150. Structure and Thermal Behaviour of Methylcyclopentadiene Dimers

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Dedicated to Dr. *G. Ohloff* on the occasion of his 65th birthday

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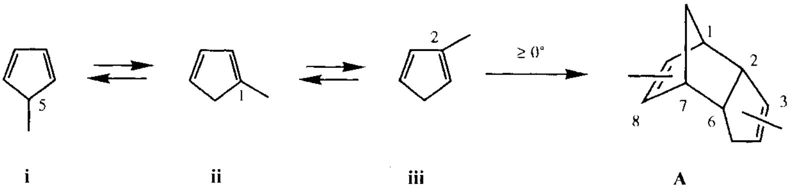
The mixture of isomeric dimethyl-*endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-dienes (**A**) resulting from *Diels-Alder* reactions of 1-, 2-, and 5-methylcyclopenta-1,3-dienes (**i–iii**, respectively) at 20° was shown by GLC analysis to consist of at least 10 components (*Table 1*). The structures of the six major isomers **1–6**, representing 96% of the total mixture, were established by ^{1}H- and ^{13}C-NMR spectroscopy. Whereas on heating up to 110° the proportions of **1**, **2**, **4**, and **6** remain nearly unaffected (±2%), the dimers **3** and **5**, formed in 22% and 24% yield, respectively, at 20°, isomerise above 70° reversibly *via* [3,3]-sigmatropic rearrangement and equilibrate at 110° to a *ca.* 10:1 ratio.

Introduction. – Owing to its large-scale availability [1], low price, and high synthetic potential, the multicomponent mixture of isomeric dimethyl-*endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-dienes (**A**; *Scheme 1*)¹) has found widespread use in organic chemistry [2] [3]. It is, therefore, surprising that neither a precise structure determination of the individual dimers nor a complete analysis of the isomeric composition of **A** has been reported.

Scheme 1



Csicsery [4] reported first on the presence of five dimers in a ratio of *ca.* 34:10:18:38:2, determined from a dimeric mixture obtained at 60°. While the *endo*-configuration of the skeleton of all these dimers was established (spectral analysis), no exact localisation of the Me groups was accomplished [4]. Despite later investigations [6a], this question has remained unresolved.

In connection with studies on structure-odour relationships in the group of fragrances with bridged tricyclic structures [7], we required as model compounds structurally well

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[1] The maximum number of possible isomers of **A** is 36, considering the fact that the three monomers **i–iii** readily isomerise at 20° *via* 1,5-H-shifts (equilibration ratio ~ 1:45:54 [5]), and that each monomer may undergo *Diels-Alder*-type self- and cross-dimerisation.

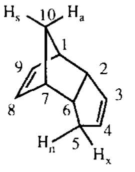
defined Me homologues of *endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-dienes, which are present in **A**. We, therefore, decided to undertake a thorough analysis of **A** and report here on the isolation, detailed structure proof, and thermal behaviour (up to ~ 110°) of the six major dimers **1**–**6**, which represent *ca.* 96% of the total dimeric mixture.

Results. – The analysis was effected on two dimeric mixtures of different origin. One (**A1**) was obtained by storage of freshly prepared methylcyclopentadienes **i**–**iii** during 7 days at 20° and the other (**A**) represents the commercially available equivalent [1]2). Capillary-column GLC (50 m, *Carbowax*-coated glass columns; 40°; He) indicated that both mixtures, except for some additional impurities (~ 5–8%) in **A** and small differences in the proportions of dimers **3** and **5**, are almost identical and contain at least 10 discernible, isomeric dimers. Their concentrations and GC retention times are presented in *Table 1*.

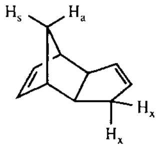
For the isolation of pure dimers **1**–**6**, mixture **A** was fractionally distilled at 1–4 Torr with bath temperature strictly maintained at $\leqslant$ 70°. Under these conditions, the main dimers **3** and **6** could be readily obtained in *ca.* 90% purity, whilst **1**, **2**, **4**, and **5** were highly enriched in the intermediate fractions. Their further purification was then achieved by prep. GLC on a *Carbowax* column (oven temp. 40°; injector: 70°).

Structural Assignment of Dimers **1**–**6**. The structural and configurational assignments of **1**–**6** were elucidated without ambiguity by interpretation of their ^{1}H- and ^{13}C-NMR spectra (decoupling and 2D experiments) and chemically from their individual behaviour when heated at 110°.

The ^{1}H-NMR data for **1**–**6** are summarised in *Table 2*; the data for *endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**iv**) and *exo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**v**) (^{1}H- [8] and ^{13}C-NMR [9]) are also presented and serve as reference spectra.



iv (*endo*)



v (*exo*)

The expected *endo*-configuration of the skeleton of **1**–**6** was confirmed by the following arguments. Firstly, the chemical shift of H_x–C(5) is 2.08–2.13 ppm and that of H_n–C(5) is 1.57–1.62 ppm; in the *exo*-isomer **v** the chemical shifts of these protons are at 2.42 and 1.86 ppm, respectively. Secondly, the chemical shift of H_a–C(10), which is between 1.19 and 1.26 ppm for **1**–**6**, is 1.51 ppm for **v**.

The C(4)-position of a Me group is indicated by the chemical shift of H_x–C(5). For **2**, **5**, and **6**, which possess a Me–C(3) group, the chemical shift of H_x–C(5) (*viz.* 2.11–2.13 ppm) is almost identical to that of the *endo*-isomer **iv**. In contrast, for **1**, **3**, and **4**, in which there is a Me–C(4) group, the signal for H_x–C(5) is shifted upfield to 2.05–2.08 ppm.

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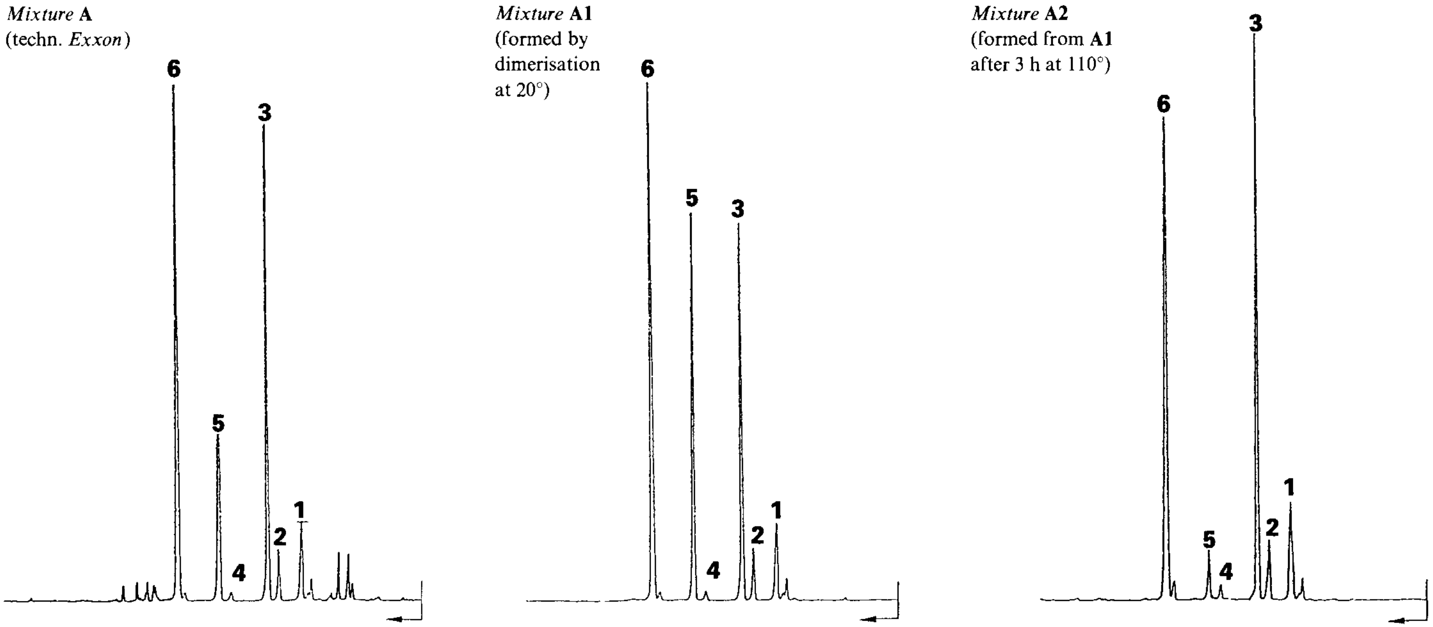
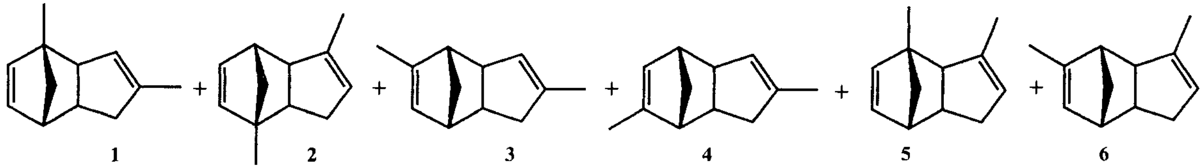
2) Obtained from *Exxon Inc.*

Table 1. *GLC Analysis*[a]) *of the Mixtures* **A**, **A1**, *and* **A2** *of Dimeric Methylcyclopentadienes* (distribution and thermal behaviour of the main dimers)



Distribution of dimers [%]



Mixture	**1**	**2**	**3**	**4**	**5**	**6**	+ unknown
A	5	3	29	2	10	36	15
A1	9	4	22	1	24	36	4
A2	7	5	42	1	4	36	5

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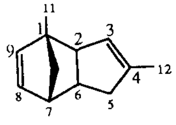
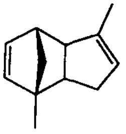
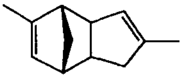
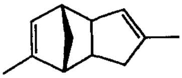
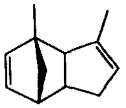
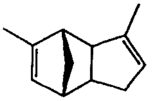
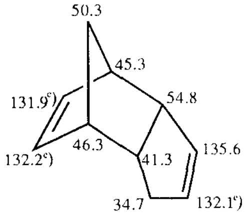
[a]) Conditions: 50-m capillary *Carbowax* column; 40°; He; t_R values 10–15 min.

Table 2. *^{1}H-NMR Assignments* (360 MHz, $CDCl_3$) *for Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene Isomers* **1–6**

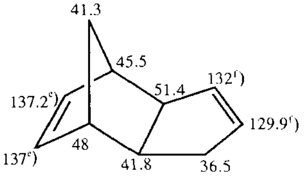
Compound	δ [ppm]	*J* [Hz]
 **1**[a]	δ(2) = 2.76; δ(3) = 5.19; δ(5x) = 2.08; δ(5n) = 1.62; δ(6) = 2.84; δ(7) = 2.78; δ(8) = 5.92; δ(9) = 5.71; δ(10a) = 1.19; δ(10s) = 1.34; δ(11) = 1.27; δ(12) = 1.57	*J*(2,3) = 2.0; *J*(2,6) = 10.0; *J*(3,12) = 1.5; *J*(5x,5n) = 17.0; *J*(5x,6) = 10.0; *J*(5n,6) = 4.0; *J*(6,7) = 4.0; *J*(7,8) = 3.0; *J*(7,10s) = 1.6; *J*(8,9) = 5.6; *J*(10a,19) = 8.0
 **2**[a]	δ(1) = 2.77; δ(2) = 3.14; δ(4) = 5.07; δ(5x) = 2.12; δ(5n) = 1.6; δ(6) = 2.42; δ(8) = 5.78; δ(9) = 5.93; δ(10a) = 1.25; δ(10s) = 1.39; δ(11) = 1.28; δ(12) = 1.59	*J*(1,2) = 3.5; *J*(1,9) = 3.5; *J*(1,10a) = 1.8; *J*(2,6) = 9.0; *J*(2,4) = 1.6; *J*(5x,5n) = 16.0; *J*(5x,6) = 9.0; *J*(5n,6) = 2.8; *J*(8,9) = 6.0
 **3**[a][b]	δ(1) = 2.5; δ(2) = 3.16; δ(3) = 5.14; δ(5x) = 2.05; δ(5n) = 1.65; δ(6) = 2.74; δ(7) = 2.72; δ(8) = 5.47; δ(10a) = 1.24; δ(10s) = 1.50; δ(11) = 1.62; δ(12) = 1.58	*J*(1,2) = 3.2; *J*(1,10a) = 1.0; *J*(1,10s) = 1.8; *J*(2,3) = 2.0; *J*(2,12) = 2.0; *J*(3,12) = 1.6; *J*(5x,5n) = 16.4; *J*(5x,12) = 1.0; *J*(5n,12) = 1.0; *J*(5x,6) = 10.0; *J*(5n,6) = 4.0; *J*(7,8) = 2.0; *J*(7,10s) = 1.8; *J*(8,11) = 1.6; *J*(10a,10s) = 8
 **4**[a]	δ(1) = 2.68; δ(2) = 3.15; δ(3) = 5.07; δ(5x) = 2.08; δ(5n) = 1.66; δ(6) = 2.74; δ(7) = 2.6; δ(9) = 5.40; δ(10a) = 1.22; δ(10s) = 1.50; δ(11) = 1.81; δ(12) = 1.58	*J*(1,2) = 3.2; *J*(1,9) = 3.2; *J*(1,10s) = 1.8; *J*(2,6) = 8.4; *J*(2,12) = 1.6; *J*(5x,5n) = 17; *J*(5x,6) = 10.0; *J*(5n,6) = 4.0; *J*(5x,12) = 1.6; *J*(5n,12) = 1.6; *J*(6,7) = 4.0; *J*(7,10) = 1.8; *J*(9,11) = 1.2; *J*(10a,10s) = 8.0
 **5**[a]	δ(2) = 2.72; δ(4) = 5.09; δ(5x) = 2.13; δ(5n) = 1.62; δ(6) = 2.91; δ(7) = 2.76; δ(8) = 5.99; δ(9) = 5.82; δ(10a) = 1.25; δ(10s) = 1.33; δ(11) = 1.38; δ(12) = 1.66	*J*(2,6) = 9.0; *J*(2,5x) = 2.1; *J*(4,5n) = 2.1; *J*(5x,5n) = 15.6; *J*(5x,6) = 9.0; *J*(5n,6) = 4.2; *J*(6,7) = 4.2; *J*(7,8) = 3.2; *J*(7,10a) = 1.6; *J*(8,9) = 6.0; *J*(10a,10s) = 8.0
 **6**[a][b]	δ(1) = 2.63; δ(2) = 3.0; δ(4) = 5.09; δ(5x) = 2.11; δ(5n) = 1.62; δ(6) = 2.74; δ(7) = 2.75; δ(8) = 5.54; δ(10a) = 1.26; δ(10s) = 1.55; δ(11) = 1.65; δ(12) = 1.65	*J*(1,2) = 4.3; *J*(1,10s) = 1.6; *J*(2,5x) = 2.2; *J*(2,5n) = 3.8; *J*(2,6) = 8.2; *J*(4,5x) = 2.0; *J*(4,5n) = 2.0; *J*(5x,5n) = 16.4; *J*(5x,6) = 9.2; *J*(5n,6) = 4.3; *J*(7,8) = 2.7; *J*(7,10s) = 1.6; *J*(10a,10s) = 7.9

[a] ^{1}H-Homo-decoupling. [b] 2D-COSY.

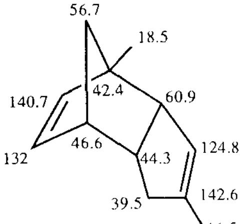
Table 3. *^{13}C-NMR Assignments* (90.55 MHz, $CDCl_3$) *for* endo- *and* exo-*Tricyclo[5.2.1.0^{2,6}]deca-3,8-diene* [9] *and Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene Isomers* **1**–**6**. Chemical shifts (δ (TMS) = 0 ppm).



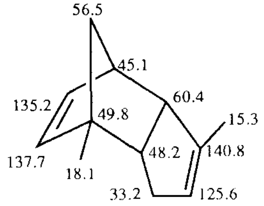
iv (*endo*) [9]



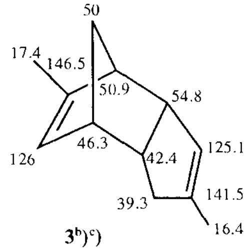
v (*exo*) [9]



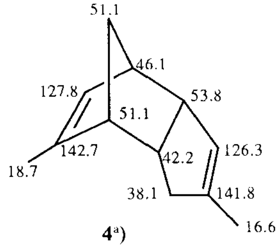
1b))



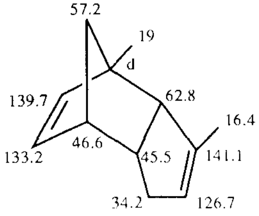
2a)



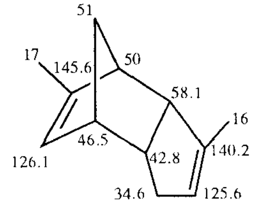
3b)c)



4a)



5a)



6b)c)

a) Compared with **1**, **3**, and **6**. b) C,H-Correlation. c) 2D-Inadequate. d) Not visible. e)f) Interchangeable.

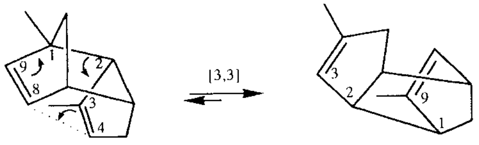
The interpretation of the ^{13}C-NMR spectra for **1**–**6** (*Table 3*) was accomplished by comparison of the chemical shifts of **iv** and **v**, CH-CORRELATION (for **1**, **2**, and **6**) and 2D-INADEQUATE experiments for **3** and **6** which subsequently became reference spectra. Confirmation of the *endo*-configuration of the skeleton and the position of the Me groups in **1**–**6** were given by inspection of the C(10) chemical shift(s). For **iv** and **v**, these values are 50 ppm and 40 ppm, respectively. For **3**, **4**, and **6**, the chemical shift lies between 50 ppm and 51.1 ppm and, for **1**, **2**, and **5**, between 56.5 ppm and 57.2 ppm, thus, exhibiting a downfield shift caused by the Me–C(1) or Me–C(7) group. In addition, in **2**, **5**, and **6** which possess a Me–C(3) group, the chemical shift of C(5) is between 33.2 ppm and 34.6 ppm (*i.e.* similar to that in **i**: 34.2 ppm). For **1**, **3**, and **4**, however, C(5) signal is shifted downfield (38.1 ppm–39.5 ppm) as a consequence of the adjacent Me–C(4) group.

The bridgehead position of a Me group in **1**, **2**, and **5** was demonstrated by the chemical shift of C(10) and its exact position (either C(1) or C(7)) determined by the downfield shift of the adjacent C-atoms. For **3**, **4**, and **6**, in which there is either a Me–C(8) or Me–C(9) group, the exact position of the Me group can be elucidated by the downfield shift of either C(7) or C(1) signal.

From the positions of the Me groups in **1**–**6**, it now follows that only 1- and 2-methylcyclopenta-1,3-diene (**ii** and **iii**, respectively) are involved in their formation. Dimers formed from 5-methylcyclopenta-1,3-diene (**i**) have not yet been identified (absence of the characteristic *doublet* for secondary Me groups at *ca.* 1.0 ppm in the ^{1}H-NMR spectrum).

Thermal Behaviour of the Dimers **1**–**6** (temperature range 20–110°). The spectrally deduced structures of **1**–**6** were further confirmed by their thermal behaviour. We observed that, on heating mixture **A1** at 110°, the proportions of **3** and **5** changed from 22% and 24% to a stable 42:4 ratio after ~ 3 h, whilst the concentrations of all other components remained almost unchanged (±2%; *Table 1*, *Mixture* **A2**). Since repetition of this thermal treatment with pure **3** or **5** led to the same result[3]), these transformations are consistent with a reversible [3,3]-sigmatropic *Woodward-Katz* rearrangement [10] (*Scheme 2*).

Scheme 2



5 **3**

Thus, **5**, the thermodynamically less stable isomer[3]), is preferentially formed by dimerisation at 20° (24%) due to kinetic control in the dimerisation process. MM-2 Calculations[4]), performed for the energy variations as a function of the distance between sp^2-C-atoms involved in the [3,3]-rearrangement of **3** and **5**, reveal a relatively small energy difference of 0.31 kcal/mol, favouring structure **3**.

Analogous isomerisation of the other dimers was not observed. It can, thus, be assumed that **2** and **4** are both the kinetically and thermodynamically preferred isomers. In the case of dimers **1** and **6**, on the other hand, a [3,3]-rearrangement may occur, but it is not discernible, since the reaction leads to structurally identical products ('*retro*-identical *Woodward-Katz* pairs').

We are grateful to Dr. *R.L. Snowden* and Dr. *A.F. Thomas* for valuable discussions and corrections of the manuscript.

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[3]) The determination of the exact thermodynamical data will be reported later.

[4]) We thank Dr. *B. Winter (Firmenich SA)* for these calculations.

Experimental Part

(With the valuable collaboration of *P. Kunz*)

General. Starting material: commercially available mixture of dimeric methylcyclopentadienes (*Exxon* [1]; mixture **A**). B.p. are uncorrected. Anal. GLC: *Varian* instrument, model *3500;* capillary columns *DB-1* and *DB-WAX* (15 m × 0.32 mm) *Hewlett Packard* instrument; Model *5890A*, quartz cap. columns *Chrompack CP Wax 57CB* (50 m × 0.2 mm). Prep. GLC: *Varian* autoprep., model *700*, glass columns (5 m × 4 mm; *Carbowax 20 M*, 10% on *Chromosorb W*. Carrier gas: He. ^{1}H- (360 MHz) and ^{13}C-NMR (90.5 MHz) spectra ($CDCl_3$): *Bruker WH-360* modified in a *AM*-model and interfaced to an *Aspect 2000* computer; δ [ppm] relative to TMS (= 0 ppm); coupling constants (J) in Hz; COSY, CH-CORRELATION, and 2D-INADEQUATE (*Bruker-Software DISN 87* (1987)).

1. *GLC of mixture* **A** *(Table 1)* was performed on the 50-m cap. *Carbowax* column (oven temp.: 40°; injector temp. 70°; flow: 4 ml He/min). Apart from some volatile impurities (*ca.* 8%), the presence of 10 isomeric methylcyclopentadiene dimers in the ratio 1:2:1:9:5:28:2:13:2:37 (increasing t_R) were detected.

2. *Isolation and Anal. Properties of Dimers* **1**–**6**. Mixture **A** (1.7 kg) was first fractionally distilled using a 1.5-m vacuum coated column (∅ 2 cm, packed with stainless steel helices) at 1–4 Torr and a bath temp. of 60°–70° (reflux ratio 1:20) to afford 25 fractions (~ 80 ml each). GLC revealed that *Fractions 8–10* and *22–24* contain the principal dimers **3** and **6**, resp. (purities of ⩾ 90%). Dimers **1** and **2** were concentrated in *Fractions 3–7*, whilst dimers **4** and **5** constitute the principal components of *Fractions 15–19*. Fractional distillation was repeated with the intermediate fractions for further enrichment of **1**, **2**, **4**, and **5**, and final purification of all six dimers was achieved by prep. GLC (5-m *Carbowax* column, 50–70°).

Dimer **5** is more conveniently obtained from dimeric mixture **A1** (see below) from which it can be separated directly by prep. GLC.

Analytical Data of **1**–**6**. The ^{1}H- and ^{13}C-NMR data of **1**–**6** are given in *Tables 2* and *3*. MS: identical for all dimers **1**–**6**.

*1,4-Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene* (**1**): peak 4; b.p. 55–56°/4 Torr. IR: 3040, 1650, 1620, 1430, 1370, 1340, 820, 720. MS: 160 (2, $M^{+\cdot}$), 115 (1), 91 (3), 80 (100), 77 (10), 51 (3), 39 (5).

*3,7-Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene* (**2**): peak 5; b.p. 55–56°/2 Torr. IR: 3040, 1650, 1620, 1440, 1380, 1350, 800, 730.

*4,9-Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene* (**3**): peak 6; b.p. 56°/2 Torr. IR: 3050, 1660, 1640, 1440, 1380, 825, 805, 730.

*4,8-Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene* (**4**): peak 7; b.p. 58°/2 Torr. IR: 3050, 1660, 1630, 1430, 1380, 1340, 820, 720.

*1,3-Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene* (**5**): peak 8; b.p. 58°/2 Torr. IR: 3040, 1650, 1630, 1440, 1380, 1350, 830, 720.

*3,9-Dimethyl-*endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene* (**6**): peak 10; b.p. 60°/2 Torr. IR: 3030, 1650, 1630, 1440, 1370, 1320, 820, 805, 720.

The minor peaks 1–3 and 9 (*Table 1, Mixture* **A**) have not yet been analysed.

3. *Dimerisation of 1-, 2- and 5-Methylcyclopenta-1,3-dienes* (**i**–**iii**, resp.) *at 20°. Preparation of Mixture* **A1**. Pure dimer **6** (100 g) was thermally cracked by slow distillation through a 1.5-m distillation column at 160° (760 Torr reflux temp. *ca.* 70°) and the resultant mixture of 1-, 2-, and 5-methylcyclopentadienes (**i**–**iii**, resp.)[1]) rapidly cooled (ice bath) and stored 7 days at 20° under N_2. GLC (*Table 1, Mixture* **A1**) then indicated *ca.* 70% dimerisation and the formation of the same 10 dimers as in **A** but with different concentrations of the dimers **3** (22%) and **5** (24%).

4. *Thermal Treatment of Mixture* **A1** (70–110°): *Formation of Mixture* **A2**. Heating of **A1** (5 g) at 110° in a glass tube under N_2 changed the concentration of **3** and **5** from the ratio 22:24 to 42:4 after *ca.* 3 h (GLC, *Table 1, Mixture* **A2**). The concentration of other dimers remained almost unaffected (±2%). Distillation (2 Torr 55–60°) yielded 4.85 g (~ 95%) of **A2**.

Heating purified **3** or **5** under identical conditions led to the same 42:4 product ratio.

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[6a] **Note added in proof.** – From a structure assignment of the 4 main dimers in mixture **A** by J. Bermejo, C.G. Blanco, M.A. Díez, J. Suárez Canga, *Afinidad* **1989,** 320, only that of dimer **1** is in agreement with ours.

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