

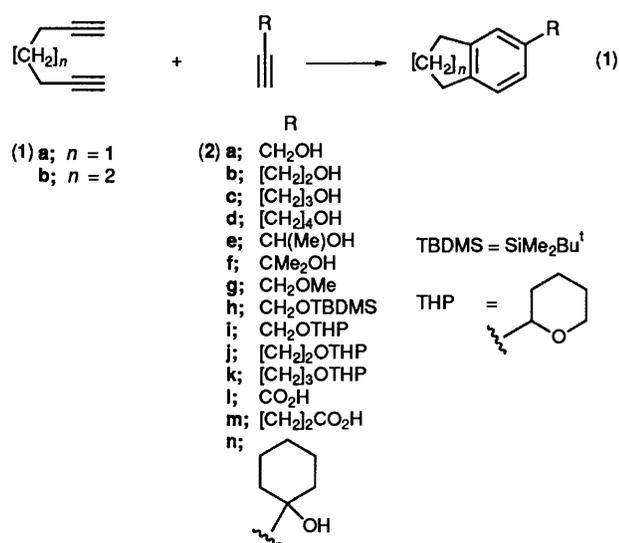
Oxygen Ligation in the Nickel-mediated [2 + 2 + 2] Co-cyclisation of a Hepta-1,6-diyne and Alkynol Derivatives

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The variation of the yields of the nickel-mediated [2 + 2 + 2] co-cyclisation of a hepta-1,6-diyne with alkynols and alkynol ethers in a regular fashion dependent on the position and steric environment of the oxygen atom is strongly indicative that this atom ligates with the metal during the reaction.

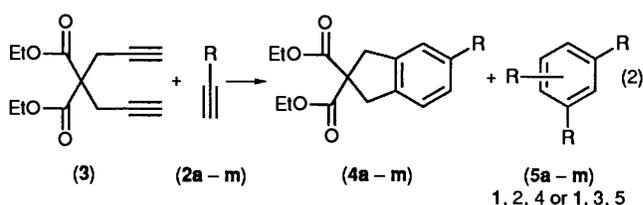
Whilst the nickel-catalysed [2 + 2 + 2] cyclotrimerisation of acetylenes to benzenes has had a productive history,¹ the corresponding co-cyclisation of α,ω -diynes (**1**) and monoacetylenes [equation (1)] has been the subject of only one report.² In that study the simple alkyl acetylenes, pent-1-yne and hept-1-yne, served as the foils to the diynes (**1a** and **b**). It is noteworthy, however, that propargyl alcohol performs well in the trimerisation catalysed by nickel(0) species^{3,4} and, accordingly, we decided to test it in a co-cyclisation reaction in the presence of a stoichiometric amount of the low-valent nickel species [probably tetrakis(triphenylphosphine)nickel(0)] generated from $\text{NiCl}_2(\text{PPh}_3)_4$ and *n*-butyl-lithium which we have previously shown to be effective in β -eliminations.⁵ For comparison with propargyl alcohol a systematic study of other alkynols and their derivatives was made in this reaction the results of which are recorded below.



Results

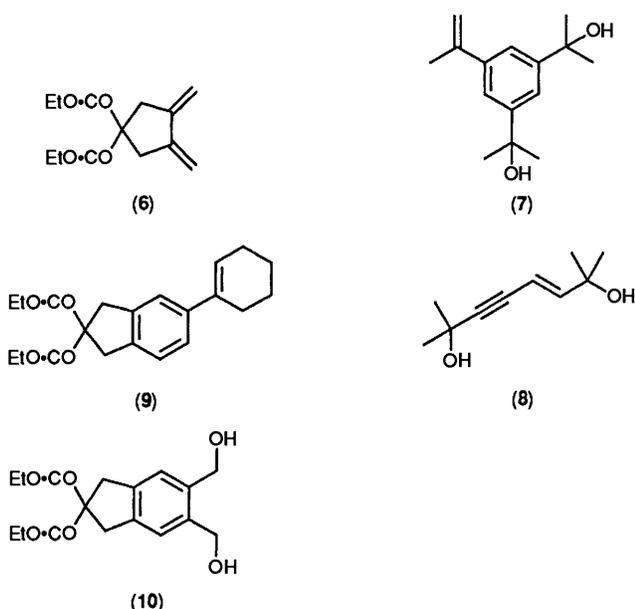
Prop-2-ynol in four-fold excess reacted reasonably well (52%) overnight with the malonate diyne (**3**) in the presence of the nickel(0) reagent (1 mol equiv.) to give the known benzylic alcohol (**4a**)⁶ [equation (2)] without any contamination from the self-condensation trimers (**5a**) of the monoyne. It was possible to carry out the reaction with 20 mol% of the nickel(0) reagent but the reaction then only went to 40–50% completion even after 2 days. Although the yield was only moderate in the stoichiometric reaction it was substantially higher than those

reported in the literature for simple alkyl acetylenes² and the product was not contaminated by large amounts of polymer. Thus again the presence of the hydroxy group appeared beneficial. The timing of the additions of the two acetylenes to the nickel(0) reagent was critical. A space of 10 min between the addition of the diyne (**3**) (first) and the addition of prop-2-ynol (**2a**) (second) was allowed to elapse. Extension of this gap to 3 h resulted in the loss of the starting diyne but with no co-cyclised product being obtained. In the absence of prop-2-ynol the only product which could be detected in small quantities in the ¹H NMR spectrum of the crude material showed two olefinic, broad singlets at δ 4.95 and 5.39. Attempted isolation of this compound by column chromatography on silica gel led to extensive loss of material. However, small amounts of this compound were obtained with little contamination in one experiment and a high-resolution mass spectrum established its molecular weight at m/z 238.120 800 0. This value and the olefinic singlets, suggest structure (**6**) for this compound (calculated value m/z 238.120 509 3).



Extension of the co-cyclisation to the alkynols (**2b–f**) and alkynol ethers (**2g–k**) under the same conditions, *i.e.* use of the nickel(0) reagent (1 mol equiv.), gave the corresponding products in generally lower yield than that with prop-2-ynol with the important exceptions of hex-5-yn-1-ol (**2d**) (62%) and methyl prop-2-ynyl ether (**2g**) (78%) (Table). Only with the methylated prop-2-ynyl alcohols (**2e**) and (**2f**) were substantial amounts of oligomers of the monoyne formed, namely trimers (**5e**)⁷ (28%) and (**7**) (26%) and dimer (**8**).⁸ Propionic acid (**2l**) and pent-4-ynoic acid (**2m**) failed to react. Indeed, these acetylenic acids appeared to destroy the nickel reagent since the reaction mixture turned rapidly from a normal red-brown colour to dark-green on their addition and only starting materials were recovered (in high yields). In the case of 1-ethynylcyclohexanol (**2n**) dehydration of the normal product occurred to give the alkene (**9**) (20%).

The only case tried of a non-terminal alkynol was but-2-yne-1,4-diol which gave the co-cyclisation product (**10**) in 15% yield only, thus indicating that disubstituted monoynes are less reactive.



Table

| Entry | R in the monoalkyne | Yield of indane (%) ^a |
|-------|---|----------------------------------|
| 1 | CH ₂ OH | 52 |
| 2 | [CH ₂] ₂ OH | 34 ^b |
| 3 | [CH ₂] ₃ OH | 28 |
| 4 | [CH ₂] ₄ OH | 62 |
| 5 | CH(Me)OH | 8 |
| 6 | C(Me) ₂ OH | 12 |
| 7 | CH ₂ OMe | 78 |
| 8 | CH ₂ OTBDMS | 32 |
| 9 | CH ₂ OTHP | 35 |
| 10 | [CH ₂] ₂ OTHP | 16 |
| 11 | [CH ₂] ₃ OTHP | 9 ^c |
| 12 | CO ₂ H | 0 ^d |
| 13 | CH ₂ CH ₂ CO ₂ H | 0 ^d |

^a Isolated yields; all new products were fully characterised by microanalysis or high-resolution mass spectrometry. ^b Compound slowly decomposed with elimination of water. ^c Admixed with some polymer of the diyne. ^d Only starting material was recovered.

Discussion

Synthetic Aspects.—We see from entries 1–4 in the Table that moving the hydroxy group from the acetylene monotonically decreases the yield until we reach hex-5-yn-1-ol, when a dramatic raise occurs. The yield is also sensitive to steric hindrance on the carbon attached to the hydroxy group (entries 5, 6). Putting bulky groups on oxygen (entries 8–11) also reduces the yield and a trend in decreasing yield is seen as the ether oxygen is progressively removed from the acetylene similar to that for the alcohols. That the effect in the ethers is primarily a steric one is indicated by the high efficiency with which methyl prop-2-ynyl ether is processed in comparison to the TBDMS or THP ethers (entry 7). Thus, from the synthetic point of view, the best type of substrate for the co-cyclisation is a sterically unhindered prop-2-ynyl ether.

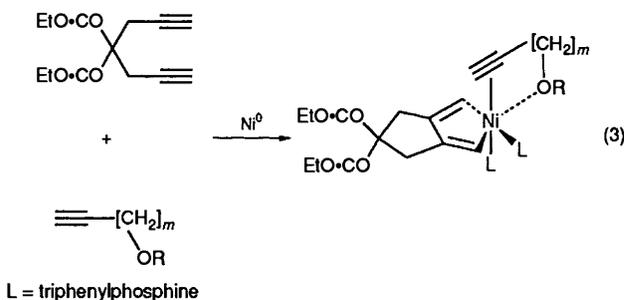
Mechanistic Aspects.—*A priori* the benefit to be gained from using prop-2-ynol (**2a**) in the nickel-mediated [2 + 2 + 2] co-cyclisation with a diyne instead of a simple alkyl acetylene may be attributed to two possible effects; namely, a through-bond inductive withdrawal of electrons from the triple

bond due to the electronegativity of oxygen or a through-space direct interaction with the nickel. The former possibility is made highly unlikely by the result with hex-5-yn-1-ol (**2d**) for which the alcohol is too far from the acetylene to have any electronic influence.

We, therefore, assume that the effect of the hydroxy group in enhancing the reaction is because it associates directly with the nickel, presumably by complexation through oxygen rather than through any effect of the OH proton since methyl prop-2-ynyl ether (**2g**) undergoes the co-cyclisation with highest efficiency. The susceptibility of the reaction yields to steric hindrance by tetrahydropyranyl and *t*-butyldimethylsilyl groups – these ethers give 15–20% lower yields than the corresponding alcohol – is consistent with the view that oxygen ligation is important. Thus, association of the monoynone through interaction of the OR function with the metal will be disfavoured by adjacent bulky R groups, especially if one or more large triphenylphosphine ligands (cone angle 145°)⁹ is still present.

Further support for this hypothesis derives from the dependence of the reaction yield on the length of chain separating the alcohol and acetylenic groups. Alignment of the orbitals required for complexation of both oxygen and the triple bond with the nickel at the correct angles necessitates that the chain be either short (prop-2-ynyl derivatives) or flexible (hex-5-yn-1-ol). Alkynols of intermediate length presumably cannot gain this entropic advantage of simultaneous binding of both functions and, therefore, behave more like simple alkyl acetylenes with consonantly lower yields.

The mechanism for the formation of benzene derivatives is still a mystery although much has been made of the intermediacy of a nickelacyclopentadiene by oxidative cyclisation of two alkynes.¹⁰ Although no such species has been isolated, this mechanism receives strong support mainly from the analogous chemistry of palladium, platinum, and iridium.^{11,12} If a nickelacyclopentadiene is truly an intermediate and at least one triphenylphosphine ligand remains on the metal during the reaction as our results suggest, then the geometry of the co-ordination sphere cannot be tetrahedral or square planar but is probably octahedral, as commonly found in nickel(II) species [equation (3)].



Experimental

M.p.s are uncorrected and were determined using a Gallenkamp apparatus. Dry tetrahydrofuran (THF) was obtained by distillation from potassium diphenylketyl under argon. Light petroleum (b.p. range 60–80 °C) used for column chromatography was distilled. May and Baker Sorbsil C60 silica gel was used for gravity column chromatography. IR spectra were recorded for samples either neat (liquids) or as Nujol mulls (solids) using a Perkin-Elmer 881 spectrophotometer. ¹H NMR spectra were recorded on a JEOL FX90Q (90 MHz) or JEOL GSX270 (270 MHz) spectrometer for solutions in CDCl₃ using SiMe₄ as internal standard. Mass spectra were recorded on an AE1 MS9 or a VG Micromass 7070 instrument.

Dichlorobis(triphenylphosphine)nickel(II) was prepared

according to the literature.⁵ Alkynols were purchased from commercial sources and their THP and TBDMS ethers made by standard procedures. Prop-2-ynyl bromide was obtained as an 80% solution in toluene from Aldrich.

Diethyl Di(prop-2-ynyl)malonate (3).—To a solution of sodium ethoxide [sodium (2.3 g, 0.1 mol) in dry ethanol (freshly distilled from CaH₂) (100 ml)] under argon was added diethyl malonate (8.07 g, 0.05 mol) during 10 min. After the solution had been stirred for 30 min at room temperature prop-2-ynyl bromide (12 g, 0.1 mol) was added dropwise at such a rate as to keep the internal temperature at 26–27 °C. A yellow suspension was formed which was then heated to reflux for 2 h. The reaction mixture was cooled to room temperature and water (100 ml) was added. The ethanol was removed under reduced pressure and the diyne was extracted with diethyl ether (3 × 30 ml). The extracts were dried (MgSO₄), filtered, and concentrated to give a yellow oil. Distillation gave the pure diyne (3) as a white solid (9.9 g, 84%), m.p. 39–40 °C; b.p. 160 °C at 0.3 mmHg (lit.,¹³ m.p. 45 °C; b.p. 129–132 °C at 0.1 mmHg); ν_{\max} 3 320 (\equiv CH), 2 120 (C \equiv C), and 1 750 cm⁻¹; δ_{H} (270 MHz) 1.1 (6 H, t, 2 × Me), 1.98 (2 H, t, *J* 1 Hz, \equiv CH), 2.8 (4 H, d, *J* 1 Hz, \equiv CCH₂), and 4.1 (4 H, q, 2 × CH₂); δ_{C} (67.6 MHz) 13.3 (Me), 22.3 (CH₂), 56 (quaternary C), 62 (CH₂O), 72 (\equiv CH), 78.4 (\equiv C), and 168.4 (CO); *m/z* 236 (*M*⁺), 197 (*M*⁺ – C₃H₃, 45%), 190 (*M*⁺ – C₂H₅OH, 70), 151 (40), and 29 (100).

Reaction of Diyne (3) with Alkynols and their Derivatives. General Procedure.—A red-brown solution of the nickel(0) reagent (0.76 mmol) in dry, degassed THF (40 ml) under argon was prepared according to the literature procedure.⁵ To this solution was added at room temperature a solution of the diyne (3) (0.76 mmol) in dry, degassed THF (5 ml) when the red tinge to the brown solution is replaced by a green tinge. After 10 min a solution of the alkynol (3.04 mmol) in dry, degassed THF (5 ml) was added at room temperature. No colour change occurred at this stage. The reaction mixture was left to stir for 17 h and then quenched with 5*M*-HCl (5 ml). The reaction vessel was then opened to air and the THF was removed on a rotary evaporator. Water (50 ml) was then added to the brown sludge and the resultant brown solution was extracted with diethyl ether until no more brown colour was extracted into the organic layer (usually 3 × 20 ml). The ethereal extracts were removed from the light green aqueous solution and were dried (MgSO₄). Filtration and evaporation gave a crude brown product. In all cases the pure product was isolated from this material by column chromatography on silica gel with 9:1 light petroleum–diethyl ether for the alkynol ethers and 1:9 light petroleum–diethyl ether for the alkynols. The following compounds were thus prepared.

Diethyl 5-(hydroxymethyl)indane-2,2-dicarboxylate (4a)⁶ as an oil (52%), ν_{\max} 3 411, 1 730, and 1 680 cm⁻¹; δ_{H} (90 MHz) 1.4 (6 H, t, 2 × Me), 2.5 (1 H, br s, OH), 3.7 (4 H, s, 2 × ring CH₂), 4.3 (4 H, q, 2 × CH₂), 4.7 (2 H, s, ArCH₂O), and 7.3 (3 H, br s, ArH); δ_{C} (22.5 MHz) 15.4 (Me), 41.6 (ring CH₂), 61.9 (quaternary C), 63.1 (ester CH₂), 66.5 (ArCH₂O), 124.3, 125, 127, 140, 141, 141.7, and 173.8 (CO); *m/z* 292 (*M*⁺, 30%), 219 (*M*⁺ – EtOCO, 42), 218 (100), 191 (24), 173 (14), 145 (21), 129 (20), 128 (19), 117 (32), 116 (21), and 115 (25).

Diethyl 5-(2-hydroxyethyl)indane-2,2-dicarboxylate (4b) as an unstable oil (34%), ν_{\max} 3 376, 1 732, and 1 653 cm⁻¹; δ_{H} (90 MHz) 1.3 (6 H, t, 2 × Me), 2.2 (1 H, br s, OH), 2.9 (2 H, t, benzylic CH₂), 3.8 (4 H, s, 2 × ring CH₂), 3.9 (2 H, t, CH₂O), 4.2 (4 H, q, 2 × CH₂), and 7.2 (3 H, br s, ArH).

Diethyl 5-(3-hydroxypropyl)indane-2,2-dicarboxylate (4c) as an oil (28%) (Found: *M*⁺, 320.163 000. C₁₈H₂₄O₅ requires *M*, 320.162 374 2); ν_{\max} 3 380, 1 734, 1 697, and 1 653 cm⁻¹; δ_{H} (90 MHz) 1.1 (6 H, t, 2 × Me), 1.6 (2 H, m, chain CH₂), 2.4 (2 H, m,

benzylic CH₂), 3.5 (4 H, br s, 2 × ring CH₂), 3.55 (2 H, t, CH₂O), 4.1 (4 H, q, 2 × CH₂), and 7.1 (3 H, br s, ArH); *m/z* 320 (*M*⁺, 7%), 246 (*M*⁺ – EtOCO, 24), 155 (45), and 111 (100).

Diethyl 5-(4-hydroxybutyl)indane-2,2-dicarboxylate (4d) as an oil (62%) (Found: C, 68.2; H, 8.0. C₁₉H₂₆O₅ requires C, 68.24; H, 7.84%); ν_{\max} 3 414, 1 729, and 1 630 cm⁻¹; δ_{H} (90 MHz) 1.1 (6 H, t, 2 × Me), 1.5 (4 H, m, 2 × chain CH₂), 2.2 (1 H, br s, OH), 2.5 (2 H, t, benzylic CH₂), 3.5 (4 H, br s, 2 × ring CH₂), 3.55 (2 H, t, CH₂O), 4.1 (4 H, q, 2 × CH₂), and 7.1 (3 H, br s, ArH); δ_{C} (22.5 MHz) 14 (Me), 27 (CH₂), 32 (CH₂), 35 (CH₂), 40 (CH₂), 61 (quaternary C), 61.8 (ester CH₂), 62.7 (CH₂O), 124, 127, 137, 140, 141, and 172 (CO); *m/z* 334 (*M*⁺, 10%), 260 (*M*⁺ – EtOCO, 34), and 85 (100).

Diethyl 5-(1-hydroxyethyl)indane-2,2-dicarboxylate (4e) as an oil (8%) (Found: *M*⁺, 306.146 500 0. C₁₇H₂₂O₅ requires *M*, 306.146 724 1); ν_{\max} 3 403, 1 731, and 1 614 cm⁻¹; δ_{H} (90 MHz) 1.1 (6 H, t, 2 × ester Me), 1.4 (3 H, d, *J* 7.7 Hz, Me), 2.2 (1 H, br s, OH), 3.5 (4 H, br s, 2 × ring CH₂), 4.1 (4 H, q, 2 × CH₂), 4.7 (1 H, q, *J* 7.7 Hz, CHMe), and 7.3 (3 H, m, ArH); δ_{C} (22.5 MHz) 14 (Me), 25 (CHMe), 40 (CH₂), 60 (quaternary C), 61 (CH₂O), 70 (CH), 121, 124, 139, 145, and 172 (CO); *m/z* 306 (*M*⁺, 39%), 232 (*M*⁺ – EtOCO, 100), 217 (68), 117 (43) and 115 (38).

Diethyl 5-(1-hydroxy-1-methylethyl)indane-2,2-dicarboxylate (4f) as an oil (12%) (Found: C, 67.7; H, 7.5. C₁₈H₂₄O₅ requires C, 67.48; H, 7.55%); ν_{\max} 3 271, 1 730, and 1 658 cm⁻¹; δ_{H} (90 MHz) 1.2 (6 H, t, 2 × Me), 1.5 (6 H, s, 2 × Me), 1.95 (1 H, br s, OH), 3.6 (4 H, br s, 2 × ring CH₂), 4.1 (4 H, q, 2 × CH₂), and 7.3 (3 H, m, ArH); δ_{C} (22.5 MHz) 14 (Me), 32 (Me), 40.4, 40.9, 61, 61.9, 73, 120, 123.5, 140, 148, and 172 (CO); *m/z* 320 (*M*⁺, 38%), 305 (*M*⁺ – Me, 96), 247 (*M*⁺ – EtOCO, 43), 246 (47), and 231 (*M*⁺ – EtOCO – Me, 100).

Diethyl 5-(methoxymethyl)indane-2,2-dicarboxylate (4g) as an oil (78%) (Found: *M*⁺, 306.146 500 0. C₁₇H₂₂O₅ requires *M*, 306.146 724 1); ν_{\max} 1 737 and 1 615 cm⁻¹; δ_{H} (90 MHz) 1.2 (6 H, t, 2 × Me), 3.3 (3 H, s, OMe), 3.6 (4 H, br s, 2 × ring CH₂), 4.1 (4 H, q, 2 × CH₂), 4.4 (2 H, s, CH₂O), and 7.1 (3 H, br s, ArH); δ_{C} (22.5 MHz) 14 (Me), 41, 58 (OMe), 61, 62, 75, 123.9, 124.3, 127, 137, 139, 141, and 172 (CO); *m/z* 306 (*M*⁺, 34%), 233 (44), and 232 (*M*⁺ – EtOCO, 100).

Diethyl 5-(*t*-butyldimethylsiloxy)indane-2,2-dicarboxylate (4h) as an oil (32%) (Found: C, 64.9; H, 8.5. C₂₂H₃₄O₅Si requires C, 64.99; H, 8.43%); ν_{\max} 1 736 cm⁻¹; δ_{H} (90 MHz) 0 (6 H, s, 2 × Me), 0.8 (9 H, s, Bu^t), 1.1 (6 H, t, 2 × Me), 3.5 (4 H, br s, ring CH₂), 3.9 (4 H, q, 2 × CH₂), 4.6 (2 H, s, CH₂O), and 7.0 (3 H, br s, ArH); δ_{C} (22.5 MHz) –5, 14, 18, 26, 40, 61, 62, 65, 122, 122, 124, 125, 140, and 172; *m/z* 405 (*M*⁺ – 1, 0.2%), 391 (*M*⁺ – Me, 1.7), 361 (5), 349 (*M*⁺ – Bu^t, 97), 275 (97), and 201 (100).

Diethyl 5-[(tetrahydropyran-2-yloxy)methyl]indane-2,2-dicarboxylate (4i) as an oil (35%) (Found: *M*⁺, 376.187 900 0. C₂₁H₂₈O₆ requires *M*, 376.188 589 0); ν_{\max} 1 734 and 1 605 cm⁻¹; δ_{H} (90 MHz) 1.1 (6 H, t, 2 × Me), 1.4–1.8 (6 H, m, 3 × CH₂), 3.5 (5 H, br s, 2 × ring CH₂ and CHHO in THP group), 3.7 (1 H, br t, CHHO in THP group), 4.1 (4 H, q, 2 × CH₂), 4.45 (2 H, ABq, CH₂O), 4.6 (1 H, br s, OCHO), and 7.1 (3 H, br s, ArH); δ_{C} (22.5 MHz) 14 (Me), 19.5, 26, 31, 40, 61, 62, 62.1, 69, 98, 123, 124, 127, 137, 140, and 172 (CO); *m/z* 376 (*M*⁺, 2.2), 292 (*M*⁺ – EtOCO, 40), 276 (32), 275 (78), 274 (59), 218 (57), 202 (60), 201 (100), 129 (57), and 128 (37).

Diethyl 5-[2-(tetrahydropyran-2-yloxy)ethyl]indane-2,2-dicarboxylate (4j) as an oil (16%) (Found: C, 67.5; H, 8.0. C₂₂H₃₀O₆ requires C, 67.67; H, 7.74%); ν_{\max} 1 740 and 1 655 cm⁻¹; δ_{H} (90 MHz) 1.1 (6 H, t, 2 × Me), 1.4–1.8 (6 H, m, 3 × CH₂), 2.7 (2 H, t, benzylic CH₂), 3.5 (4 H, br s, 2 × ring CH₂), 3.5–3.9 (4 H, m, 2 × CH₂O), 4.1 (4 H, q, 2 × CH₂), 4.6 (1 H, br s, OCHO), and 7.2 (3 H, br s, ArH); δ_{C} (22.5 MHz) 14 (Me), 20, 26, 31, 36, 40, 40.5, 61, 62, 68, 99, 124, 125, 128, 137, 140, and 172 (CO); *m/z* 390 (*M*⁺, 0.5%), 290 (16), 288 (*M*⁺ – THPOH, 20), and 85 (THP⁺, 100).

Diethyl 5-[3-(tetrahydropyran-2-yloxy)propyl]indane-2,2-dicarboxylate (4k) as an oil (9%) (Found: C, 67.9; H, 8.1. $C_{23}H_{32}O_6$ requires C, 68.29; H, 7.97%); ν_{\max} 1 737, 1 653, and 1 614 cm^{-1} ; δ_H (90 MHz) 1.1 (6 H, t, $2 \times$ Me), 1.5–2.0 (6 H, m, $3 \times$ CH₂), 2.6 (2 H, dt, CH₂), 3.3 (2 H, m, CH₂O), 3.5 (4 H, br s, $2 \times$ ring CH₂), 3.6–3.9 (2 H, m, CH₂O), 4.1 (4 H, q, $2 \times$ CH₂), 4.5 (1 H, br s, OCHO), and 7.0 (3 H, br s, ArH); δ_C (22.5 MHz) 14 (Me), 20, 26, 31, 31.6, 32, 40, 40.5, 62, 62.4, 68, 76, 99, 124, 124.3, 128, 141, and 172 (CO); m/z 404 (M^+ , 9%), 320 ($M^+ + H - THP$, 23), 302 ($M^+ - THPOH$, 33), 228 (48), and 85 (THP⁺, 100).

Diethyl 3,4-dimethylenecyclopentane-1,1-dicarboxylate (6) as an oil (Found: M^+ , 238.120 800 0. $C_{13}H_{18}O_4$ requires M , 238.120 509 3); ν_{\max} 1 732 and 1 652 cm^{-1} ; δ_H (90 MHz) 1.25 (6 H, t, $2 \times$ Me), 3.0 (4 H, br s, $2 \times$ ring CH₂), 4.15 (4 H, q, $2 \times$ CH₂), 4.95 (2 H, br s, $2 \times =CHH$), and 5.39 (2 H, br s, $2 \times =CHH$); m/z 238 (M^+ , 0.1%), 86 (64), and 84 (100).

5-Isopropenyl- $\alpha,\alpha,\alpha',\alpha'$ -tetramethylbenzene-1,3-dimethanol (7) as a solid, m.p. 135 °C (26%) (Found: M^+ , 234.162 500 0. $C_{15}H_{22}O_2$ requires M , 234.161 980 2); ν_{\max} 3 380, 1 626, and 1 594 cm^{-1} ; δ_H (90 MHz) 1.5 (12 H, s, $4 \times$ Me), 2.2 (3 H, br s, allylic Me), 5.1 (1 H, br s, =CH), 5.4 (1 H, br s, =CH), and 7.4–7.6 (3 H, m, ArH); δ_C (22.5 MHz) 22 (Me), 32, 73, 122, 129, 130, and 160; m/z 234 (M^+ , 31%), 219 ($M^+ - Me$, 79), 159 (32), 57 (41), and 43 (100).

Diethyl 5-(cyclohex-1-enyl)indane-2,2-dicarboxylate (9) as an oil (20%) (Found: M^+ , 342.184 000 0. $C_{21}H_{26}O_4$ requires M , 342.183 109 6); ν_{\max} 1 591 and 1 562 cm^{-1} ; δ_H (90 MHz) 1.2 (6 H, t, $2 \times$ Me), 1.5 (4 H, m, $2 \times$ CH₂), 2.0 (4 H, m, allylic CH₂), 3.5 (4 H, br s, $2 \times$ ring CH₂), 4.1 (4 H, q, $2 \times$ CH₂), 6.0 (1 H, m, =CH), and 7.1 (3 H, m, ArH); δ_C (22.5 MHz) 14, 22, 23, 25, 28, 40, 40.5, 61, 62, 76, 77, 79, 121, 123, 124, 136, 138, and 172; m/z 342 (M^+ , 64%) and 268 ($M^+ - EtOCOH$, 100).

Diethyl 5,6-Bis(hydroxymethyl)indane-2,2-dicarboxylate (10) as a pale yellow oil (15%) (Found: C, 63.7; H, 6.9. $C_{17}H_{22}O_6$ requires C, 63.34; H, 6.88%); ν_{\max} 3 339 and 1 731 cm^{-1} ; δ_H (90 MHz) 1.1 (6 H, t, $2 \times$ Me), 3.5 (4 H, br s, $2 \times$ ring CH₂), 4.1 (4

H, q, $2 \times$ CH₂), 4.6 (4 H, s, $2 \times$ CH₂O), and 7.1 (2 H, s, ArH); δ_C (22.5 MHz), 14, 40, 61, 62, 64, 125, 138, 140, and 172; m/z 322 ($M^+ - 2$, 34%), 278 (37), 277 (75), 249 (48), 248 (50), 230 (100), 221 (32), 158 (38), 157 (38), 129 (60), and 128 (39).

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