Pergamon

Tetrahedron Vol. 51, No. 9, pp. 2689-2698, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01115-X

A Study of the Scope of the Bismethoxycarbonylation of Norbornene Systems

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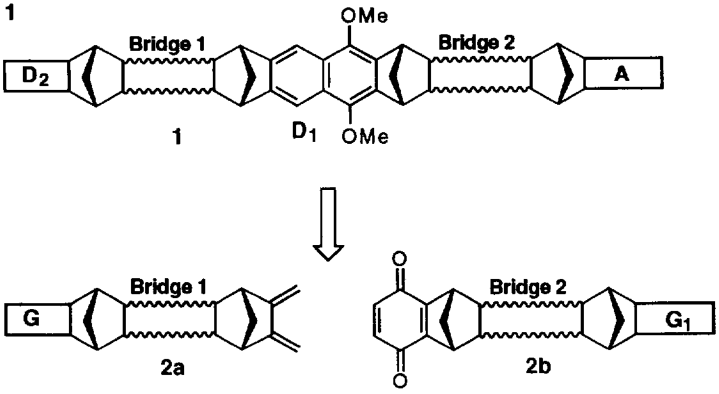
Abstract: Stille–Vogel bismethoxycarbonylation of a series of norbornene–type monoenes, **9** – **15**, and nonconjugated dienes, **16** and **17** was studied. Three significant findings are: (1) Bismethoxycarbonylation reactions may be carried out using CO at atmospheric pressure. (2) The sensitive *p*–methoxybenzyl protecting group withstands the Stille–Vogel reaction conditions. (3) The bismethoxycarbonylation reaction may be carried out using THF as a cosolvent, although reaction times are longer.

INTRODUCTION

There is intense interest in the rational design of molecules and supramolecular assemblies that are capable of achieving photoinduced charge separation over large distances and with efficiencies comparable to that found in nature, *e.g.* the photosynthetic reaction centre.[1a,b] Such molecular photovoltaic systems would have widespread applications in molecular electronics devices.[1c] A major approach towards achieving this goal is the construction of rigid polychromophoric systems in which the chromophores (redox active centres) are connected in serial *via* a series of bridges.[2] For example, a trichromophoric system could be D_2—D_1—A, in which the primary donor group (D_1) is connected to the secondary donor, D_2, by a bridge and to the acceptor, A, by a different bridge. In such systems, light–induced intramolecular electron transfer takes place *via* a cascade of redox processes to give the final charge separated state, $^+D_2$—D_1—A^-.

Our recent efforts in this area are focused on the general triad, **1** in which the primary donor is a dimethoxynaphthalene group which is connected to the other chromophores by a series of polynorbornyl-type bridges.[3,4] These triads have the advantage of synthetic convergency in that both bridge units, **2a** and **2b** can be synthesized separately and then joined to form the naphthalene ring, through Diels–Alder methodology (Scheme 1). Synthesis of the bridge unit **2a**, which contains the bismethylene group may be approached in two ways, as indicated in Scheme 2. In one approach (Scheme 2a), one begins with a suitably protected 5,6–bishydroxymethylnorbornene, **3**, onto which the polynorbornane-bicyclo[2.2.0]hexane bridge is constructed in the usual way[5] (using a series of tandem Mitsudo–Smith reactions [6,7]), to give **4**. The progenitor of the chromophore, G, is then fused to the norbornene double bond of **4** to give **5** . The protected bishydroxymethyl groups can then be converted into the bismethylene system, **2a**, through the sequence of deprotection, bistosylation, and finally, bisdehydrotosylation. This strategy has been successfully employed in the synthesis of the first trichromophoric system of the type **1**.[4]

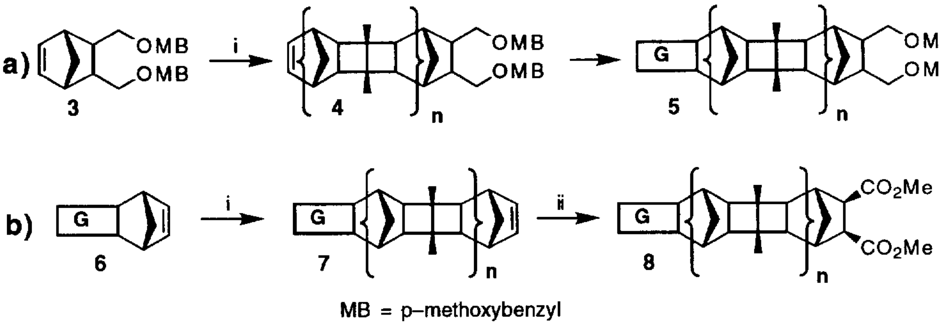
Scheme 1



However, this approach suffers from the constraint that the chromophore progenitor, G, must be readily attached to the double bond of the terminal norbornene group of **4**. Since this is not the case for many groups, G, the alternative method, shown in Scheme 2b has been devised.

In this approach, one begins with **6**, in which the progenitor chromophore, G, is already fused to the norbornene system. The availablity of compounds of the type **6** is not normally a problem since they should be obtainable from Diels–Alder reactions between cyclopentadiene and appropriate dienophiles. Application of the bridge building technology to **6** then gives **7**. The success of this approach depends on the ability to effect bismethylenation of the double bond in **7**, to give **2a**. This might be achievable through bismethoxycarbonylation of the double bond of **7** to give **8**.

Scheme 2

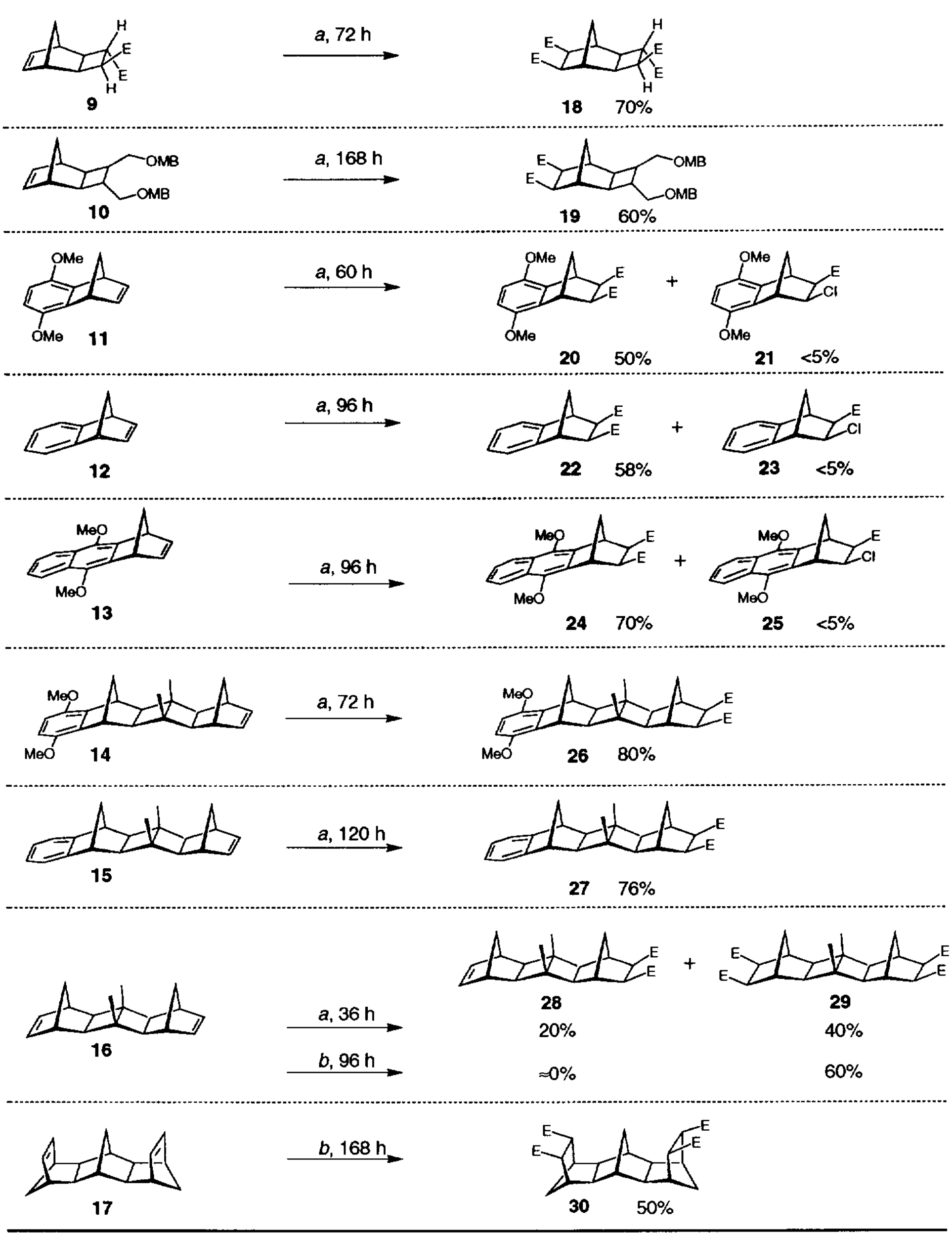


MB = p–methoxybenzyl

i Mitsudo–Smith tandem reaction[5–7] ii Pd/C, $CuCl_2$, MeOH, CO 1atm

Stille *et al.*have reported palladium catalysed bismethoxycarbonylation of a number of acyclic and cyclic olefins with carbon monoxide and methanol.[8] This method originally used catalytic amounts of $PdCl_2$ and a stoichiometric quantity of $CuCl_2$, but Vogel *et al.* have improved the process by replacing $PdCl_2$ with 10% Pd/C.[9] Several useful bismethoxycarbonylations of simple bicyclo[2.2.1]heptene systems have been reported, including norbornene,[8a] benzonorbornadiene,[10] and the anhydrides of norbornene[11] and 7–oxabicyclo[2.2.1]heptene.[9]

Chart E = CO_2Me; MB = *p*-methoxybenzyl



a: 4 equivalents each of $CuCl_2$ and NaOAc. *b*: 8 equivalents each of $CuCl_2$ and NaOAc

Although highly promising, the Stille–Vogel bismethoxycarbonylation procedure has not been applied to either molecules bearing sensitive protecting groups (such as *p*–methoxybenzyl), or to large polycyclic molecules that may experience solubility problems under the usual Stille–Vogel conditions. Herein, we address these issues by studying bismethoxycarbonylation of the series of substrates, **9** – **17**. Of particular interest in the context of our work on the synthesis of polychromophoric systems are **10** (it has two *p*–methoxybenzyl groups), **14** and **15** (these have very poor solubility in methanol), and **16** and **17** (hopefully, tetrakismethoxycarbonylation may occur in these dienes).

RESULTS AND DISCUSSION

The bismethoxycarbonylation reactions were carried out in methanol (with THF as cosolvent in some cases), under 1 atm CO (balloon), using a catalytic amount of 5% Pd/C (*ca* 100 mg per 3 mmol of olefin), and 4 equivalents each of $CuCl_2$ and NaOAc per double bond. The presence of a base such as NaOAc was found to be essential since, in its absence only low yields of a complex mixture of products were obtained.[12] The results are presented in the Chart. Yields refer to purified products.

In the past, bismethoxycarbonylation reactions have generally been carried out under 2–4 atm pressure of CO. However, Yamada *et al.* recently reported that bismethoxycarbonylation of the *endo*–anhydride of norbornene occurs in high yield under 1 atm CO.[11] For convenience, we also carried out our reactions at atmospheric pressure and our results show that bismethoxycarbonylations of a variety of substrates proceed in reasonable yields under 1 atm pressure of CO. Indeed, our yield of **22** is identical to that reported by Atasoy *et al.*[10] who carried out the bismethoxycarbonylation of **13** at 4–5 atm pressure of CO.

As expected,[8–11] bismethoxycarbonylation of all substrates, **9** – **17** proceeded with *exo,exo* stereochemistry which was evident from the ^1H nmr spectra of the products (see experimental). The carbonylation of **11** – **13** gave, in addition to the bis–esters, small amounts of the *exo,exo*–β–chloro esters, **21**, **23**, and **25**, respectively. In general, however, carrying out the bismethoxycarbonylation reactions under fairly dilute conditions (*ca* 35 mM) gave little or no β–chloroester.

Importantly, the carbonylation reaction conditions did not affect the sensitive *p*–methoxybenzyl protecting groups in **10**; the *exo,exo*-bis–ester **19**, with the protecting groups intact, was isolated in acceptable yield (60%). Addition of THF as cosolvent in the reactions involving **10**, **14** – **18** (which have limited solubility in neat methanol) appears to have no adverse effect on product yields. In the case of **10**, the THF:methanol ratio was as high as 70:100 (by volume). However, the reaction is more sluggish in MeOH/THF solvent systems, requiring seven days to complete in the case of **10**.

Dienes **16** and **17** offer the possibility of controlled formation of either bismethoxycarbonylated or tetrakismethoxycarbonylated products. The results for **16** show that this aim was only partially successful. In the presence of four equivalents of $CuCl_2$/NaOAc per mole of **16** (*ie*, two equivalents per double bond), both bis– and tetrakismethyl esters were formed (all ester groups having *exo* stereochemistry) in a 1:2 ratio, respectively. Attempts to increase the relative amount of bis–ester in the product were unsuccessful. Reasonable yields of the tetrakismethoxycarbonylated products were obtained from **16** and **17** using eight equivalents of $CuCl_2$/NaOAc.

CONCLUSION

Our studies have demonstrated that the Stille–Vogel bismethoxycarbonylation of double bonds is a remarkably versatile and powerful reaction. Three important conclusions may be drawn from our work. Firstly, bismethoxycarbonylation reactions may be carried out using CO at atmospheric pressure with no adverse effect on product yield. Secondly, the sensitive *p*–methoxybenzyl protecting group withstands the Stille–Vogel reaction conditions. This augers well for many other protecting groups. Thirdly, the bismethoxycarbonylation reaction may be carried out using THF as a cosolvent. The product yields are good, although the reaction proceeds more slowly.

EXPERIMENTAL

Melting points were determined with a Mel-Temp (II) apparatus and are uncorrected. Microanalyses were performed by Dr H. P. Pham of the University of New South Wales.

^{1}H n.m.r. spectra were obtained on a Bruker AC300F (300 MHz) spectrometer. ^{1}H data is reported as follows: chemical shifts (δ) measured in parts per million (ppm) down field from TMS; proton count; multiplicity; observed coupling constant (J) in Hertz (Hz); proton assignment. Multiplicities are reported as singlet (s), broad singlet (bs), doublet (d), triplet (t) and multiplet (m).

^{13}C spectra were obtained on a Bruker AC300F (75.47 MHz) spectrometer. ^{13}C chemical shifts (δ) are reported in parts per million (ppm) down field from TMS and identifiable signals are given. Assignment was determined with the aid of 90° DEPT and 135° DEPT experiments.

Mass spectra were recorded on a VG Quattro mass spectrometer with a 70eV ionising voltage and an ion source temperature of 210°C. The ion peaks m/z are reported together with their intensities relative to the base peak as percentages.

Chromatography was performed using gravity columns packed with Merck silica gel 7734 60 (70 - 230 mesh).

Anhydrous methanol was distilled and stored over 4Å molecular sieves. Anhydrous tetrahydrofuran was distilled from sodium and benzophenone. N,N-Dimethylformamide was dried over $MgSO_4$, distilled under reduced pressure and stored over 4Å molecular sieves.

The following abbreviation is used: DMF - N,N-Dimethylformamide.

Tetramethyl-tricyclo[4.2.1.0.^{2,5}]nonane-3-endo,4-exo,7-exo,8-exo-tetracarboxylate, **18**. To a solution of the diester **9**[13] (1.0 g, 4.2 mmol), anhydrous copper (II) chloride (2.3 g, 16.9 mmol) and anhydrous sodium acetate (1.39 g, 16.9 mmol) in anhydrous methanol (75 cm^3) was added 5% Pd/C catalyst (Fluka, 0.10 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture stirred at room temperature for 72 h. Dichloromethane (100 cm^3) and H_2O (100 cm^3) were added to the mixture and the resulting suspension was filtered through a pad of Celite and the aqueous layer extracted with dichloromethane (2 x 50 cm^3). The combined organic extracts were washed with water (50 cm^3) and a saturated solution of sodium bicarbonate (3 x 50 cm^3) until the blue colour disappeared, then dried (Na_2SO_4) and solvent removed under reduced pressure to give a yellow oil which was purified by column chromatography (ethyl acetate / light petroleum; 1:1) to yield the tetraester **18** as a colourless oil (1.50 g, 70%), b.p. > 250°C, 1mm Hg. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74 (1H,d, $J_{9,9}$ 12.1 Hz, H9), 2.10 (1H, d, $J_{9,9}$ 12.1 Hz, H9), 2.41 (1H, m, H2), 2.50 (1H, m, H5), 2.54 (2H, d, J 1.8 Hz, H7 and H8), 2.57 (1H, s, H1 or H6), 2.62 (1H, s, H1 or H6), 3.06 (1H, dd, J 4.8 Hz, J 7.8 Hz, H3), 3.60 (3H, s, $OC\underline{H}_3$), 3.60 (3H, s, $OC\underline{H}_3$), 3.64 (1H, m, H4), 3.68 (3H, s, $OC\underline{H}_3$), 3.71 (3H, s, $OC\underline{H}_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 30.44 (CH_2), 39.88 (CH), 40.34 (CH), 40.94 (CH), 41.23 (CH), 41.93 (CH), 42.50 (CH), 48.47 (CH), 49.20 (CH), 51.78 (OCH_3 x 2), 51.93 (OCH_3), 52.15 (OCH_3), 171.89 (C=O), 172.70 (C=O), 172.77 (C=O), 174.01 (C=O). m/z 354 (M^+, 2), 323 (20), 295 (23), 145 (100).

3-endo,4-exo-Di(hydroxymethyl)-tricyclo[4.2.1.0.^{2,5}]non-7-ene **(10, OMB = OH)**. A solution of the diester **9**[13] (50 g, 210 mmol) in anhydrous tetrahydrofuran (250 cm^3) was added dropwise to an ice cold suspension of lithium aluminium hydride (12.5 g, 330 mmol) in anhydrous tetrahydrofuran (250 cm^3) under an argon atmosphere. The resulting mixture was warmed to room temperature and then refluxed for 16 h. The mixture was cooled in an ice bath and the reaction quenched by the dropwise addition of 1M K_2CO_3 (70 cm^3). The resulting mixture was refluxed for 10 min then filtered hot through a pad of Celite. The Celite was extracted with boiling diethyl ether (100 cm^3) and the combined organic extracts dried (Na_2SO_4). The solvent was removed under reduced pressure to yield a colourless solid which was recrystallised from chloroform to yield the diol **(10, OMB = OH)** (37 g, 98%), m.p. 116-118°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (1H, td, $J_{9,2}$ 1.3 Hz, $J_{9,9}$ 9.5 Hz, H9), 1.64-1.81 (2H, m, H9 and H2), 1.97 (1H, dd, J 8.73 Hz, J 7.41 Hz, H5), 2.26-2.37 (4H, m, H3, H4 and $O\underline{H}$ x2), 2.72 (2H, bs, H1 and H6), 3.45 - 3.76 (4H, m, $C\underline{H}_2OH$ x 2), 5.96 (2H, m, H7 and H8). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 35.79 (CH), 36.60 (CH), 39.74 (CH), 40.97 (CH), 41.13 (CH), 42.60 (CH_2), 43.68 (CH), 60.54 (CH_2), 66.71 (CH_2), 135.01 (CH), 136.52 (CH). m/z 180 (M^+, 3), 66 (100). Found C, 73.1; H, 9.0. $C_{11}H_{16}O_2$ requires C, 73.3; H, 9.0.

3-endo, 4-exo, Di[(p-methoxybenzyloxy)methyl]-tricyclo[4.2.1.0.^{2,5}]non-7-ene, **10**. To a solution of the diol **10 (OMB = OH)** (35 g, 0.19 mol) in DMF (230 cm^3) and monoglyme (115 cm^3) at 0°C under an argon atmosphere was added sodium iodide (20.99 g, 0.14 mol) and the resulting yellow solution stirred for 30 min. *p*-Methoxybenzyl chloride (73.80 g, 0.47 mol) was then added and the mixture stirred for 3 h. Sodium hydride (47 g, 55% oil dispersion, 1.08 mol) was washed with light petroleum and collected by filtration. The dried sodium hydride was then added to the cooled reaction mixture in portions and the mixture stirred for a further 16 h. The reaction was quenched by the dropwise addition of H_2O (100 cm^3) and the resulting mixture extracted with diethyl ether (5 x 150 cm^3). The combined organic extracts were washed with H_2O (2 x 150 cm^3) and a saturated solution of sodium bicarbonate (3 x 100 cm^3) then dried (Na_2SO_4) and the solvent removed under reduced pressure to yield the dibenzyloxy compound **10** as a colourless oil which solidified on standing (70.4 g, 92%), m.p. 42-44°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (1H, d, $J_{9,9}$ 9.2 Hz, H9), 1.57-1.78 (3H, m, H9, H2 and H5), 1.95 (1H, m, H3), 2.39 (1H, m, H4), 2.70 (1H, s, H1 or H6), 2.73 (1H, s, H1 or H6), 3.39-3.58 (4H, m, $C\underline{H}_2OCH_2Ar$ x 2), 3.81 (6H, s, $OC\underline{H}_3$ x 2), 4.43 (4H, d, *J* 5.3 Hz, $OC\underline{H}_2Ar$ x 2), 5.97 (2H, m, H7 and H8), 6.87 (4H, m, ArH), 7.25 (4H, m, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 34.69 (CH), 36.08 (CH), 37.43 (CH), 38.50 (CH), 41.14 (CH), 42.32 (CH_2), 43.83 (CH), 55.19 (CH_3), 68.56 (CH_2), 72.51 (CH_2), 74.48 (CH_2), 113.66 (CH), 113.72 (CH), 129.06 (CH), 129 (CH), 130.69 (Cq), 130.73 (Cq), 135.33 (CH), 136.52 (CH), 158.99 (Cq), 159.02 (Cq). m/z 299 (16), 121 (100). Found C, 77.1; H, 7.7. $C_{27}H_{32}O_4$ requires C, 77.1; H, 7.7.

3-endo,4-exo-Di[(p-methoxybenzyloxy)methyl]-dimethyl-tricyclo[4.2.1.0.^{2,5}]nonane-7-exo,8-exo-dicarboxylate, **19**. To a solution of the olefin **10** (1.01 g, 2.6 mmol), anhydrous copper (II) chloride (1.46 g, 11 mmol) and anhydrous sodium acetate (0.90 g, 11 mmol) in anhydrous methanol (100 cm^3) and anhydrous THF (70 cm^3) was added 5% Pd/C (Fluka, 0.1 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was then attached to the flask and the mixture was stirred vigorously for 7 d with more carbon monoxide being added when necessary. Dichloromethane (50 cm^3) and H_2O (50 cm^3) were added and the mixture filtered through a pad of Celite. The aqueous layer was extracted with dichloromethane (2 x 75 cm^3) and the combined organic extracts were washed with a saturated solution of sodium bicarbonate (5 x 100 cm^3) and H_2O (1 x 100 cm^3) until the blue colour disappeared. The solution was then dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (ethyl acetate / light petroleum, 35:65) to yield the diester **19** as a colourless oil which solidified upon standing in the freezer (0.83 g, 60%), m.p.62-64°C.^{1}H NMR (300 MHz, $CDCl_3$): δ 1.82 - 1.93 (2H, m, H9 and H2), 2.05 - 2.16 (3H, m, H3, H5 and H9), 2.40 - 2.51 (5H, m, H1, H4, H6, H7 and H8), 3.32 - 3.60 (4H, m, $C\underline{H}_2OCH_2Ar$ x 2), 3.60 (3H, s, $C(=O)OC\underline{H}_3$), 3.61 (3H, s, $C(=O)OC\underline{H}_3$), 3.80 (6H, s, $OC\underline{H}_3$ x 2), 4.40 (4H, m, $OC\underline{H}_2Ar$ x 2), 6.85 (4H, d, *J* 8.5 Hz, ArH), 7.23 (4H, d, *J* 8.5 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 32.27 (CH_2), 37.63 (CH), 38.83 (CH), 39.60 (CH), 39.80 (CH), 42.22 (CH), 42.28 (CH), 49.12 (CH), 50.11 (CH), 51.64 (CH_3), 55.27 (CH_3), 68.34 (CH_2), 72.61 (CH_2), 72.66 (CH_2), 73.65 (CH_2), 113.76 (CH), 129.13 (CH), 129.26 (CH), 130.55 (Cq), 130.64 (Cq), 159.12 (Cq), 159.15 (Cq), 173.30 (C=O), 173.41 (C=O). m/z 507 (0.8), 417 (8), 121 (100). Found C, 69.4; H, 7.3. $C_{31}H_{38}O_8$ requires C, 69.1; H, 7.1.

3,10-Dimethyl-tetramethyl-hexacyclo[10.2.1.1.^{5,8}0.^{2,11}0.^{3,10}0.^{4,9}]hexadecane-6-exo,7-exo,13-exo,14-exo-tetracarboxylate, **29**, and *3,10-Dimethyl-dimethyl-hexacyclo[10.2.1.1.^{5,8}0.^{2,11}0.^{3,10}0.^{4,9}]hexadec-6-ene-13-exo,14-exo-dicarboxylate,* **28**,. To a solution of the bis-olefin **16**^{5e} (0.5 g, 2 mmol), anhydrous copper (II) chloride (2.30 g, 17 mmol) and anhydrous sodium acetate (1.40 g, 17 mmol) in anhydrous methanol (75 cm^3) and anhydrous tetrahydrofuran (10 cm^3) was added 5% Pd/C (Fluka, 0.20 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture stirred at room temperature for 96 h. Dichloromethane (50 cm^3) and H_2O (50 cm^3) were added to the mixture and the resulting suspension was filtered through a pad of Celite and the aqueous layer extracted with dichloromethane (2 x 50 cm^3) . The combined organic extracts were washed with H_2O (50 cm^3) and a saturated solution of sodium bicarbonate (3 x 50 cm^3) until the blue colour disappeared, then dried (Na_2SO_4) and the solvent removed under reduced pressure to give a yellow solid which was filtered through a pad of silica and recrystallised from dichloromethane / methanol to yield the tetraester **29** as a colourless crystalline solid (0.55 g, 60%), m.p. 226-228°C.^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78 (6H, s, $C\underline{H}_3$ x 2), 1.62 (2H, d, *J* 9.9 Hz, H15 and H16), 2.04 (4H, s, H2, H4, H9 and H11), 2.07 (2H, d, *J* 9.9Hz, H15 and H16), 2.44 (4H, s, H1, H5, H8 and H12), 2.60 (4H, d, $J_{6,16}$ 1.5Hz, H6, H7, H13 and H14), 3.62 (12H, s, $OC\underline{H}_3$ x 4). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 9.51 (CH_3), 32.48 (CH_2), 40.00 (CH), 45.25 (Cq), 49.67 (CH), 51.53 (CH), 51.66 (CH_3), 173.42 (C=O). m/z 443 (19), 59 (33), 145 (100). Found C, 65.5; H, 7.4. $C_{26}H_{34}O_8$ requires C, 65.8; H, 7.2.

Under the same conditions using only 4 equivalents of copper (II) chloride and sodium acetate the diester **28** was also obtained in 20% yield whilst the tetraester **29** was obtained in 40% yield. m.p. 131-133°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78 (6H, s, CH_3), 1.17 (1H, d, *J* 8.8 Hz, H16), 1.30 (1H, d, *J* 8.8 Hz, H16), 1.63 (1H, d, *J* 11.4 Hz, H15), 1.73 (2H, s, H4 and H9), 1.97 (2H, s, H2 and H11), 2.08 (1H, d, *J* 11.9 Hz, H15), 2.49 (2H, s, H1 and H12), 2.60 (2H, d, *J* 1.8 Hz, H13 and H14), 2.72 (2H, s, H5 and H8), 3.62 (6H, s, $OC\underline{H}_3$ x 2), 6.00 (2H, s, H6 and H7).^{13}C NMR (75.47MHz, $CDCl_3$): δ 9.36 (CH_3), 32.48 (CH_2), 40.27 (CH), 41.80 (CH), 42.26 (CH_2), 42.77 (Cq), 47.80 (CH), 49.78 (CH), 51.62 (CH_3), 51.62 (CH), 135.92 (CH), 173.59 (C=O). m/z 356 (M^+, 1), 357 (M^++1, 0.5), 325 (13), 106 (100). Found C, 74.4; H, 8.2. $C_{22}H_{28}O_4$ requires C, 74.1; H, 7.9.

Tetramethyl-(1α,4α,4aα,8aα,9aα,9β,10aα,10β)-1,2,3,4,4a,5,6,7,8,8a,9,9a,10,10a-tetradecahydro-1,4:5,8:9,10-trimethanoanthracene-2-exo,3-exo,6-exo,7-exo-tetracarboxylate, **30**. To a solution of the bis-olefin **17**^{5f} (0.5 g, 2.2 mmol), anhydrous copper (II) chloride (1.25 g, 9.2 mmol) and anhydrous sodium acetate (0.78 g, 9.5 mmol) in anhydrous methanol (50 cm^3) and anhydrous tetrahydrofuran (10 cm^3) was added 5% Pd/C (Fluka, 0.10 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture stirred at room temperature for 7 d. Dichloromethane (50 cm^3) and water (50 cm^3) were added to the mixture and the resulting suspension was filtered through a pad of Celite and the aqueous layer extracted with dichloromethane (2 x 50 cm^3) . The combined organic extracts were washed with water (50 cm^3) and a saturated solution of sodium bicarbonate (3 x 50 cm^3) until the blue colour disappeared, then dried (Na_2SO_4) and the solvent removed under reduced pressure to give a yellow oil which was purified by column chromatography (ethyl acetate / light petroleum; 1:9) to yield the tetraester **30** as a colourless crystalline solid (0.51 g, 50%), m.p. 199-201°C.^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (2H, s, H13 x 2), 1.31 (2H, d, *J* 10.2 Hz, H11 and H12), 1.65 (4H, m, H4a, H8a, H9a and H10a), 2.09 (2H, d, *J* 10.2 Hz, H11 and H12), 2.17 (2H, s, H9 and H10), 2.54 (4H, s, H1, H4, H5 and H8), 3.07 (4H, d, *J* 2.0 Hz, H2, H3, H6 and H7), 3.60 (12H, s, $OC\underline{H}_3$ x 4). ^{13}C NMR (75.47MHz, $CDCl_3$): δ 29.98 (CH_2), 36.11 (CH), 40.01 (CH_2), 43.98 (CH), 45.49 (CH), 51.30 (CH), 51.68 (CH_3), 173.81 (C=O). m/z 460 (M^+, 0.3), 429 (18), 59 (100) . Found C, 65.2; H, 7.1. $C_{25}H_{32}O_8$ requires C, 65.2; H, 7.0.

Dimethyl (1α,4α,4aβ,4bα,4cβ,5α,10α,10aβ,10bα,10cβ)–6,9–dimethoxy-4b,10b–dimethyl–1,2,3,4,4a,4c,5,10,10a,10c-decahydro-1,4:5,10-dimethanobenzo[3',4']cyclobuta[1,2-b]-napthalene-2-exo,3-exo-dicarboxylate, **26**. To a suspension of the olefin **14**^{5b} (0.52 g, 1.4 mmol), anhydrous copper (II) chloride (0.77 g, 5.7 mmol) and anhydrous sodium acetate (0.47 g, 5.7 mmol) in anhydrous methanol (45 cm^3) and anhydrous tetrahydrofuran (35 cm^3) was added 5% Pd/C (Fluka, 0.03 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture stirred at room temperature for 72 h then poured into water (50 cm^3) and dichloromethane (50 cm^3) and the resulting suspension filtered through a pad of Celite. The aqueous layer was extracted with dichloromethane (3 x 50 cm^3) and the organic layers combined and washed with water (50 cm^3) and a saturated sodium bicarbonate solution (3 x 50 cm^3) until the blue colour disappeared. The solution was dried (Na_2SO_4) and the solvent removed under vacuum to yield the diester **26** as a colourless crystalline solid which was recrystallised from dichloromethane / methanol (0.55 g, 80%), m.p. 248-250°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (6H, s, $C\underline{H}_3$ x 2), 1.53 (1H, d, $J_{12,12}$ 9.2 Hz, H12), 1.68 (2H, m, H11 and H12), 1.96 (4H, s, H4a, H4c, H10a and H10c), 2.09 (1H, d,

$J_{11,11}$ 9.2 Hz, H11), 2.47 (2H, s, H1 and H4), 2.55 (2H, d, $J_{2,11}$ 1.8Hz, H2 and H3), 3.49 (2H, s, H5 and H10), 3.61 (6H, s, C(=O)OC$\underline{H}_3$, x 2), 3.79 (6H, s, OC$\underline{H}_3$ x 2), 6.67 (2H, s, H7 and H8). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 9.35 (CH_3), 32.51 (CH_2), 40.10 (CH), 40.13 (CH), 43.36 (CH_2), 43.70 (CH), 49.86 (CH), 49.72 (CH), 51.43 (CH), 51.60 (C(=O)O$\underline{C}H_3$ x 2), 56.03 (O$\underline{C}H_3$ x 2), 109.02 (CH), 136.50 (Cq), 147.75 (Cq), 173.50 (C=O). m/z 466 (M^+, 1.5), 435 (10), 176 (100). Found C, 72.3; H, 7.5. $C_{28}H_{34}O_6$ requires C, 72.1; H, 7.4.

Dimethyl-9,10-Dimethoxy-1,2,3,4-tetrahydro-1,4-methanoanthracene-2-exo,3-exo-dicarboxylate, **24** *and 2-Methyl, 3-exo-chloro-9,10-dimethoxy-1,2,3,4-tetrahydro-1,4-methanoanthracene-2-exo-carboxylate,* **25**. To a solution of the olefin **13**[14] (0.51 g, 2.0 mmol), anhydrous copper (II) chloride (1.05 g, 7.9 mmol) and anhydrous sodium acetate (0.66 g, 7.9 mmol) in anhydrous methanol (75 cm^3) was added 5% Pd/C (Fluka, 0.10 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture stirred at room temperature for 96 h. Dichloromethane (50 cm^3) and H_2O (50 cm^3) were added to the mixture and the resulting suspension was filtered through a pad of Celite and the aqueous layer extracted with dichloromethane (2 x 50 cm^3) . The combined organic extracts were washed with H_2O (50 cm^3) and a saturated solution of sodium bicarbonate (3 x 50 cm^3) until the blue colour disappeared, then dried (Na_2SO_4) and the solvent removed under reduced pressure to give a yellow oil which was purified by column chromatography (ethyl acetate / light petroleum; 1:9) to yield two compounds. The first compound to be eluted from the column was the *exo,exo*-chloro-ester **25** which was isolated as a colourless crystalline solid (<5%), m.p. 116-118°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (1H, m, H11), 2.72 (1H, m, H11), 3.04 (1H, bs, H2), 3.77 (3H, s, C(=O)OC$\underline{H}_3$), 3.98 (3H, s, OC$\underline{H}_3$), 4.04 (3H, s, OC$\underline{H}_3$), 4.08 (1H, dd, J 3.1 Hz, J 7.83 Hz, H1), 4.14 (1H, m, H4), 4.30 (1H, s, H3), 7.49 (2H, m, H7 and H8), 8.09 (2H, M, H6 and H9). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 39.21 (CH_2), 41.88 (CH), 51.65 (C(=O)$\underline{C}H_3$), 52.39 (CH), 58.25 (CH), 59.61 (CH), 61.81 (O$\underline{C}H_3$), 62.00 (O$\underline{C}H_3$), 122.19 (CH), 122.28 (CH), 125.77 (CH), 126.10 (CH), 128.02 (Cq), 128.63 (Cq), 129.64 (Cq), 131.97 (Cq), 144.43 (Cq), 145.23 (Cq), 170.76 (C=O x 2). m/z 346 (M^+, ^{35}Cl, 100), 348 (M^+, ^{37}Cl, 30). Found C, 66.1; H, 5.8. $C_{26}H_{34}O_8$ requires C, 65.8; H, 5.5.

The second compound which was eluted from the column was found to be the diester **24** which was isolated as a colourless crystalline solid (0.73 g, 70%), m.p. 120-121°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90 (1H, td, $J_{1,11}$ 1.8 Hz, $J_{11,11}$ 10.0 Hz, H11), 2.57 (1H, td, $J_{11,11}$ 9.7 Hz, $J_{11,2}$ 1.6 Hz, H11), 2.94 (2H, d, $J_{2,11}$ 1.8 Hz, H2 and H3), 3.72 (6H, s, C(=O)OC$\underline{H}_3$ x 2), 3.99 (6H, s, OC$\underline{H}_3$ x 2), 4.03 (2H, t, $J_{1,11}$ 1.5 Hz, H1 and H4),7.47 (2H, m, H7 and H8), 8.09 (2H, m, H6 and H9).^{13}C NMR (75.47 MHz, $CDCl_3$) 44.03 (CH), 45.04 (CH_2), 49.42 (CH), 52.07 (C(=O)O$\underline{C}H_3$ x 2), 61.93 (O$\underline{C}H_3$ x 2), 122.23 (CH), 125.68 (CH), 128.31 (Cq), 133.45 (Cq), 144.68 (Cq), 173.19 (C=O). m/z 370 (M^+, 80), 371 (M^++1, 15), 211 (100). Found C, 68.2; H, 6.1. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.0.

Dimethyl 5,8-Dimethoxy-1,2,3,4-tetrahydro-1,4-methanonapthalene-2-exo,3-exo-dicarboxylate, **20** *and 2-Methyl,3-exo-chloro-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-methanonapthalene-2-exo-dicarboxylate,* **21**. To a solution of the olefin **11**[15] (0.5 g, 2.6 mmol), anhydrous copper (II) chloride (1.34 g, 10.0 mmol) and anhydrous sodium acetate (0.82 g, 10.0 mmol) in anhydrous methanol (75 cm^3) was added 5% Pd/C (Fluka, 0.08 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture stirred at room temperature for 60 h with more carbon monoxide being introduced when necessary. The mixture was poured into H_2O (50 cm^3) and dichloromethane (50 cm^3) and the resulting suspension filtered through a pad of Celite. The aqueous layer was extracted with dichloromethane and the organic layers combined and washed with H_2O (50 cm^3) and a saturated sodium bicarbonate solution (3 x 50 cm^3) until the blue colour disappeared. The resulting solution was dried (Na_2SO_4) and the solvent removed under reduced pressure to give a yellow solid which was purified by column chromatography (ethyl acetate / light petroleum, 1:9) to yield the *exo,exo*-chloro-ester **21** as a colourless crystalline solid (<5%), m.p. 110-112°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (1H, m, H9), 2.53 (1H, m, H9), 2.91 (1H, s, H2), 3.71 (3H, s, C(=O)OC$\underline{H}_3$), 3.75 (3H, s, OC$\underline{H}_3$), 3.78 (3H, s, OC$\underline{H}_3$), 3.87 (2H, m, H1 and H4), 4.09 (1H, s, H3), 6.63 (2H, m, H6 and H7). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 37.75 (CH_2), 41.26 (CH), 51.42 (CH_3), 51.82 (CH), 55.84 (CH_3), 56.05 (CH_3), 57.99 (CH), 60.66 (CH), 109.78 (CH), 111.07 (CH), 132.29

(Cq), 135.71 (Cq), 147.42 (Cq), 147.88 (Cq), 171.02 (C=O). m/z 296 (M^+, ^{35}Cl, 40), 298 (M^+, ^{37}Cl, 13), 234 (100).

Increasing the solvent polarity (ethyl acetate / light petroleum, 1:4) yielded the diester **20** as a colourless crystalline solid (0.40 g, 50%), m.p. 140-142°C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.78 (1H, td, $J_{2,9}$ 1.8 Hz, $J_{9,9}$ 9.5 Hz, H9), 2.42 (1H, td, $J_{1,9}$ 1.5 Hz, $J_{9,9}$ 9.5 Hz, H9), 2.74 (2H, d, $J_{2,9}$ 1.8 Hz, H2 and H3), 3.68 (6H, s,C(=O)OC$\underline{H}_3$), 3.77 (6H, s, OC$\underline{H}_3$), 3.81 (2H, t, $J_{1,9}$ 1.5 Hz, H1 and H4), 6.60 (2H, s, H6 and H7). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 43.56 (CH), 46.23 (CH_2), 48.64 (CH), 51.88 (C(=O)O$\underline{C}H_3$ x 2), 55.95 (O$\underline{C}H_3$ x 2), 109.98 (CH), 136.12 (Cq), 147.74 (Cq), 173.60 (C=O). m/z 320 (M^+, 22) 321 (M^++1, 5), 289 (8) 176 (100). Found C, 63.7; H, 6.5. $C_{17}H_{20}O_6$ requires C, 63.71; H, 6.3.

Dimethyl-1,2,3,4-tetrahydro-1,4-methanonapthalene-2-exo,3-exo-dicarboxylate, **22** *and 2-Methyl,3-exo-chloro-1,2,3,4-tetrahydro-1,4-methanonapthalene-2-exo-dicarboxylate,* **23**. To a solution of the olefin **12**[16] (0.5 g, 3.5 mmol), anhydrous copper (II) chloride (1.89g, 14.0 mmol) and anhydrous sodium acetate (1.15 g, 14.0 mmol) in anhydrous methanol (75 cm^3) was added 5% Pd/C (Fluka, 0.06 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture was stirred at room temperature for 96 h with more carbon monoxide being introduced when necessary. The mixture was poured into H_2O (50 cm^3) and dichloromethane (50 cm^3) and the resulting suspension filtered through a pad of Celite. The aqueous layer was extracted with dichloromethane (3 x 50 cm^3) and the organic layers combined and washed with H_2O (50 cm^3) and a saturated sodium bicarbonate solution (3 x 50 cm^3) until the blue colour disappeared. The resulting solution was dried (Na_2SO_4) and the solvent removed under vacuum to give a yellow solid which was purified by column chromatography (ethyl acetate / light petroleum; 1:9) to yield two compounds. The first compound eluted from the column was the *exo,exo*-chloro-ester **23** which was isolated as a colourless crystalline solid (<5%), m.p. 125-127°C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.05 (1H, M, H9), 2.57 (1H, m, H9), 2.98 (1H, s, H2), 3.68 (1H, d, J 3.8 Hz, H1), 3.73 (3H, s, OC$\underline{H}_3$), 3.90 (2H, m, H3 and H4), 7.10-7.21 (4H, m, H5, H6, H7 and H8). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 38.29 (CH_2), 44.79 (CH), 51.50 (CH_3), 55.58 (CH), 58.44 (CH), 60.98 (CH), 121.11 (CH), 121.84 (CH), 126.45 (CH), 127.34 (CH), 143.70 (Cq), 146.73 (Cq), 171.07 (C=O). m/z 236 (M^+, ^{35}Cl, 17), 238 (M^+, ^{37}Cl, 5%), 174 (100).

The second compound to be eluted from the column was the diester **22** which was isolated as a colourless crystalline solid (0.52 g, 58%), m.p. 106-108°C, literature m.p. 107-108°C [10]. ^1H NMR (300 MHz, $CDCl_3$): δ 1.85 (1H, td, $J_{9,2}$ 1.8 Hz, $J_{9,9}$ 9.7 Hz, H9), 2.47 (1H, dt, $J_{9,1}$ 1.8 Hz, $J_{9,9}$ 9.7 Hz, H9), 2.75 (2H, d, $J_{2,9}$ 1.8Hz, H2 and H3), 3.60 (2H, t, $J_{1,9}$ 1.8 Hz, H1 and H4), 3.69 (6H, s, OC$\underline{H}_3$ x 2), 7.10 (2H, m, H6 and H7), 7.21 (2H, m, H5 and H8).

Dimethyl (1α,4α,4aβ,4bα,4cβ,5α,10α,10aβ,10bα,10cβ)-4b,10b-dimethyl-1,2,3,4,4a,4c,5,10,10a,10c-decahydro-1,4:5,10-dimethanobenzo[3',4']cyclobuta[1,2-b]-napthalene-2-exo,3-exo-dicarboxylate, **27**. To a suspension of the olefin **15**[17] (0.50 g, 1.7 mmol), anhydrous copper (II) chloride (0.93 g, 6.8 mmol) and anhydrous sodium acetate (0.57 g, 6.8 mmol) in anhydrous methanol (45 cm^3) and anhydrous tetrahydrofuran (20 cm^3) was added 5% Pd/C (Fluka, 0.05 g) and the flask flushed with carbon monoxide. A balloon of carbon monoxide was attached and the mixture stirred at room temperature for 120 h then poured into water (50 cm^3) and dichloromethane (50 cm^3) and the resulting suspension filtered through a pad of Celite. The aqueous layer was extracted with dichloromethane (3 x 50 cm^3) and the organic layers combined and washed with water (50 cm^3) and a saturated sodium bicarbonate solution (3 x 50 cm^3) until the blue colour disappeared. The solution was dried (Na_2SO_4) and the solvent removed under reduced pressure to yield a colourless oil which was purified by column chromatography (ethyl acetate / light petroleum; 1:9) to yield the diester **27** as a colourless crystalline solid (0.53 g, 76%), m.p. 182-184°C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (6H, s, CH_3), 1.58 (1H, d, $J_{12,12}$ 9.5 Hz, H12), 1.67 (1H, d, $J_{11,11}$ 11.3 Hz, H11), 1.76 (1H, d, $J_{12,12}$ 9.5 Hz, H12), 1.94 (2H,s, H4c and H10a or H4a and H10c), 1.96 (2H, s H4c and H10a or H4a and H10c), 2.10 (1H, d, $J_{11,11}$ 11.0 Hz, H11), 2.49 (2H, s, H1 and H4), 2.56 (2H, d, $J_{2,11}$ 1.8 Hz, H2 and H3), 3.23 (2H, s, H5 and H10), 3.62 (6H, s, OC$\underline{H}_3$), 7.05-7.17 (4H, m, H6, H7, H8 and 9). ^{13}C NMR (75.47 MHz, $CDCl_3$) 9.43 (CH_3), 32.49 (CH_2), 40.13 (CH), 43.58 (CH), 43.75 (CH_2), 46.69 (CH), 50.44 (CH), 51.47 (CH), 51.60 O$\underline{C}H_3$ x 2), 120.67 (CH), 125.41 (CH), 147.63 (Cq), 173.48 (C=O). m/z 406 (M^+, 23), 375 (7), 116 (100). Found C, 76.9; H, 7.6.$C_{28}H_{30}O_4$ requires C, 76.8; H, 7.4.

ACKNOWLEDGEMENTS

The support of the Australian Research Council is gratefully acknowledged.

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(*Received in UK* 6 *December* 1994; *accepted* 21 *December* 1994)