

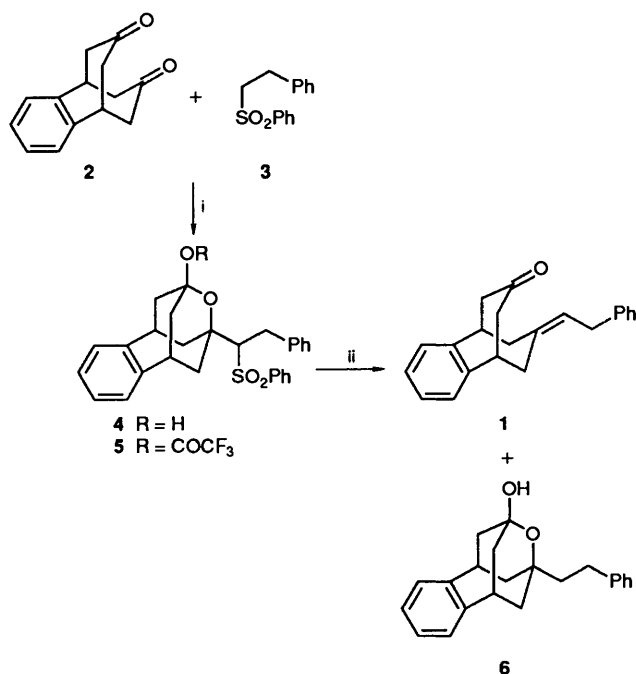
Transannular Cyclisation Products of a 7-Ethylidenebicyclo[3.3.2]decan-3-one

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Reaction of the enone **1** with toluene-*p*-sulphonic acid in solvent toluene at reflux furnished the products of ring closure **7–11**.

We have synthesized the enone **1** with the purpose of using it as a model for studying the stereochemistry of the S_E reaction.¹ In the course of investigating its cyclisation, which was to form the basis of our stereochemical studies, we observed the formation of a number of unexpected products when enone **1** was heated at reflux in solvent toluene in the presence of varying amounts of toluene-*p*-sulphonic acid (PTSA). This paper reports the structure of these compounds and speculates on their mode of formation.

The enone **1** was prepared as follows: reaction of the dione **2**² with the lithium salt of phenethyl phenyl sulphone **3**³ in tetrahydrofuran (THF) at -78°C furnished the hemiacetal sulphone **4** in almost quantitative yield. It was found essential to quench the reaction at below -40°C , otherwise yields of product **4** were poor. The trifluoroacetate **5**, formed quantitatively when a solution of compound **4** in anhydrous THF was treated with trifluoroacetic anhydride (TFAA) at 20°C for



Scheme 1 Reagents: i, BuLi; ii, Na/Hg

24 h, was dissolved in a mixture of buffered dry THF and methanol and was then reduced with sodium amalgam, furnishing the enone **1**, C₂₂H₂₂O, m.p. $160\text{--}162^\circ\text{C}$ in 83% yield, accompanied by the hemiacetal **6**^{4,5} (Scheme 1). The structure of the enone was supported, *inter alia*, by an intense peak in the IR spectrum at 1685 cm^{-1} (C=O), a triplet in the ¹H NMR spectrum at δ 5.5 (>C=CHCH₂Ph), and a signal at δ 210.75 (C=O) in the ¹³C NMR spectrum. Enone **1** when heated in toluene for 52 h under argon in a sealed tube afforded the expected enol **7** as sole product. Addition, in separate

experiments, of increasing amounts of PTSA, afforded, progressively, compounds **7–11**, compounds **7** and **8** being formed at low acid concentration and compounds **9–11** at higher acid concentration (see Experimental section). The structures of these products are supported by microanalysis, high-resolution MS, and salient spectroscopic characteristics as follows: the styrenol **7**, C₂₀H₂₂O, m.p. $169\text{--}171^\circ\text{C}$, had λ_{max} 253 nm (ϵ 17 600) (PhCH=CHR); $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3590 (π -bonded OH); δ_{H} 6.30 and 6.53 (ABq, J 16 Hz) (*trans*-CH=CH); δ_{C} 90.3 (s) ($\geq\text{C-OH}$), 129.4 (d) (PhCH=CH) and 136.2 (d).†

Diol **8**, C₂₂H₂₄O₂, m.p. $143\text{--}144^\circ\text{C}$, had $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3600 (unbonded OH); δ_{H} 1.68 (2 H, s, D₂O-exchangeable) (2 \times OH); δ_{C} 58.9 (1 C, d) [$>\text{C}(\text{OH})\text{CHC}(\text{OH})$] and 74.6 (2 C, s). Close inspection of the ¹³C NMR spectrum confirms the equivalence, as required, of only those pairs of C-atoms that are enantiotopic with respect to the plane defined by the fused aromatic ring, *i.e.* AA', BB' and CC'.

The tetrahydrofuran **9**, C₂₂H₂₂O, m.p. $159\text{--}161^\circ\text{C}$, had δ_{H} 1.75 (1 H, dd, J 12 and 11.6 Hz), 2.26 (1 H, dd, J 12 and 5 Hz) (OCHCH₂C-) and 5.24 (1 H, dd, J 11.6 and 5 Hz). This AX₂ spectrum was located by a 2D COSY experiment.

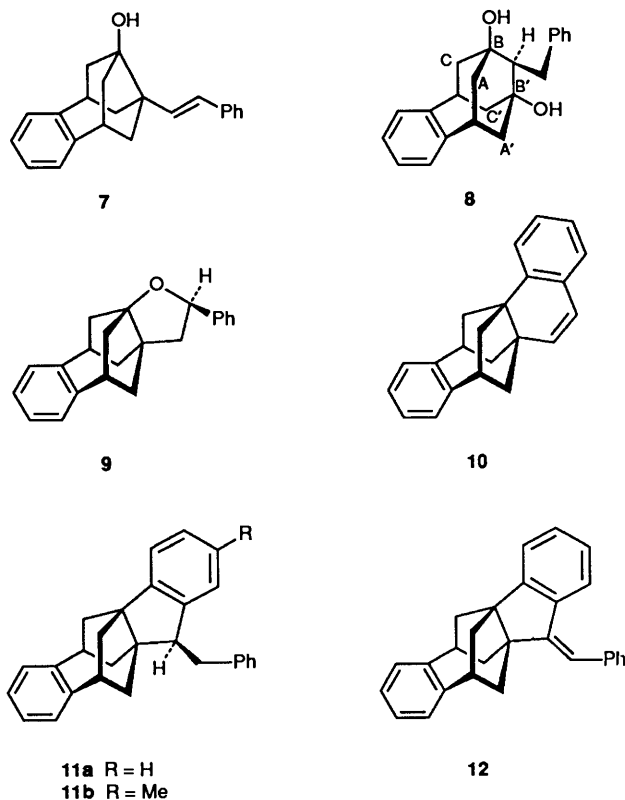
The styrene **10**, C₂₀H₂₀, m.p. $211\text{--}212^\circ\text{C}$, had $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1490, 1450, 791 and 758 (mono- and *ortho*-disubstituted benzenes); δ_{H} 6.12 (1 H, d, J 9 Hz) and 6.27 (1 H, d, J 9 Hz) (*cis*-CCH=CHC-).

In accord with the plane of symmetry passing through the styrene system, the ¹³C NMR spectrum has only *one* aromatic C-atom of double intensity (δ_{C} 145.9), *two* aromatic CHs of double intensity (δ_{C} 125.7, 129.6), *one* non-aromatic CH (δ_{C} 43.3), *two* CH₂s (δ_{C} 52.0, 53.7) and *four* unique aromatic CHs (δ_{C} 125.5, 126.7, 127.0, 127.7). The two olefinic carbons (δ_{C} 120.4, 135.2) were identified by a 2D $\delta_{\text{C}}/\delta_{\text{H}}$ direct correlation experiment.

Hydrocarbons **11a**, C₂₈H₂₆, m.p. $169\text{--}171^\circ\text{C}$, and **11b**, C₂₉H₂₈, m.p. $150\text{--}152^\circ\text{C}$, were obtained respectively by reflux of enone **1** in either benzene or toluene at high acid concentration (10 mg cm⁻³). They have virtually identical ¹H and ¹³C NMR spectra, but for the differences arising from the tolyl methyl group in species **11b**. They are tentatively formulated on the basis of their likely mode of formation (see below), their ¹³C NMR spectra and the conversion of hydrocarbon **11a** into the styrene **12**. The high-resolution MS of compound **11a** has its base peak at m/z 271.1479, corresponding to the loss of benzyl from the parent ion. In accord with the proposed structure, hydrocarbon **11a**, when

† Multiplicities (q, t, d, s) refer to off-resonance H-decoupled spectra and denote H-substitution (Me, CH₂, CH, C).

heated with *N*-bromosuccinimide (NBS) at reflux in CCl_4 , led directly to the styrene **12**, $\text{C}_{28}\text{H}_{24}$, m.p. 207–209 °C, *via* the benzylic bromide that could be detected in the high-resolution MS of the crude product [m/z 438.0991/440.0979: $\text{C}_{28}\text{H}_{25}^{79}\text{Br} - \text{H}^+/\text{C}_{28}\text{H}_{25}^{81}\text{Br} - \text{H}^+$].



The ^1H spectrum of product **12** showed one sharp singlet at δ 6.09 (1 H) (=CHPh) and a complex multiplet, superficially a triplet of quartets centred at δ 3.20, corresponding to the quartet of quartets centred at δ 3.23 in the spectrum of the parent **11a** (bridgehead CHs). The ^{13}C NMR spectrum showed the equivalence of carbons enantiotopic with respect to the plane passing through the dihydroindene system and the required number of non-aromatic CH_2 , CH and C signals (δ_{C} 40.3, 43.5, 41.4, 44.6) and olefinic and aromatic CH and C signals (δ_{C} 118.8, 121.2, 121.3, 123.8, 126.3, 126.5, 126.6, 128.0, 128.2, 142.8, 146.5, 154.0, 161.1 and 163.3).

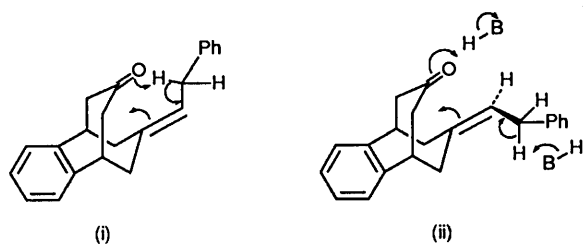


Fig. 1

The formation of compounds **7**–**11** from the enone **1** merits some comment. The enol **7** can be generated by two pathways: (i) an ene reaction [Fig. 1(i)] or (ii) an S_{E} reaction [Fig. 1(ii)]. Our detailed study^{6,7} of this cyclisation suggests that the purely thermal cyclisation (toluene at reflux without added PTSA) proceeds by an ene mechanism [Fig. 1(i)], while the acid-catalysed S_{E} reaction [Fig. 1(ii)] comes progressively into play with increasing concentrations of added acid. Formation of diol

8 is in accord with the mechanism indicated in Fig. 2, which we have observed to function when enone **1** is treated with acidic reagents. Thus X can be Cl when the reagent is trimethyloxonium hexachloroantimonate, or $\text{OCH}_2\text{CH}_2\text{OH}$ in the product

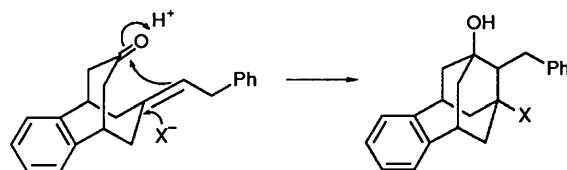
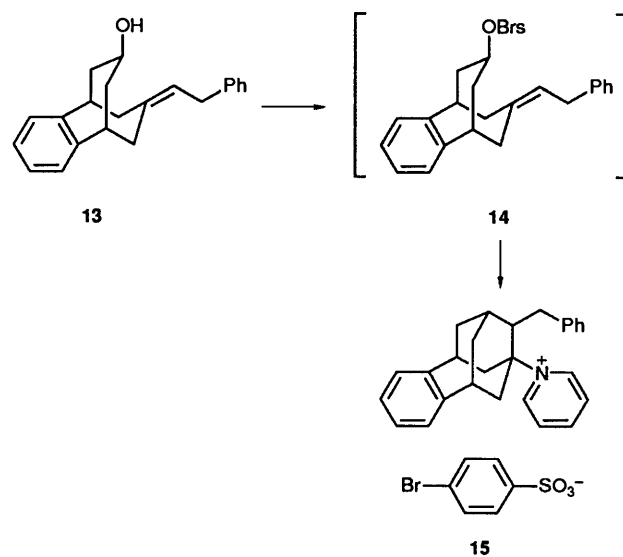


Fig. 2

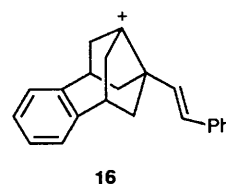
of attempted acetalisation under standard conditions.⁶ In the formation of diol **8** under 'anhydrous' conditions the source of X = OH is presumably hydrated PTSA. The propensity to generate the benzo-fused tricyclo[3.3.2.1]undecane system **8** was even more strikingly demonstrated in attempts to form the brosylate **14** under normal conditions from the alcohol **13**, when the salt **15** was the only product, obtained in high yield (Scheme 2).⁶ The tetrahydrofuran **9** is unproblematic since it



Scheme 2

represents the acid-catalysed cyclisation product of the enol **7** and is readily and irreversibly formed from enol **7** under the reaction conditions.

The hydrocarbons **10** and **11a,b** are perhaps the most interesting, being the most unexpected products. Both must depend for their formation on the availability of the bridgehead cation **16** from protonated enol **7**. Cyclisation to the



spirodihydronaphthalene **10** must be preceded by *Z* to *E* isomerisation (*via* a benzylcyclopropyl cation?) and arylation at the bridgehead. Formation of species **11a** and **11b** presumably involves arylation of the same cation **16** by solvent benzene or toluene and then internal arylation at the styryl β -carbon atom. Interestingly, both hydrocarbons **10** and **11** are formed from diol **8** at high acid concentration, presumably *via* the enol **7**.

Table 1 Product mixtures

	Product					
	7	8	9	10	11a	11b
i	+++					
ii	+++	+++				
iii	+	++				
iv	+	+++				
v			+	+		+++
vi			+	+	+++	

* Signs indicate relative amounts.

Experimental

All m.p.s were determined on a Kofler hot-stage apparatus, and are uncorrected. Routine IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer. ^1H NMR spectra were obtained for solutions in CDCl_3 , unless otherwise stated, with tetramethylsilane as internal standard, at 100 MHz on a Varian XL 100 spectrometer and at 200 MHz on a Bruker WP 200 SY spectrometer, both employing a deuterium lock system setting either chloroform (CHCl_3) in CDCl_3 at δ 7.25 or methanol (MeOH) in CD_3OD at δ 3.35 as internal standard. J -Values are given in Hz. ^{13}C NMR spectra were recorded at 55 MHz on the Bruker WP 200 SY spectrometer, either in deuteriochloroform setting the reference CDCl_3 signal at δ_{C} 77.0, in perdeuteriomethanol setting the reference CD_3OD signal at δ_{C} 49.0, or in perdeuteriodimethyl sulphoxide setting the reference $(\text{CD}_3)_2\text{SO}$ signal at δ_{C} 40.0. Hydrogen-substitution patterns (Me, CH_2 , CH, C) were obtained by off-resonance decoupling or from DEPT spectra and are shown as (q), (t), (d) and (s), respectively. High-resolution mass spectra were recorded on a V.G./Kratos M.S. 9025 spectrometer. Preparative TLC (PLC) were run, using the developing solvents indicated, on precoated Merck Kiesel gel 60-F254 20 \times 20 cm, 0.25 mm plates.

Dione 2.—Prepared according to the method of Fohlisch,² this had m.p. 196–198 °C (lit.,² 196–199 °C); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1705; $\delta_{\text{H}}(100 \text{ MHz})$ 2.85 (8 H, d, J 4), 3.22 (2 H, m) and 7.18 (4 H, s).

Hemiacetal Sulphone 4.—The sulphone **3**³ (1.9 g, 7.7 mmol) was dissolved in anhydrous THF (15 cm^3) under dry argon and the solution was stirred and cooled to -70°C . Butyllithium (5.2 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 7.8 mmol) was added and the yellow solution was allowed to warm to 0°C and was then recooled to -70°C . A solution of the dione **2** (1.7 g, 7.9 mmol) in dry THF (35 cm^3) was added to the reaction mixture in one portion and the mixture was stirred for 2 h. Saturated aq. ammonium chloride (25 cm^3) was added to the mixture at -70°C , which was then allowed to warm to room temperature, and the product was isolated by extraction into methylene dichloride to give a solid (3.6 g, 100%). A portion of this was recrystallised from ethanol to give crystals of the hemiacetal sulphone **4**, m.p. 238.5–240 °C (Found: C, 72.8; H, 6.0; S, 6.75. $\text{C}_{28}\text{H}_{28}\text{O}_4\text{S}$ requires C, 73.0; H, 6.15; S, 7.0%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3350, 1495, 1300, 1160, 1140 and 735; $\delta_{\text{H}}(100 \text{ MHz})$ 1.75–2.10 (6 H, m), 2.30–2.45 (2 H, m), 3.13–3.40 (4 H, m), 3.53–3.65 (1 H, m), 6.84–7.30 (9 H, m), 7.30–7.60 (3 H, m) and 7.65–7.80 (2 H, m).

Enone 1.—The hemiacetal sulphone **4** (0.5 g, 1.1 mmol) was dissolved in anhydrous THF (30 cm^3) and TFAA (5 cm^3) was added. The reaction mixture was stirred for 24 h under an inert atmosphere and the solvent and reagent were then removed under reduced pressure to give the trifluoroacetate **5** (608 mg,

100%); $\nu_{\text{max}}(\text{thin film})/\text{cm}^{-1}$ 1785; δ_{H} 2.10–2.60 (8 H, m), 3.15–3.43 (4 H, m), 3.65 (1 H, t, J 5), 7.00–7.20 (9 H, m), 7.35–7.55 (3 H, m) and 7.67–7.80 (2 H, m).

This trifluoroacetate was used without further purification. It was dissolved in a mixture of anhydrous THF (30 cm^3) and dry methanol (20 cm^3) and disodium hydrogen orthophosphate (200 mg) was added to the stirred mixture cooled to -70°C . Sodium amalgam⁸ (3 g) was added, and the reaction mixture was gradually allowed to warm to -20°C over a period of several hours, kept at -20°C for 3 h and then allowed to warm to room temperature, when it was stirred for a further 8 h. Work-up gave the enone **1** (273 mg, 83%), m.p. 160–162 °C (Found: C, 87.15; H, 7.45%; M^+ , 302.1671. $\text{C}_{22}\text{H}_{22}\text{O}$ requires C, 87.35; H, 7.35%; M , 302.1671); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1685, 1600, 1580, 1495, 760 and 755; $\delta_{\text{H}}(100 \text{ MHz})$ 2.0–2.8 (8 H, m), 2.9–3.7 (4 H, m), 5.5 (1 H, t, J 8) and 7.2 (9 H, s); δ_{C} 33.89 (t), 34.65 (t), 40.85 (d), 42.29 (d), 44.08 (t), 48.59 (2t), 125.98 (d), 127.40 (d), 128.54 (d), 132.68 (d), 134.82 (s), 140.65 (s), 144.74 (s) and 210.75 (s).

A common by-product of this reaction was the hemiacetal **6**, m.p. 218–220 °C (Found: C, 82.4; H, 7.55%; M^+ , 320.1781. $\text{C}_{22}\text{H}_{24}\text{O}_2$ requires C, 82.45; H, 7.55%; M , 320.1776); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3330, 1170, 1115, 1000, 770 and 700; $\delta_{\text{H}}(100 \text{ MHz})$ 1.50–2.10 (10 H, m), 2.57–2.80 (2 H, m), 2.93 (1 H, s), 3.10–3.35 (2 H, m) and 7.10–7.30 (9 H, m).

Cyclisation Experiments.—Each of five 20 cm^3 glass ampoules (i)–(v) was charged with enone **1** (60 mg) and dry toluene (6 cm^3 , dried over sodium wire and kept over 4 Å molecular sieves). PTSA monohydrate (Aldrich) (mg) was added as follows: i (0); ii (2); iii (6); iv (12); v (22); in ampoule v—as v, but with dry benzene instead of toluene. The ampoules were sealed under argon and heated in an oil-bath at 120°C for 52 h. Work-up was by dilution with diethyl ether (10 cm^3), washing successively with aq. NaHCO_3 (sat., 2 \times 10 cm^3) and brine (2 \times 10 cm^3), drying over anhydrous Na_2SO_4 , and removal of solvent under reduced pressure. The product mixtures (see Table 1) were analysed by NMR spectroscopy. Analytical samples were obtained by PLC with ethyl acetate–hexane mixtures as eluent.

Styrenol 7.—M.p. 169–171 °C (Found: C, 87.5; H, 7.5%; M^+ , 302.168. $\text{C}_{22}\text{H}_{22}\text{O}$ requires C, 87.4; H, 7.3%; M , 302.167); $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$ 253 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 17 600); $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3590, 2950, 1495, 1490, 1450 and 1090; $\delta_{\text{H}}(200 \text{ MHz})$ 1.63–2.75 (4 H, m), 3.05–3.30 (2 H, t, J 7, 6.30 and 6.53 (2 H, q, J 16) and 7.05–7.50 (9 H, m); $\delta_{\text{C}}(55 \text{ MHz})$ 45.0 (d), 48.0 (t), 50.7 (t), 55.2 (s), 90.3 (s), 126.97 (d), 127.2 (d), 128.5 (d), 128.6 (d), 129.4 (d), 136.2 (d), 137.5 (s) and 144.7 (s).

Diol 8.—M.p. 143–144 °C (Found: C, 82.3; H, 7.7. $\text{C}_{22}\text{H}_{24}\text{O}_2$ requires C, 82.5; H, 7.6%; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3600, 1495, 1030, 755 and 700; $\delta_{\text{H}}(200 \text{ MHz})$ 1.68 (2 H, s, D_2O -exchangeable) and 1.75–2.40 (9 H, m); $\delta_{\text{C}}(55 \text{ MHz})$ 30.1 (t), 36.6 (2 C, t), 38.8 (d), 39.3 (d), 45.4 (2 C, t), 58.9 (d), 74.6 (2 C, s), 125.8 (d), 126.8 (d), 128.1 (d), 128.2 (d), 128.6 (d), 129.2 (d), 144.0 (s), 144.9 (s) and 145.7 (s).

Tetrahydrofuran 9.—M.p. 159–161 °C (Found: C, 87.5; H, 7.25%; M^+ , 302.1671. $\text{C}_{22}\text{H}_{22}\text{O}$ requires C, 87.4; H, 7.3%; M , 302.1670); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1495, 1490, 1450, 1080, 1031, 1018, 764, 700 and 547; $\delta_{\text{H}}(200 \text{ MHz})$ 1.7–2.6 (10 H, m), 3.39 (1 H, t, J 12), 3.53 (1 H, t, J 12), 5.24 (1 H, dd, J 11.6, 5) and 7.1–7.5 (9 H, m); $\delta_{\text{C}}(55 \text{ MHz})$ 46.7 (t), 47.6 (d), 47.9 (t), 48.3 (t), 49.5 (t), 50.8 (t), 52.5 (d), 84.1 (d), 126.0 (d), 126.3 (d), 127.5 (d), 128.3 (d), 129.3 (d), 129.5 (d), 141.1 (s), 144.8 (s) and 145.1 (s).

Styrene 10.—M.p. 211–212 °C (Found: C, 92.7; H, 7.3%; M^+ ,

284.1575. $C_{22}H_{20}$ requires C, 93.0; H, 7.05%; M , 284.1565; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1490, 1450, 1049, 792 and 758; $\delta_{\text{H}}(200 \text{ MHz})$ 2.0–2.4 (8 H, m), 2.96 (2 H, m), 6.12 (1 H, d, J 9), 6.27 (1 H, d, J 9) and 7.06–7.25 (8 H, m); $\delta_{\text{C}}(55 \text{ MHz})$ 43.4 (d), 52.0 (t), 53.7 (t), 120.4 (d), 125.5 (d), 125.7 (d), 126.7 (d), 127.0 (d), 127.7 (d), 129.6 (d), 135.2 (d), 145.1 (s) and 145.8 (s).

Hydrocarbon 11a.—M.p. 169–171 °C (Found: C, 92.85; H, 7.2%; M^+ , 362.2051. $C_{28}H_{26}$ requires C, 92.8; H, 7.2%; M , 362.2034); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1492, 1444, 758, 732 and 699; $\delta_{\text{H}}(200 \text{ MHz})$ 1.5–3.3 (13 H, m) and 7.05–7.5 (13 H, m); $\delta_{\text{C}}(55 \text{ MHz})$ 30.9 (t), 32.1 (t), 36.2 (t), 39.1 (t), 40.0 (s), 41.0 (d), 41.8 (d), 45.7 (s), 46.3 (d), 55.3 (d), 121.0 (d), 125.2 (d), 125.5 (d), 125.8 (d), 126.2 (d), 126.3 (d), 126.4 (d), 127.8 (d), 128.2 (d), 128.3 (d), 141.8 (s), 146.8 (s), 147.3 (s), 149.0 (s) and 153.9 (s).

Hydrocarbon 11b.—M.p. 150–152 °C (Found: C, 92.4; H, 7.4%; M^+ , 376.2201. $C_{29}H_{28}$ requires C, 92.55; H, 7.45%; M , 376.2191); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1516, 1492, 1471, 1452, 1447, 758 and 735; $\delta_{\text{H}}(200 \text{ MHz})$ 1.5–3.3 (13 H, m), 2.34 (3 H, s) and 7.05–7.35 (12 H, m); $\delta_{\text{C}}(55 \text{ MHz})$ 20.87 (q), 30.9 (t), 32.2 (t), 36.2 (t), 39.0 (t), 39.6 (s), 41.0 (d), 41.8 (d), 45.6 (s), 55.3 (d), 121.0 (d), 125.1 (d), 125.2 (d), 125.5 (d), 126.2 (d), 126.3 (d), 126.4 (d), 127.7 (d), 128.1 (d), 128.3 (d), 129.0 (d), 135.1 (s), 141.8 (s), 146.1 (s), 146.8 (s), 147.4 (s) and 153.9 (s).

Styrene 12.—M.p. 207–209 °C (Found: M^+ , 360.1870.

$C_{28}H_{24}$ requires M , 360.1878); $\delta_{\text{H}}(200 \text{ MHz})$ 1.5–1.62 (2 H, m), 2.17–2.52 (6 H, m), 3.20 (2 H, tq), 6.08 (1 H, s) and 7.03–7.58 (13 H, m); $\delta_{\text{C}}(55 \text{ MHz})$ 40.3 (t), 41.4 (d), 43.5 (t), 44.6 (s), 118.8 (d), 121.2 (d), 123.8 (d), 126.4 (d), 126.6 (d), 128.0 (d), 128.3 (d), 142.8 (s), 146.5 (s), 154.0 (s), 161.1 (s) and 163.3 (s).

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