, m, merged with a d at 1.32, J = 7 Hz), 3.95 (2H, s) and 4.07 (2H, q, 7 Hz) and the starting lactone 32 (0.3 g).

Methyl-cis-endo-3-(chloromethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (36). The lactone 35 (0.6 g, 4 mmol) on reaction with $SOCl_2$ in MeOH afforded the chloro-ester 36 (0.28 g, 61%, based on consumed lactone) as a liquid; ν_{max} 1730 cm^{-1}; δ (60 MHz) 1.37 (H_A, AB_q, J = 8 Hz), 1.54 (H_B, AB_q, J = 8 Hz), 2.5-3.36 (4H, m), 3.46-3.83 (5H, m, merged with a sharp singlet at 3.60) and 6.28 (2H, m) and the starting lactone 35 (0.3 g).

Reaction of the chloro-esters with tributyltinhydride : exo-Methyl-6-methylene-bicyclo[5.2.1]dec-8-ene-2-carboxylate (12). A solution of the chloro-ester 5 (0.24 g, 1 mmol) in benzene (40 ml) was refluxed with TBTH (0.58 g, 2 mmol) and AIBN (catalytic amount) for 6 h, under N_2 atomsphere. Benzene was then removed under reduced pressure. To the residue were added ether (30 ml) and saturated aqueous KF solution (20 ml). The resulting mixture was vigorously stirred for 20 h. The precipitated solid was filtered off and the ether layer was separated. The aqueous layer was extracted with ether (3 x 30 ml). The combined ether extract was dried and concentrated to afford a liquid which was found to be a mixture of two components in ca. 90-95 : 10-5 ratio (from integration of the CO_2Me singlets in ^1H NMR). The mixture after column chromatography [ether-petroleum (1:19)] afforded the diene 12 (180 mg, 87%) as a liquid; ν_{max} 1730, 1630 cm^{-1}; δ (100 MHz) 1.12-2.60 (8H, m), 2.78 (1H, q, J = 4 Hz), 3.40 (2H, m), 3.68 (3H, s), 4.62 (2H, m) and 5.76 (2H, s). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found : C, 75.83; H, 8.58%

Methyl-10-isopropylidene-6-Methylenebicyclo[5.2.1]dec-8-ene-2-carboxylate (17). Following the above procedure, reaction of the chloro-ester 16 (70 mg, 0.25 mmol) in benzene with TBTH (140 mg, 0.5 mmol) and AIBN (cat) afforded a chromatographically inseparable mixture (40 mg, 65%) comprising mainly a diastereoisomeric mixture 17; ν_{max} 1730 cm^{-1}; δ (200 MHz) (from the mixture) 1.46-2.46 (12H, m), 2.56 (1H, m), 2.76-3.06 (1H, m), 3.66, 3.68 (3H, boths), 3.92, 3.98 (2H, both br s), 4.56-4.88 (2H, m) and 5.66-6.04 (2H, m) and the reduced product 18; δ (200 MHz) 1.26 (Me, s),

3.72 (CO_2Me, s); m/z (%) (of the mixture of 17 and 18), 246 (M^+, 15), 231(33), 187(22), 186(22), 171(17), 159(12), 145(28), 131(23), 117(12), 106(100), 91(48), 79(18) and 55(12).

Methyl-cis-endo-6-Methyl-3,4-Benzotricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2-carboxylate (25) and exo-Methyl-6-Methylene-3,4-benzobicyclo[5.2.1]dec-8-ene-2-carboxylate (24). Following the above procedure reaction of the chloro-ester 23 (0.140 g, 0.5 mmol) in benzene with TBTH (0.29 g, 1 mmol) and AIBN (cat) afforded a liquid which was found to be a mixture of two components in ca. 1:1 ratio (from integration of the CO_2Me singlets in ^1H NMR), difficult to separate by column chromatography. This mixture (80 mg, 0.32 mmol) was treated with 2% methanolic NaOH (4 ml) at r.t. for 7 h. After removing MeOH, the residue was dissolved in H_2O (5 ml) and extracted with ether. Removal of ether after drying afforded 25 (25 mg, 31%) as a liquid; ν_{max} 1725 cm^{-1}; δ(60 MHz) 1.15 (3H, s), 1.05-2.26 (2H, m), 2.45 (1H, br s), 3.0 (3H, br s), 3.53 (3H, s), 6.10 (1H, dd, J = 2.5 and 6 Hz), 6.41 (1H, dd, J = 2.5 and 6 Hz) and 7.10 (4H, s); m/z (%), 254 (M^+, 8), 195(8), 188(100), 165(14), 156(17), 181(77), 115(11), 77(3) and 66(4).

The basic aqueous part left after ether extraction was acidified with cold 6N HCl and extracted with ether. The ether extract after washing with brine and drying was concentrated. The semi - solid mass obtained was treated with ethereal diazomethane. The resulting mass was purified by preparative TLC [ether-petroleum (1:19)] to afford 24 (20 mg, 25%) as a colourless liquid; ν_{max} 1735, 1630 cm^{-1}; δ (100 MHz), 1.12-2.20 (2H, m), 3.0-3.52 (3H, m), 3.52-4.12 (2H, m), 3.78 (3H, s), 4.84 (2H, dd, J = 16 and 2 Hz), 5.20 (1H, br s), 5.62 (1H, br s) and 6.60-7.68 (4H, m), m/z (%), 254(32), 195(86), 188(38), 179(73), 165(54), 153(17), 141(17), 129(100), 115(22), 102(8), 91(16), 77(10), 67(5).

Ethyl-4-exo-Methyl-cis-endo-6-Methyltricyclo[5.2.1,$0^{2,6}$]decane-2-carboxylate (34). Reaction of the chloro-ester 33 (220 mg, 0.8 mmol) in benzene with TBTH (400 mg, 1.25 mmol) and AIBN (cat) afforded 34 (160 mg, 83%); b.p. 110°C (0.1 mm of Hg) bath. temp.; ν_{max} 1725 cm^{-1}; δ(60 MHz) 1.06 (3H, t, J = 7Hz), 1.26 (3H, s), 1.32 (3H, d, J = 7 Hz), 1.16-2.46 (13H, m) and 4.05 (2H, q, J = 7 Hz). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found : C, 76.47; H, 10.34.

Methyl-cis-endo-3-Methylbicyclo[2.2.1]hept-5-ene-2-carboxylate ((37). Reaction of the chloro-ester 36 (200 mg, 1 mmol) in benzene with TBTH (580 mg, 2 mmol) and AIBN (cat) afforded 37 (130 mg, 79%) as a colourless liquid; ν_{max} 1730 cm^{-1}; δ (60 MHz) 0.77 (3H, d, J = 7 Hz), 1.13-1.70 (2H, m), 2.13-3.23 (4H, m), 3.56 (3H, s), 6.06 (1H, dd, J = 2 and 6 Hz) and 6.38 (1H, dd, J = 2 and 6 Hz). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.06; H, 8.49. Found : C, 72.06; H, 8.31%

endo-Methyl-6-Methylenebicyclo[5.2.1]dec-8-ene-2-carboxylate (13). The ester 12 (100 mg, 0.5 mmol) was treated with 10% NaOMe in MeOH (5 ml) at rt for 16 h. After removing MeOH, the residue on acidification (6N HCl) was worked up with ether to

afford the corresponding acid of the epimerised ester 13 (60 mg, 65%), m.p. 91°C; δ (100 MHz) (of methylester) 1.12-2.92 (9H, m), 3.14 (1H, d, J = 10 Hz), 3.46 (1H, d, J= 10Hz), 3.67 (3H, s), 4.66 (m, 2H), 5.80 (1H, m) and 5.96 (1H, m). Anal. Calcd for $C_{12}H_{16}O_2$ (for acid): C, 74.97; H, 8.39. Found : C, 74.76; H, 8.37.

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