Electronic Supplementary information:

Diastereomeric cyclic tris-allenes

Hussein H. Mustafa, Mark S. Baird, Juma'a R. Al Dulayymi and Viacheslav V. Tverezovsky

4,4,8,8,12,12-Hexabromotetracyclo[9.1.0.0^{3,5}.0^{7,9}]dodecane

Sodium hydroxide solution (17.0 g, 425 mmol, 50 %) was added slowly to a stirred solution of (1*Z*,4*Z*,7*Z*)-cyclonona-1,4,7-triene (2.0 g, 16.6 mmol), bromoform (42.0 g, 14.5 ml, 166.6 mmol) and cetremide (0.5 g, 1.35 mmol) in dichloromethane (20 ml). The mixture was stirred rapidly for 72 hrs at room temperature. The product was extracted with dichloromethane (3 x 100 ml) and the combined organic layers were washed with water and brine (150 ml), dried over MgSO₄ and the solvent was evaporated. The bromoform was removed by distillation under vacuum (.5 mmHg), then the oily residue was treated with dichloromethane to give a white precipitate which was 4,4,8,8,12,12-hexabromotetracyclo[9.1.0.0^{3,5}.0^{7,9}]dodecane **4** (6.5 g, 61%), as a white solid, mp 247-250 °C [lit ^[1] m.p 240-246 °C]; $\delta_{\rm H}$ (400 MHz): 2.45 (3H, d, *J* 14.8 Hz), 1.82 (6H, br.q, *J* 9.3 Hz), 0.78 (3H, m); $\delta_{\rm c}$ (126 MHz): 32.4, 31.7, 24.6; $v_{\rm max}/{\rm cm}^{-1}$: 1465, 895, 777, 698, 515, 494.

The filtrate was concentrated under reduced pressure to give a residue, 4,4,11,11-tetrabromo tricyclo[8.1.0.0^{3,5}]undec-7-ene **5** (1.5 g, 20%) as a colourless solid which was one spot by tlc, mp 155-157 °C [Found M⁺: 459.7529; (C₁₂H₁₂Br⁷⁹₄)⁺ requires: 459.7672]. This showed $\delta_{\rm H}$ (400 MHz): 5.66 (2H, br.pent., *J* 10.48 Hz), 2.54 (1H, d, *J* 14.8 Hz), 2.40 (2H, dd, *J* 4.0, 13.56 Hz), 1.8 (2H, m), 1.68 (4H, m), 1.0 (1H, m); $\delta_{\rm c}$ (126 MHz): 128.0, 34.4, 33.8, 31.6, 24.5; $v_{\rm max}$ / cm⁻¹: 3017, 1662, 1465, 783, 485; m/z 460, 462, 464, 466, 468.

1. C. D. Poulter, R. S. Boikes, J. I. Brauman, S. Winstein, J. Amer. Chem. Soc., 1972, 94, 2291-2296.

Preparation of (R,R,R) & (R,R,S)-Cyclododeca-1,2,5,6,9,10-hexaene

Methyl lithium in ether (10.4 ml, 15.7 mmol) was added to a stirred suspension of 4,4,8,8,12,12-hexabromotetracyclo[9.1.0.0^{3,5}.0^{7,9}]dodecane **4** (1.0 g, 1.6 mmol) in dry ether (20 ml) at room temperature under a dry nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5 min, cooled to -20 °C and quenched with water (5 ml), then allowed to reach room temperature. The mixture was extracted with ether (3 x 15 ml), and the combined organic layers were dried and the solvent evaporated. The residue was purified by column chromatography over silica gel eluting with petrol : ethyl acetate (10:1). The product was obtained as a mixture (0.2 g, 81%) of two diastereoisomers. Silica gel (25 g) was added

to silver nitrate (10 g) in acetonitrile (90 ml) in a flask covered with aluminium foil and stirred for 10 min. The solvent was evaporated to give the silica powder which used for the column. The mixture was separated by column chromatography, eluting with petrol : ethyl acetate (10:1) to give two fractions. The first fraction was a racemic mixture of (S,S,R) and (R,R,S)-cyclododeca-1,2,5,6,9,10-hexaene 8 (0.09 g, 37% from 4) as an oil which was a single spot on TLC on silver nitrate impregnated silica gel plates [Found (M+H)⁺: 157.1010; $(C_{12}H_{12}+H)^+$ requires: 157.1012].** This showed δ_H (400 MHz, CDCl₃): 5.3 (4H, m), 5.2 (2H, m), 2.74 (2H, complex m, $H_{8,12}$), 2.63 (2H, m, $H_{4,4'}$), 2.53 (2H, complex m, $H_{8',12'}$); δ_c (126 MHz): 206.7 $(C_{2,6})$, 205.8 (C_{10}) , 91.7, 90.2, 89.8, 28.2 (C_4) , 27.7 $(C_{8,12})$; δ_H (400 MHz, C_6D_6) : 5.24 (2H, m, including J ca. 5 Hz); 5.18 (2H, m, including J ca. 5 Hz), 5.13 (2H, m), 2.70 (2H, m, H_{8,12}), 2.49 (distorted septet, J ca. 4 Hz, H_{4,4}), 2.25 (2H, complex m, H_{8',12'});* v_{max}/cm^{-1} : 2910, 1963, 1434, 790, 720. The second fraction was (S,S,S) and (R,R,R)-cyclododeca-1,2,5,6,9,10-hexaene 7 (0.02 g, 8% from 4), a colourless solid, m.p 53-55 °C [Found $(M+H)^+$: 157.1010; $(C_{12}H_{12}+H)^+$ requires: 157.1012].** This showed $\delta_{\rm H}$ (400 MHz, CDCl₃): 5.22 (6H, complex m, including J ca. 4 Hz), 2.62 (6H, complex m, including J ca. 4 Hz); δ_H (400 MHz, C₆D₆): 5.18 (6H, complex m, including J ca. 4 Hz), 2.47 (6H, complex m, including J ca. 4 Hz); δ_c (126 MHz, $CDCl_3$: 206.5, 89.8, 27.8; v_{max}/cm^{-1} : 2919, 2852, 1964, 1715, 1438, 871, 721.

Compound 7 could also be partly separated from 8 by partial crystallisation from methanol.

* Selective decoupling of the signal at $\delta_{\rm H}$ 5.17 caused the signals at 2.70 and 2.25 to appear as two broad doublets (*J ca.* 15 Hz). Irradiation at 5.23 caused these signals to be reduced to doublets of quartets (*J ca.* 16, 4 Hz) and the signal at 2.49 was partly decoupled a broad singlet.

** Thanks are due to the EPSRC Mass Spectrometry service in Swansea for obtaining these accurate mass values

Hydrogenation of cyclododeca-1,2,5,6,9,10-hexaenes

Palladium, (10 %) on carbon (0.5 g, 4.69 mmol) was added to a stirred solution of a crude mixture of cyclododeca-1,2,5,6,9,10-hexaenes **7** and **8** (0.20 g, 1.28 mmol). The mixture was stirred at room temperature for 16 hrs under hydrogen then filtered and evaporated under reduced pressure to give cyclododecane (0.18 g, 90 %); M^+ m/z: 168; δ_H (400 MHz): 1.34 (24H, s); δ_c (126 MHz): 23.7.

Proton and carbon NMR data

(all proton data shown were obtained at 400 MHz, carbon at 126 MHz)

The tris-allene (8)

In C₆D₆







Proton-proton correlation



Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013

Proton-carbon correlation:



In CDCl₃



7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 f1(ppm)



Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013



The trisallene (7)









In CDCl₃





Selective decoupling at 2.6:



Selective decoupling at 5.2:

Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013





Quantum mechanical calculations

Preliminary semi-empirical calculations out on the allene (7) using the AM1 method showed that the C_3 form was an energy minimum, with the D_3 form a third order transition state some 6.7 kcal/mol higher in energy. The symmetry axes for the D_3 form are shown below:



The atomic coordinates for the D_3 form are as below:

С	0.00000000	0.00000000	0.00000000
С	1.23615418	0.64926705	0.49199445
С	2.43815418	0.56726705	-0.00000555
С	3.64015418	0.64926705	-0.49200555
С	4.87630836	-0.00000000	-0.00001109
С	4.82051471	-1.39517348	0.49198630
С	4.14849895	-2.39513698	-0.00000944
С	3.61851135	-3.47710049	-0.49200550
С	2.43815418	-4.22300692	-0.00000555
С	1.25779701	-3.47710049	0.49199440
С	0.72780942	-2.39513698	-0.00000166
С	0.05579365	-1.39517348	-0.49199739
Н	-0.63284582	-1.59873295	-1.33700555
Н	0.73719248	-3.97169836	1.33700531
Н	2.07315418	-4.89873295	-0.82800555
Н	2.80315418	-4.89873295	0.82799445
Н	4.13911588	-3.97169836	-1.33701640
Н	5.50915418	-1.59873295	1.33699445
Н	5.64400145	0.02176538	-0.82801367
Н	5.27900710	0.65396066	0.82798882
Н	3.80818336	1.34742440	-1.33701565
Н	1.06812500	1.34742440	1.33700456
Н	-0.76769309	0.02176538	0.82800258
Н	-0.40269874	0.65396066	-0.82799991

Preliminary calculations *ab initio* were also carried out on the allene (7) (personal communication, R. A. Davies and J. Morris), using Gaussian 03 with a HF/6-31G(d) basis set this gave similar results. Calculations with a higher level basis set are on-going.

Tetrabromide 5





Selective decoupling of methylene protons between cyclopropanes:



