*Bull Soc Chim Fr* (1996) 133, 283-293
© Elsevier, Paris

# Intramolecular Diels–Alder reaction of cyclenic trienes: stereoselectivity and NMR structure determination

Alain Blond[1], Nicole Platzer[1*], Alain Guy[2*], Hélène Dhotel[2], Laurence Serva[2]

[1] *Laboratoire de chimie organique structurale, 4, place Jussieu, 75252 Paris cedex 05;*
[2] *Laboratoire de chimie organique, Conservatoire national des arts et métiers,*
*292, rue Saint-Martin, 75141 Paris cedex 03, France*

(Received 17 July 1995; accepted 27 February 1996)

**Summary** — A series of trienes possessing an internally cyclenic dienophilic group undergo thermal intramolecular Diels–Alder (IMDA) reaction with high selectivity for the *cis*-fused products. A concentrated solution of $LiClO_4$ in diethyl ether catalyzes the IMDA reaction of cyclenic nitrotrienes, giving rise to the *trans*-fused compounds. The stereochemical outcome of these various processes are rationalized in terms of a minimization of the steric interactions between the ring and the chain on the one hand and the *endo*-stabilization from the nitro group on the other. The structures of the cycloadducts have been carefully determined by NMR $^1H$ and $^{13}C$ spectroscopy: dipolar interactions, detected via nuclear Overhauser effects, and criteria based on scalar coupling and moreover on chemical shifts have been employed. Conformational preferences were observed.

**intramolecular Diels–Alder / selectivity / NMR / configuration / conformation**

**Résumé — Réaction de Diels–Alder intramoléculaire : stéréosélectivité et détermination structurale par RMN.** *Des triènes comportant un reste diénophile engagé dans un cycle conduisent par cyclisation de Diels et Alder intramoléculaire (DAIM), par voie thermique, aux produits de cyclisation à jonction* cis. *Par contre le DAIM de ces mêmes triènes catalysée par $LiClO_4$ dans l'éther conduit uniquement aux composés à jonction* trans. *Le contrôle stéréochimique de ces différents processus est expliqué en terme de minimisation des interactions stériques entre le cycle et la chaîne d'une part (contrôle stérique), et la stabilisation* endo *due au groupement nitro (contrôle électronique). La structure des différents cycloadduits a été déterminée précisément par RMN $^1H$ et $^{13}C$ à partir des interactions dipolaires mises en évidence par effet Overhauser nucléaire et les informations basées sur les couplages scalaires et les déplacements chimiques. Des conformations privilégiées ont été mises en évidence à partir de ces observations.*

**Diels–Alder intramoléculaire / sélectivité / RMN / configuration / conformation**

## Introduction

Since the mid-1970s, the use of the intramolecular Diels–Alder (IMDA) reaction — in which the diene and dienophile are tethered by a connecting chain — has become widespread in organic synthesis [1]. This success is associated with the increased reactivity observed during the reaction (due to favorable entropy considerations), and the heightened regioselectivity and stereoselectivity imposed by the constraint of the connecting chain. The dominant stereochemical control element in these intramolecular reactions is the minimization of strains and nonbonding interactions involving the three- or four-atom chain separating the diene and dienophile in the transition state.

As part of our program aimed at the development of methods for the construction of polycyclic ring systems based on the IMDA reaction [2], we have been interested in the intramolecular cycloaddition of cyclenic trienes, in order to establish the role played by a ring incorporated in the tether chain on the diastereoselectivity of the reaction. In theory four racemic adducts can be formed. In practice we have found that only one or two stereoisomers are isolated, depending on the nature of the substituents. A major problem of this investigation was to determine the relative configurations of the carbons situated at the A/B and B/C junctions of the products. Crystals suitable for X-ray analysis were obtained in one case only (that of **12b**). High-field NMR studies have thus been undertaken in order to determine the structures of all other tricyclic compounds synthesized.

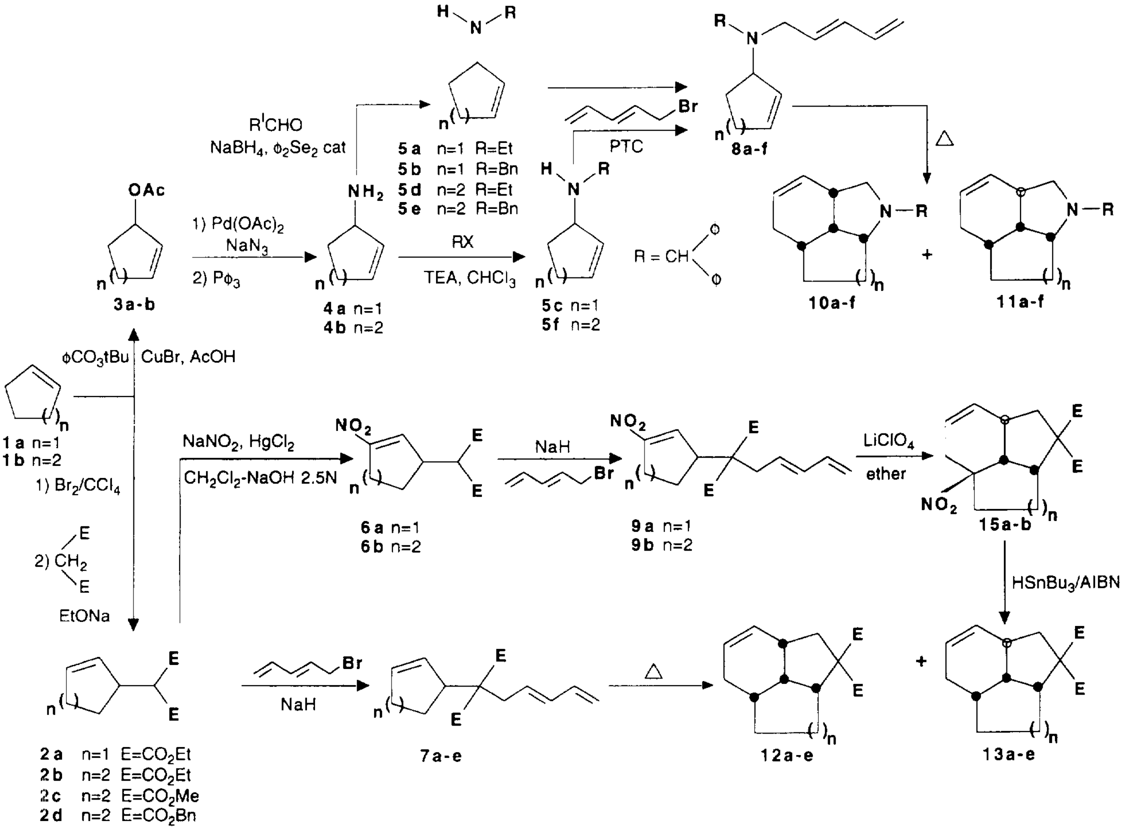
## Chemical results

### *Synthesis of the trienes*

The dienophilic moiety is prepared by a multistep procedure from either cyclopentene or cyclohexene and then alkylated by 1-bromopenta-2,4-diene to give the trienes **7**. Primary allylic amines **4a,b** were ob-

---

* Correspondence and reprints



Scheme 1

tained in good yield by reduction of the cycloalkenyl azides using the conditions of Murahashi [3]. Reductive amination using a previously described method gave the *N*-benzyl cycloalkenylamines **8b,e** [4]. The *N*-benzhydrylamines **8c,f** were obtained by direct alkylation of the primary amine by benzhydryl bromide. The nitrodienophilic moieties **6** were prepared in three steps from the corresponding cycloalkene by a procedure reported by Corey [5]. All these procedures are summarized in scheme 1.

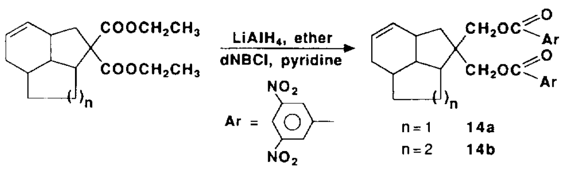
### *Cyclization of the trienes*

The IMDA cyclizations of trienes **7a–e** and **8a–f** were performed on carefully degassed, dilute toluene solutions in a sealed tube at the temperatures indicated in tables I and II. In these intramolecular examples the rate of cycloaddition across the unactivated olefin was often sluggish, owing to the poor HOMO-LUMO interactions. High temperatures are therefore needed for the reaction to proceed.

It is apparent (see table II) that incorporation of a sterically-bulky group on the nitrogen enhances the reaction. In this manner the frequency of encounters between the diene and the dienophile is considerably favored. This phenomena is less marked in the carbotriene series, probably because secondary orbital interactions between the diene and the carbonyl group are in competition with the steric effect favorable to the more reactive conformation, and the population of conformers disposed toward cycloaddition is thus lower. Reduction of the carbonyl function, or increasing the bulkiness of the ester function, slightly increases the rate of the reaction.

The catalytic IMDA reaction of nitrotrienes **9a,b** was undertaken at room temperature for 24 h in the presence of a concentrated solution of $LiClO_4$ in diethyl ether (5 M). The cycloadduct obtained was reduced by $HSnBu_3$ and AIBN to lead to **13a** and **b** which are the *anti* H *exo* stereoisomers. These diastereoisomers are the minor compounds obtained during the thermal cyclization of the unactivated trienes **7a,b**.

For high field NMR studies, the cycloadducts **12a** and **13b** were converted to **14a** and **14b** by reduction ($LiAlH_4$) and esterification with 3,4-dinitrobenzoyl chloride (dNBCl) [9].



### *Selectivity control during the cyclization*

During the intramolecular Diels–Alder reaction, the presence of an additional asymmetric center on the

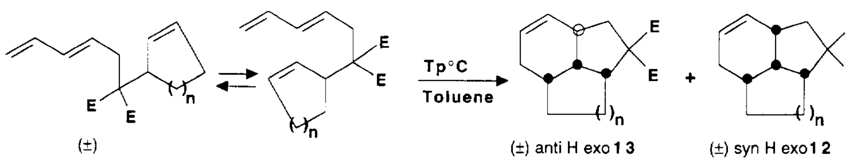
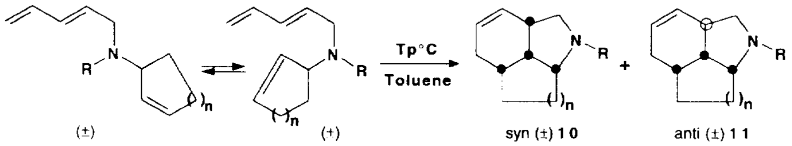


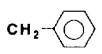
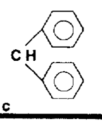
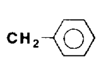
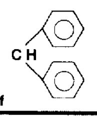
**Table I.** Cyclization of carbotrienes **7a–e**.

| *n* | *E* | *Compound* | *Solvent* | T (°C) | *Time (h)* | *Cyclization yield* | anti *H* exo | syn *H* exo |
|---|---|---|---|---|---|---|---|---|
| 1 | COOEt | **7a** | toluene | 110 | 47<br>168 | 77%<br>91% | 6%<br>16% | 71%<br>75% |
| 2 | COOEt | **7b** | toluene | 140 | 23<br>30 | 93%<br>94% | 12%<br>14% | 81%<br>80% |
| 2 | COOEt | **7b** | toluene | 160 | 6<br>24 | 94%<br>93% | 13%<br>13% | 81%<br>80% |
| 2 | COOEt | **7b** | toluene | 180 | 3 | 95% | 14% | 81% |
| 2 | COOEt | **7b** | acetonitrile | 160 | 7<br>24 | 62%<br>87% | 7%<br>12% | 55%<br>75% |
| 2 | COOEt | **7b** | toluene | 160 | 168 | 96% | 35% | 61% |
| 2 | $COOCH_3$ | **7c** | toluene | 160 | 168 | 100% | 34%* | 66% |
| 2 | $COOCH_2Ph$ | **7d** | toluene | 160 | 6<br>70 | 100%<br>100% | 15%*<br>14%* | 85%<br>86% |
| 2 | $CH_2OH$ | **7e** | toluene | 160 | 7 | 100% | 25% | 75% |

* Not isolated.

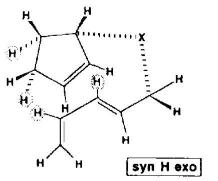
**Table II.** Cyclization of azatrienes **8a–f**.

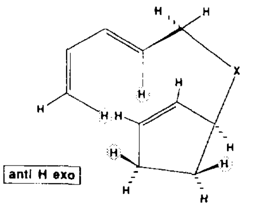


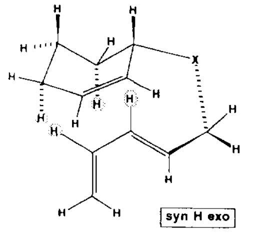
| n | R | Tp°C | Time | Cyclization yield | syn H exo | anti H exo |
|---|---|---|---|---|---|---|
| 1 | 8a $CH_2CH_3$ | 195 | 1h | Polymerization | — | — |
|  |  <br>8b | 115 | 15h | 52% | 74% | 26% |
|  |  | 195 | 4h | 95% | 71% | 29% |
|  |  | 230 | 2h | 95% | 70% | 30% |
|  |  <br>8c | 115 | 4h | 84% | 82% | 18% * |
|  |  | 195 | 45min | 95% | 72% | 28% * |
|  |  | 230 | 30min | 95% | 74% | 26% * |
| 2 | 8d $CH_2CH_3$ | 195 | 3h | 85% | 59% | 41% |
|  |  <br>8e | 115 | 30h | 69% | 100% | — |
|  |  | 195 | 2h30 | 92% |  |  |
|  |  <br>8f | 115 | 4h30 | 83% | 100% | — |
|  |  | 195 | 2h | 93% |  |  |

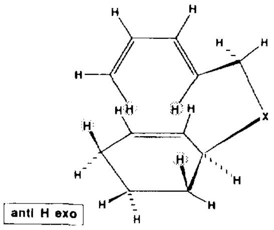
*Not isolated

chain connecting the diene and the dienophile could in principle result in the formation of four diastereomeric products. The presence of a ring on the linking chain introduces supplementary steric and torsional strain, which defavors some of the possible transition states.









From the results obtained during the cyclization of all the cyclenic trienes studied, it is immediately apparent that each of the cyclizations occurs preferentially via a transition state in which the H on the carbon of the ring which bears the chain connecting the diene adopts an *exo* position relative to the diene. We suggest that this orientation is preferred as a consequence of strain involving the CH axial in the *endo* position and the diene, which destabilizes the two alternative transition states.

The diastereoselectivity of the reaction is mainly due to the 1–3 diaxial destabilizing interactions between the diene and the ring system. These interactions are more important in the cyclohexane ring than in the flat cyclopentane, as evidenced by the lower diastereoselectivity exhibited by this latter series.

## Physicochemical results

### *X-ray study*

Crystals were obtained only for **12b**, and its structure was determined by X-ray analysis. The Ortep view is shown in figure 1. It is clearly established that all the ring junctions are *cis*.

### *NMR study*

Stereochemical problems are usually best approached by examining $^1$H–$^1$H dipolar interactions via nuclear Overhauser effects (NOE) [10]. However, in several cases severe overlap occurs for the signals of protons situated at the ring junctions. It was thus necessary to resort to alternative criteria based on scalar coupling together with $^1$H and $^{13}$C chemical shifts to resolve this problem. Conformational information was also obtained for the all *cis* compounds, which are less constrained than the isomers with *trans* junctions.

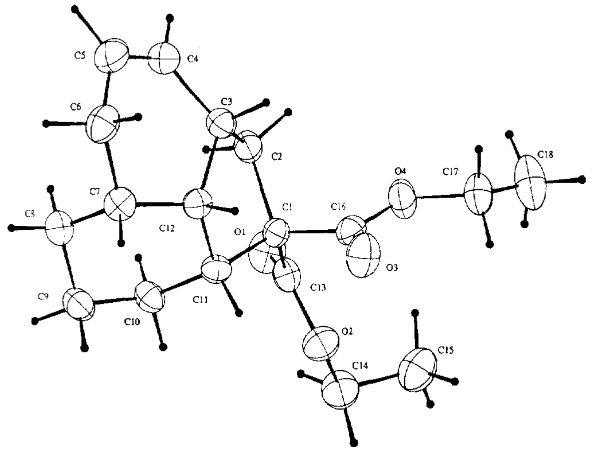
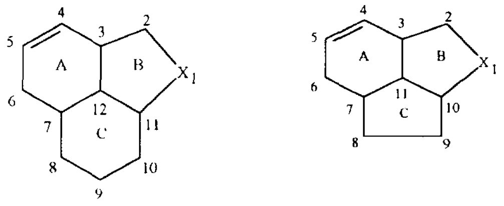


**Fig 1.** Ortep drawing of compound **12b**. Ellipsoids are shown at the 30% probability level.

For ease of comparison the following numbering of the atoms (different from IUPAC nomenclature) will be employed:



**Scheme 2**

### *Spectral assignments*

Most compounds show complex $^1$H multiplet patterns. Thus, prior to further analysis the methine protons and the groups of geminated protons were identified using 2D $\delta^{13}$C–$\delta^1$H correlations. Inverse HMQC (Heteronuclear Multiple Quantum Correlation) experiments were preferred due to the low solubility of most compounds. The HMQC method was used without decoupling of the $^{13}$C resonances [11].

- *$^1$H NMR spectra*

The resonance assignments were first made on the basis of chemical shifts, multiplicity patterns and by use of the 2D COSY 45 experiment [12]. The signals of the ethylenic protons are readily assigned (in the range 5.6–6.2 ppm). In one case only, that of **12b**, the frequencies were identical. In all the other cases the H-5 proton coupled to the geminal H-6 protons showed a more complex pattern than H-4, which has only one vicinal interaction with H-3. Correlations with these protons allowed assignment of protons H6 and H3. Starting from the signal of H3 the signals of the geminated protons H2 were then assigned. They do not exhibit further correlations except their geminal correlation with the typical orientation of the signal. As regards the methine protons, the central one H12 (or H11 when C is a five-membered ring) was determined from the correlation

**Table III.** $^1$H NMR chemical shifts $\delta$ ppm with respect to TMS.

| *no* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* | *11* | *12* | *Other protons* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **10b** | 2.60*<br>2.35* | 2.44 | 5.65 | 5.81 | 2.09*<br>1.98* | 2.00 | 1.49*<br>1.77* | 1.31<br>*1.77* | 3.07 | **2.60** | | CH$_2$: 3.87; 3.23 | o: 7.43<br>m: 7.26; p: 7.17 |
| **11b** | 2.16<br>*3.12* | *2.40* | 6.16 | 5.76 | 2.34<br>*1.83* | 1.94 | 1.75*<br>1.60* | 1.54*<br>1.70* | 2.94 | **1.94** | | CH$_2$: 3.72; 3.75 | o: 7.45<br>m: 7.28; p: 7.19 |
| **10c** | 2.78<br>*2.33* | 2.59 | 5.71 | 5.77 | 2.13*<br>1.92* | 1.90 | 1.43<br>*1.54* | 1.12<br>*1.84* | 3.63 | **2.59** | | CH: 4.66 | o: 7.59; 7.52<br>m: 7.21; p: 7.07 |
| **10d** | 2.79<br>*2.33* | 2.67 | 5.86 | 5.95 | 1.86*<br>2.29* | 1.83 | 1.47<br>*1.57* | 1.25<br>*1.68* | 1.47<br>*1.57* | 2.42 | **2.36**[a] | CH$_2$: 1.92; 2.75<br>CH$_3$: 1.09 | |
| **11d** | 2.18<br>*3.34* | *2.70* | 5.83 | 5.61 | 2.32<br>*1.71* | 1.85 | 1.30eq<br>*1.19ax* | 1.07ax<br>*1.57eq* | 1.80eq<br>*1.48ax* | 2.65 | **1.72** | CH$_2$: 2.61<br>CH$_3$: 1.14 | |
| **10f** | 2.87<br>*2.38* | 2.64 | 5.67 | 5.79 | 1.93*<br>±0.02 | 1.76 | 1.28eq<br>*1.20ax* | 0.85ax<br>*1.54eq* | 1.54eq<br>*1.18ax* | 3.20 | **2.57** | CH: 4.70 | o: 7.59; 7.52<br>m: 7.21; p: 7.07 |
| **12b** | 2.37<br>*2.10* | 2.35 | 5.70 | 5.70 | 2.00*<br>1.90* | 1.94 | 1.39eq<br>*1.03ax* | 1.15ax<br>*1.63eq* | 1.39eq<br>*0.74ax* | 2.75 | **2.75** | CH$_3$: 1.23<br>CH$_2$: 4.12; 4.18<br>4.12; 4.21 | |
| **13b** | 1.39<br>*2.93* | *2.55* | 5.73 | 5.53 | 2.37<br>*1.77* | 2.07 | 1.39eq<br>*1.24ax* | 1.24ax<br>*1.71eq* | 1.39eq<br>*1.10ax* | 2.85 | **1.77** | CH$_3$: 1.24<br>CH$_2$: 4.11; 4.19<br>4.11; 4.21 | |
| **14b** | 1.38<br>*2.02* | *2.72* | 5.79 | 5.61 | 2.47<br>*1.86* | 2.13 | 1.55eq<br>*1.34ax* | 1.34ax<br>*1.84eq* | 1.66eq<br>*1.50ax* | 2.08 | **1.95** | CH$_2$: 4.41; 4.53<br>*CH$_2$: 4.58; 4.60* | o: 9.11<br>p: 9.24 |
| **13a** | 1.50<br>*2.87* | *2.11* | 5.99 | 5.69 | 2.40<br>*1.82* | 2.24 | 1.97<br>*1.50* | 1.82<br>*1.32* | 3.21 | **1.82** | | CH$_3$: 1.23<br>CH$_3$: 1.24<br>CH$_2$: 4.14; $4.13_5$<br>CH$_2$: $4.22_2$; 4.20 | |
| **14a** | 2.09<br>*1.26* | 2.78 | 5.77 | 5.73 | 1.99*<br>2.25* | 2.28 | 1.61<br>*1.46* | 1.79<br>*1.71* | 2.61 | **2.80** | | CH$_2$: 4.45; 4.51<br>CH$_2$: *4.48; 4.70* | o: $9.11_5$; $9.13_8$<br>p: $9.24_3$; $9.24_5$ |

[a] Bold characters are used for the central proton, H12 or H11; [b] italic characters are used for the *endo* protons whenever it was possible to discriminate their position (within pairs of geminated protons on the skeleton) between the two substituents at C1; * is used when the position *exo/endo* could not be determined.

with H3, except when overlap occurs as is the case for **10c** or **14a**. It might nevertheless be identified because it is coupled to the last two methine protons. The signal of H7 was directly assigned from the correlations to the geminated H6 protons, except when overlap occurs with one of them as is the case for **10c,d**, **12b** and **14a**. The last methine proton H11 (or H10 when C is a five-membered ring) is coupled to a group of geminated protons which are less deshielded than the H6 protons. It was thus assigned and distinguished from H7 in the particular cases outlined above. Finally, for the assignments of the protons in ring C there are two possible pathways obtained from the correlation map, starting either from H7 or from H11 (or H10).

The distinction between the signals corresponding to geminal protons as a function of their position on the *exo* or *endo* face of the molecule is much more difficult. In some cases for the more rigid compounds, eg, **12b**, **11d** and **10f**, rather well-dispersed first-order multiplets were observed in the region 1–2 ppm. Taking into account the axial and equatorial coupling interactions found in rigid cyclohexane systems, the signals of the geminated protons in ring C could then be unambiguously ascribed to the proton situated on the *exo* or *endo* face of the rigid skeleton. For example, in the spectrum of **12b** the signal assigned to H8 at 1.03 ppm is a quadruplet of doublets ($^2J_{\text{H8-H8}'} = {}^3J_{\text{H8-H9ax}} = {}^3J_{\text{H8-H7}} = 12.5$ Hz and $^3J_{\text{H8-H9eq}} = 3.0$ Hz), the signal assigned to H10 at 0.74 ppm is a quadruplet of doublets ($^2J_{\text{H10-H10}'} = {}^3J_{\text{H10-H9ax}} = {}^3J_{\text{H10-H11}} = 13.0$ Hz and $^3J_{\text{H10-H9eq}} = 3.6$ Hz), but the signal assigned to H9 at 1.15 ppm ($^2J_{\text{H9-H9}'} = 13.0$ Hz) appears as a quadruplet of triplets. The multiplet patterns are only consistent with axial positions for these three protons as well as for the two methine protons H7 and H11. The methine proton H7 always being situated on the *exo* face of the skeleton, the axial protons H8, H9, H10 and H11 are respectively in *endo*, *exo*, *endo* and *exo* positions.

Alternatively nuclear Overhauser effects were used, starting from protons such as H7*exo* and H12*exo* (or H11) at the A/C junction. The differentiation was completed in conjunction with the determination of the positions of the protons at the ring junctions (see below). The signals of the substituents were obvious and easily assigned. Diastereotopic effects have been observed even for protons far remote from the asymmetric centres and can be very different for the various isomers.

The data are presented in table III.

- *$^{13}$C NMR spectra*

With the assignments of the $^1$H spectrum completed, the heteronuclear $\delta^{13}$C–$\delta^1$H correlations were used for the $^{13}$C assignments. The data are presented in table IV.

**Table IV.** $^{13}C$ NMR chemical shifts δ ppm with respect to TMS.

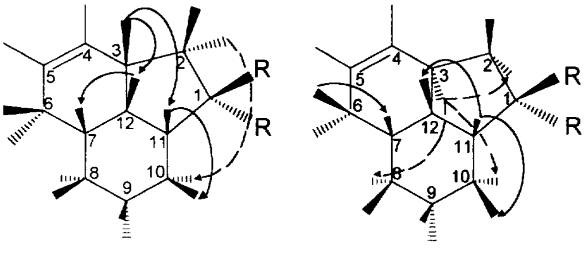
| *No* | *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* | *11*[a] | *12*[a] | *Other carbons* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **10b** | | 61.19 | 35.67 | 131.95 | 126.20 | 26.31 | 37.21 | 32.58 | 30.26 | 71.44 | **44.49** | | $CH_2$: 58.75 | o: 129.44<br>m: 128.95<br>p: 127.55 |
| **11b** | | 57.66 | 39.53 | 130.48 | 129.91 | 29.66 | 35.20 | 32.59 | 34.54 | 68.82 | **54.84** | | $CH_2$: 61.20 | o: 129.84; m: 128.87<br>p: 127.58 |
| **10c** | | 58.07 | 36.05 | 129.40 | 125.77 | 26.82 | 37.09 | 33.24 | 27.98 | 68.12 | **44.18** | | CH: 71.27 | o: 128.5; 129.04<br>m: 128.7<br>p: 128.5 |
| **10d** | | 61.37 | 35.78 | 131.97 | 128.61 | 31.21 | 31.76 | 29.96 | 18.04 | 25.04 | 64.30 | **39.85** | $CH_2$: 44.59<br>$CH_3$: 14.24 | |
| **11d** | | 58.49 | 34.33 | 127.13 | 128.12 | 32.09 | 32.04 | 29.77 | 25.07 | 31.54 | 62.17 | **44.45** | $CH_2$: 50.81<br>$CH_3$: 14.58 | |
| **10f** | | 55.22 | 36.02 | 130.88 | 127.28 | 32.02 | 32.09 | 29.99 | 22.10 | 23.61 | 60.00 | **39.05** | CH: 69.87 | o: 128.2; 129.2<br>m: 128.8; 129.2<br>p; 127.5 |
| **12b** | 64.63 | 37.19 | 33.80 | 130.55 | 126.06 | 30.73 | 31.22 | 29.28 | 23.77 | 26.10 | 43.05 | **37.06** | $CH_2$: 61.25; 61.02<br>$CH_3$: 14.08; 14.16 | C=O: 171.66; 170.08 |
| **13b** | 62.82 | 38.04 | 32.94 | 127.71 | 126.94 | 31.77 | 31.79 | 28.22 | 25.79 | 23.75 | 42.91 | **45.81** | $CH_2$: 61.07; 60.97<br>$CH_3$: 14.00; 14.14 | C=O: 172.92; 170.97 |
| **14b** | 47.68 | 36.67 | 32.85 | 127.70 | 127.49 | 31.89 | 31.98 | 28.59 | 26.01 | 23.86 | 42.83 | **45.06** | $CH_2$: 67.39; 70.07 | C=O: 162.53<br>ipso: 133.69; o: 129.43<br>m: 148.9; p: 122.68 |
| **13a** | 64.10 | 39.34 | 38.82 | 130.06 | 129.01 | 29.90 | 34.48 | 32.86 | 27.96 | 47.23 | **55.28** | | $CH_2$: 60.94; 61.19<br>$CH_3$: 14.10; 14.23 | C=O: 171.4; 172.8 |
| **14a** | 48.93 | 38.61 | 34.78 | 128.32 | 124.73 | 26.34 | 37.23 | 32.67 | 26.67 | 49.12 | **43.68** | | $CH_2$: 67.61; 68.02 | C=O: 162.41; 162.61<br>ipso: 133.56; 133.69<br>o: 129.41; 129.46<br>m: 148.85; p: 122.72 |

[a] Bold characters are used for the central carbon atom (C11 or C12).

### *Nuclear Overhauser effects*

Nuclear Overhauser effects, NOE, provide an easy method for the determination of relative configurations if the signals of interest are well separated. With a *cis* junction between rings B and C the three methine protons of ring C lie on the *exo* face of the molecule. For rings A and B, H3 lies on the same face as the other methine protons of ring A if the junction is *cis*. With a *trans* junction, which might be expected to result in a very rigid structure, H3 lies on the *endo* face and modeling shows that it becomes proximate to the *endo* protons of ring C. The NOE detected for a couple of isomers **12b** and **13b** are shown in figure 2.

The observation of NOE between the methine protons of ring C allowed us to establish that the B/C junction is *cis* for all the compounds. The *trans* A/B ring junction was established for compounds **11b**, **11d**, **13a**, **13b** and **14b** by observation of dipolar interactions between H3 and *endo* protons of ring C, and by the absence of interaction of H3 with the other methine protons. Dipolar interactions detected between all the methine protons established the position of H3 on the *exo* face of the molecule for **10d** and **10f**; the A/B junction is *cis*. For **10b**, **10c**, **14a** superimposition with other signals for the resonances of interest, ie, that of H3 and the central proton, precluded an unambiguous conclusion.



**12b** **13b**

**Fig 2.** Nuclear Overhauser effects observed for the isomers **12b** and **13b** (R = $CO_2CH_2CH_3$).

Whenever possible the dipolar interactions were also used to allow the ready attribution of the protons in

**Table V.** Effect of the A/B ring junction on the chemical shifts of various nuclei or on shift differences between selected nuclei. Ranges are given respectively for $\delta$ in ppm or $\Delta\delta$ in ppm.

| | *A/B* trans | *A/B* cis | *A/B unknown* |
|---|---|---|---|
| Central methine $\delta$H12 (or $\delta$H11) | $1.72 \longleftrightarrow 1.95$ | $2.36^* \longleftrightarrow 2.75$ | $2.59 \longleftrightarrow 2.80$ |
| Central methine | | | |
| $\delta$C12 | $44.45 \longleftrightarrow 45.06$ | $37.06 \longleftrightarrow 39.85^*$ | |
| $\delta$C11 | $54.84 \longleftrightarrow 55.28$ | | $43.68 \longleftrightarrow 44.49$ |
| $\delta$H4–$\delta$H5 | $0.18 \longleftrightarrow 0.40$ | $0 \longleftrightarrow -0.12$ | $0.04 \longleftrightarrow -0.16$ |
| $\delta$C4–$\delta$C5 | $-0.99 \longleftrightarrow 1.05$ | $3.36^* \longleftrightarrow 4.49$ | $3.59 \longleftrightarrow 5.75$ |
| $\delta$H6exo–$\delta$H6endo | $0.51 \longleftrightarrow 0.61^a$ | $0.10 \longleftrightarrow 0.43^{*b}$ | $0.11 \longleftrightarrow 0.26^b$ |
| $\delta$H2endo–$\delta$H2exo | $0.64 \longleftrightarrow 1.54$ | $-0.27 \longleftrightarrow -0.49$ | $-0.25 \longleftrightarrow -0.83$ |

[a] The difference is positive; [b] absolute value: it was not possible to assign the signals unequivocally to the *endo* or *exo* position. * denotes cases where an extreme value corresponds to **10d**.

each of the methylene pairs to the *exo* or *endo* position. All the results obtained in this way are reported in table III. Finally it is worth noting that upon irradiation of the *exo* methine proton H11 (or H10), or upon irradiation of the H2 protons, NOE were also observed for some protons of the substituent. When a carbon is situated at position 1, as for **14a** and **14b**, it was thus possible to distinguish the two identical substituents as a function of their *exo* or *endo* position.

### *Secondary criteria*

Due to distorsions from the typical geometry of the rings in polycyclic systems, the rules usually applied for the interpretation of substituent shift effects cannot be used. Thus a semi-quantitative approach was preferred, taking into account $^1$H deshielding, and contrarily $^{13}$C shielding, as a result of steric constraints.

The chemical shifts of a number of carbons and protons were found to vary systematically as a function of the *trans* or *cis* nature of the A/B ring junction. The results are given in table V.

For the central methine group the CH bond nearly eclipses the bond C3–H3 when the A/B junction is *cis*. In addition, further flattening of the six-membered ring C results in low values of the dihedral angles H12–C12–C7–H7 and H12–C12–C11–H11. These geometrical features induce significant steric interactions. They disappear or are minimized when the A/B junction is *trans*. The proton of the central methine group is thus systematically more deshielded in the first case. As regards the central carbon the comparison must involve on one hand six-membered ring C compounds and on the other hand five-membered ring C compounds, since chemical shift increases systematically with ring strain. In both series the central carbon is more shielded when the A/B junction is *cis*.

When the A/B junction is *cis* the H6 *endo* proton lies nearly in the plane of the double bond and the steric interactions are significant for H5. In contrast, in the case of a *trans* junction the C5–H5 bond approximately bisects the angle H6–C6–H6 and thus steric interactions are reduced for H5. As a result H5 is more deshielded than H4 for an A/B *cis* junction and the reverse is true for an A/B *trans* junction. There are two exceptions: **12b**, where the two protons are equivalent, and **14a**, where the difference $\delta$H4 – $\delta$H5 is positive but remains significantly much smaller than for all the compounds with a *trans* A/B junction. As regards the carbon resonances, the difference $\delta$C4 –$\delta$C5 is greater for an A/B *cis* junction.

For the protons H2 the difference $\delta$H2 *exo* – $\delta$H2 *endo* is always positive for the A/B *cis* junction and becomes negative for the *trans* junction. Furthermore these protons, deshielded by the nitrogen atom at position 1 or by indirect effects of the substituents, gave in most cases well-isolated multiplets. For an A/B *trans* junction the multiplicities correspond to a doublet of doublets and to a triplet. The coupling constant between H2 *exo* and H3 *endo* in antiperiplanar situation, ca 12.5 Hz, is always greater than the coupling constant between the *syn* protons H3 and H2 *endo*, ca 8 Hz. When there is a carbon at position 1 the geminal constant $^2J$ has a high value (ca 12.5 Hz), and as a result a triplet is observed for H2 *exo* and a doublet of doublets for H2 *endo*. The reverse is true when position 1 is occupied by a nitrogen atom, since the geminal constant decreases (ca 8 Hz). For an A/B *cis* junction the multiplet pattern is different. The coupling constants of H3 with H2 *endo* or H2 *exo* and the geminal coupling constant have the same value. As a result two triplets are observed. The lone exception is **10d** (see below).

Comparison of the data for the compounds with unknown geometry with the data for compounds with either *trans* or *cis* A/B ring junctions clearly allowed us to conclude that the junction is *cis* for **10b**, **10c** and **14a**.

### *Diastereotopic effects*

Strong diastereotopic effects were observed for the substituents of the compounds bearing a nitrogen atom at position 1 when the A/B junction is *cis*. In **10b** and **10d**, where the substituent bears a methylene group in the $\alpha$ position, the protons were separated by 0.64 and 0.83 ppm respectively. In **10c** and **10f** the two phenyl groups linked to the $\alpha$ methine carbon are diastereotopic with a difference of 0.07 ppm for the *ortho* protons. Significant diastereotopic effects are also observed for the $^{13}$C resonances: up to 0.7 ppm for the *meta* carbons and 1.0 ppm for the *ortho* carbons. The diastereotopic effects are very small or absent for the *trans* compounds.

In the compounds bearing a carbon at position 1, the diastereotopic effects are much smaller. Nevertheless they are still observed for **14a** and **14b** within the protons of each methylene group: 0.22 and 0.06 ppm and 0.12 and 0.02 ppm respectively, the effect being greater for the *endo* substituent of the compound with an A/B *cis* junction. For **12b** and **13b**, where the methylene groups are in the $\gamma$ position, the difference remains detectable within the protons in each group: respectively 0.09 and 0.06 and 0.10 and 0.07 ppm.

### *Conformation*

Whereas some flexibility might be expected for the compounds with all *cis* junctions, the multiplicities observed for the protons of ring C are in favor of a strongly preferred chair conformation with H12 in equatorial position. The conformation of ring B is of the envelope type with the nitrogen atom *exo*. The lone exception is **10d**. The protons of ring C for this compound did not show the typical multiplicities expected for a cyclohexanic ring constrained in one chair conformation. It should also be noted that for **10d** the values of the above parameters for the effect of the A/B ring junction lie in most cases at the edges of the intervals characteristic of the *cis* junction. The multiplet patterns for the signals of the H2 protons are atypical, with a triplet for H2 *endo* (8.7 Hz) and a doublet of doublets for H2 *exo* (8.7 and 3.5 Hz). This molecule bears the smallest substituent and a conformational equilibrium involving ring inversion of ring C and pseudo rotation of ring B is most likely to occur.

It is worth noting that the skeletons of the all *cis* compounds exhibit a significant concavity, which results in strong diastereotopic effects. When there was a nitrogen at position 2 it was sometimes possible to detect a preferential orientation of the substituent by observing specific NOE. For **10f** and **10c**, irradiation of the *exo* methine (H11 and H10 respectively) gave a positive response for the methine of the substituent and, moreover, the *ortho* protons of the most shielded phenyl group. In the ethyl group of **10d** only the most shielded methylene proton underwent a strong enhancement upon irradiation of H11. In contrast, for **10b** the two diastereotopic protons of the methylene linked to a phenyl group were simultaneously enhanced upon irradiation of H10.

## Conclusion

From the results obtained for all cyclenic trienes studied, it is apparent that each cyclization occurs preferentially via a transition state in which the H on the carbon of the ring bearing the chain connecting the diene adopts an *exo* position relative to the diene. The diastereoselection of the reaction is dependent mainly on the 1-3 diaxial destabilizing interactions between the diene and the ring system. Besides the NMR information leading to the determination of the relative configurations of all the carbons in the compounds studied in this paper, the chemical shifts and coupling effects presented above might be of prime value for the study of tricyclic skeletons of similar geometry.

## Experimental section

### *X-ray structure determination*

- *Crystal parameters*

Crystal system monoclinic, space group $P2_1/n$, $a = 8.376(2)$ Å, $b = 13.820(4)$ Å, $c = 14.777(6)$ Å, $\beta = 101.05(3)°$, $V = 1\,679(1)$ Å$^3$, $Z = 4$, $\rho$ calc: 1.21 g cm$^{-3}$, $\mu = 0.79$ cm$^{-1}$. Data collection: diffractometer Nonius CAD4, monochromator graphite, radiation Mo$K\alpha$, scan type $\omega$-$2\theta$, scan width $0.8 + 0.34 \tan\theta$. $\theta$ range: 1–25°, number of measured reflections 2 945, number of reflections used $I > 3\sigma(I)$ 2 004, min–max height in final $\Delta\rho$, e Å$^{-3}$, number of refined parameters 280. Refinement $R = [\Sigma|\Delta F|/\Sigma F_o] = 0.046$. $R_\omega[\Sigma\omega(\Delta F)^2/\Sigma\omega(F_o)^2]^{1/2} = 0.042$. $\omega = 1$.

### *NMR data*

$^1$H and $^{13}$C NMR spectra of the trienes were recorded on a Bruker WM 200 spectrometer in chloroform-*d*. All coupling constants are presented in hertz (Hz). Chemical shifts are reported relative to TMS as internal standard. IR spectra were recorded on a Philips PU 9716 spectrometer. Analysis were performed by Wolff Laboratories (92583 Clichy, France).

The $^1$H and $^{13}$C NMR spectra of the tricyclic compounds were recorded on a Bruker AM 500 spectrometer in $C_6D_6$. Standard Bruker programs were used for the 2D experiments.

### *Chemical data*

All synthetic manipulations involving air-sensitive compounds were performed under a dry, inert $N_2$ atmosphere using standard Schlenk techniques. THF and $Et_2O$ were dried and distilled from sodium/benzophenone prior to use. The cosolvents were dried according to literature methods [7], distilled and stored over molecular sieves (3 Å). Diisopropylamine and hexamethyldisilazane were distilled at atmospheric pressure and stored over molecular sieves (3 Å).

Nitrotrienes **9a** and **b** were prepared as previously described [2d]. Azatrienes **8a–f** were prepared in the same way as the procedure described in references [2d, 4]. Trienes **7a–d** were prepared according to refs [6, 8]. All the trienes **8** and **7** are oily compounds.

- *Diethyl 2-(cyclopent-2-enyl)-2-(2*E*-penta-2,4-dienyl)malonate* **7a**

Yield: 90%.

$^1$H NMR $\delta$: 1.19 (t, 6H, $J = 7$ Hz), 2.05 (m, 2H), 2.25 (m, 2H), 2.65 (d, 2H, $J = 8$ Hz), 3.40 (m, 1H), 4.08 (q, 4H, $J = 7$ Hz), 4.97 (dd, 1H, $J = 10, 2$ Hz), 5.10 (dd, 1H, $J = 17, 2$ Hz), 5.60 (m, 1H), 5.75 (m, 2H), 6.10 (dd, 1H, $J = 16, 10$ Hz), 6.30 (dt, 1H, $J = 17, 10, 10$ Hz).

$^{13}$C NMR $\delta$: 14.0, 25.0, 31.6, 36.3, 49.1, 60.8, 60.9, 61.0, 115.9, 128.8, 131.0, 132.0, 134.3, 136.6, 170.6, 170.8.

IR (film): 1 740, 1 700, 1 590 cm$^{-1}$.

- *Diethyl 2-(cyclohex-2-enyl)-2-(2*E*-penta-2,4-dienyl)malonate* **7b**

Yield: 90%.

$^1$H NMR $\delta$: 1.23 (t, 6H, $J = 7$ Hz), 1.20–1.90 (m, 4H), 1.96 (m, 2H), 2.70 (d, 2H, $J = 8$ Hz), 2.90 (m, 1H), 4.16 (q, 4H, $J = 7$ Hz), 4.97 (dd, 1H, $J = 10, 2$ Hz), 5.10 (dd, 1H, $J = 17, 2$ Hz), 5.65 (m, 3H), 6.10 (dd, 1H, $J = 16, 10$ Hz), 6.30 (dt, 1H, $J = 17, 10, 10$ Hz).

$^{13}$C NMR $\delta$: 14.0, 22.3, 24.1, 24.8, 35.9, 39.4, 60.8, 60.9, 61.2, 115.9, 128.0, 129.0, 134.2, 136.7, 170.5.

IR (film): 1 740, 1 700, 1 590 cm$^{-1}$.

- *Dimethyl 2-(cyclohex-2-enyl)-2-(2*E*-penta-2,4-dienyl)malonate* **7c**

Yield: 95%.

$^1$H NMR $\delta$: 1.20–1.90 (m, 4H), 1.94 (m, 2H), 2.71 (d, 2H, $J = 8$ Hz), 2.90 (m, 1H), 3.68 (s, 3H), 3.69 (s, 3H), 4.97 (dd, 1H, $J = 10, 2$ Hz), 5.10 (dd, 1H, $J = 17, 2$ Hz), 5.65 (m, 3H), 6.10 (dd, 1H, $J = 16, 10$ Hz), 6.30 (dt, 1H, $J = 17, 10, 10$ Hz).

$^{13}$C NMR $\delta$: 22.2, 24.3, 24.8, 36.0, 39.6, 51.8, 52.0, 61.7, 116.0, 128.0, 134.2, 136.6, 170.7, 171.0.

IR (film): 1 740, 1 700, 1 590 cm$^{-1}$.

- *Dibenzyl 2-(cyclohex-2-enyl)-2-(2*E*-penta-2,4-dienyl)malonate* **7d**

Yield: 95%.

$^1$H NMR $\delta$: 1.20–1.90 (m, 4H), 1.95 (m, 2H), 2.74 (d, 2H, $J = 8$ Hz), 2.90 (m, 1H), 4.97 (dd, 1H, $J = 10, 2$ Hz), 5.10 (m, 1H), 5.10 (s, 2H), 5.11 (s, 2H), 5.60 (m, 3H), 6.10 (dd, 1H, $J = 16, 10$ Hz), 6.30 (dt, 1H, $J = 17, 10, 10$ Hz), 7.29 (m, 10H).

$^{13}$C NMR $\delta$: 22.2, 24.1, 24.8, 36.0, 39.5, 61.6, 66.8, 116.1, 128.0, 134.4, 135.0, 136.6, 170.1, 170.3.

IR (film): 1 740, 1 710, 1 590 cm$^{-1}$.

- *2-(Cyclohex-2-enyl)-2-(2*E*-penta-2,4-dienyl) propane-1,3-diol* **7e**

Yield: 88%.

$^1$H NMR $\delta$: 1.20–1.90 (m, 4H), 1.95 (m, 2H), 2.19 (dd, 2H, $J = 8,1$ Hz), 2.45 (m, 1H), 2.53 (bs, 2H), 3.72 (m, 4H), 4.97 (dd, 1H, $J = 10, 2$ Hz), 5.10 (dd, 1H, $J = 17, 2$ Hz), 5.73 (m, 3H), 6.30 (dt, 1H, $J = 17, 10, 10$ Hz).

$^{13}$C NMR $\delta$: 22.6, 23.5, 25.1, 33.3, 36.6, 44.3, 67.2, 67.3, 115.4, 127.0, 130.0, 133.8, 136.8.

IR (film): 3 300, 1 690, 1 530 cm$^{-1}$.

- N-*Benzyl*-N-*(2*E*-penta-2,4-dienyl)cyclopent-2-enylamine* **8b**

Yield: 60%.

$^1$H NMR $\delta$: 1.90 (m, 2H), 2.40 (m, 2H), 3.05 (m, 1H), 3.20 (m, 1H), 3.42 (d, 1H, $J = 14$ Hz), 3.64 (d, 1H, $J = 14$ Hz), 4.15 (m, 1H), 5.15 (m, 2H), 5.85 (m, 3H), 6.33 (m, 2H), 7.27–7.37 (m, 5H).

$^{13}$C NMR $\delta$: 23.7, 31.6, 52.5, 54.0, 56.8, 115.8, 126.6, 128.0, 128.6, 131.9, 132.7, 133.1, 133.15, 136.8, 140.4.

IR (film): 1 580, 1 630 cm$^{-1}$.

- N-*Benzylhydryl*-N-*(2*E*-penta-2,4-dienyl)cyclopent-2-enylamine* **8c**

Yield: 51%.

$^1$H NMR $\delta$: 1.70 (m, 2H), 2.30 (m, 2H), 3.18 (d, 2H, $J = 6$ Hz), 4.30 (m, 1H), 5.04 (s, 1H), 5.10 (m, 2H), 5.43 (m, 1H), 5.77 (m, 2H), 6.25 (m, 2H), 7.25–7.44 (m, 10H).

$^{13}$C NMR $\delta$: 25.7, 31.3, 48.2, 56.3, 65.0, 68.2, 115.5, 126.6, 128.0, 128.9, 131.8, 132.4, 132.7, 134.8, 136.9, 142.5.

IR (film): 1 580, 1 630 cm$^{-1}$.

- N-*Ethyl*-N-*(2*E*-penta-2,4-dienyl)cyclohex-2-enylamine* **8d**

Yield: 68%.

$^1$H NMR $\delta$: 1.07 (t, 3H, $J = 7$ Hz), 1.45 (m, 2H), 1.76 (m, 2H), 1.95 (m, 2H), 2.50 (m, 2H), 3.07 (m, 1H), 3.25 (m, 1H), 3.50 (m, 1H), 5.08 (m, 2H), 5.70 (m, 3H), 6.30 (m, 2H).

$^{13}$C NMR $\delta$: 14.1, 21.8, 23.4, 25.2, 44.0, 52.2, 56.3, 115.6, 129.6, 130.6, 132.1, 133.9, 136.6.

IR (film): 1 580, 1 630 cm$^{-1}$.

- N-*Benzyl*-N-*(2*E*-penta-2,4-dienyl)cyclohex-2-enylamine* **8e**

Yield: 80%.

$^1$H NMR $\delta$: 1.60 (m, 2H), 1.90 (m, 2H), 2.05 (m, 2H), 3.23 (m, 2H), 3.50 (m, 1H), 3.55 (d, 1H, $J = 14$ Hz), 3.85 (d, 1H, $J = 14$ Hz), 5.15 (m, 1H), 5.80 (m, 3H), 6.35 (m, 2H), 7.29–7.48 (m, 5H).

$^{13}$C NMR $\delta$: 21.6, 23.4, 25.3, 52.0, 53.8, 55.5, 115.7, 126.5, 128.1, 128.4, 129.9, 130.9, 132.3, 133.8, 136.7, 140.9.

IR (film): 1 580, 1 630 cm$^{-1}$.

- N-*Benzhydryl*-N-*(2*E*-penta-2,4-dienyl)cyclohex-2-enylamine* **8f**

Yield: 48%.

$^1$H NMR $\delta$: 1.50 (m, 2H), 1.72 (m, 2H), 1.95 (m,2H), 3.27 (d, 2H, $J = 6$ Hz), 3.65 (m, 1H), 5.05 (m, 2H), 5.07 (s, 1H), 5.55 (m, 2H), 5.70 (m, 1H), 5.95 (m, 1H), 6.30 (m, 1H), 7.21–7.46 (m, 10H).

$^{13}$C NMR $\delta$: 22.2, 25.2, 26.5, 49.1, 55.3, 69.0, 115.3, 126.65, 126.70, 126.75, 128.05, 128.3, 128.6, 131.2, 135.4, 137.0, 143.0, 143.4.

IR (film): 1 580, 1 630 cm$^{-1}$.

### *Thermal cyclization of trienes* **7a–d** *and* **8a–f**

A degassed solution of triene (40 mM/L) in dry toluene was heated in the presence of a trace of hydroquinone in a sealed tube for the time and at the temperature indicated in tables I and II. The organic phase was evaporated and the residue was chromatographed on silica gel (heptane/EtOAc, 96:4) to give **12a,b** and **13a,b** or (heptane/EtOAc, 80:20) to give **10a–f** and **11a–f**.

### *IMDA reaction of nitrotrienes and subsequent denitration [13]*

To a solution of nitrotriene **9a,b** (1.7 mmol) in Et$_2$O (40 mL) was slowly added LiClO$_4$ (21 g, 200 mmol). The mixture was stirred for 24 h at room temperature prior to cooling to 5 °C and washing with water. The organic phase was dried and evaporated to yield cycloadduct **15a,b** (70%).

Cycloadducts **15a,b** (0.66 mmol), HSnBu$_3$ (0.4 mL, 1.5 mmol) and AIBN (15 mg, 0.09 mmol) in dry toluene (11 mL) were refluxed for 5 h. After cooling, H$_2$O was added and the mixture was extracted with EtOAc. The organic phase was washed with H$_2$O, dried and evaporated. The residue was chromatographed on silica gel (heptane/EtOAc, 96:4) to give **13a,b**.

- *1-Benzyl-2,2a,5,5a,6,7,7a,7b-octahydro-1*H*-cyclopenta[*cd*]isoindole* **10b–11b**

$^1$H and $^{13}$C NMR spectral data are presented in tables III and IV.

Anal calc for C$_{17}$H$_{21}$N: C, 85.30; H, 8.85; N, 5.85. Found **10b**: C, 85.60; H, 8.90; N, 5.72.

- *1-Benzhydryl-2,2a,5,5a,6,7,7a,7b-octahydro-1H-cyclopenta[cd]isoindole* **10c**

$^1H$ and $^{13}C$ NMR spectral data are presented in tables III and IV.

Anal calc for $C_{23}H_{25}N$: C, 87.56; H, 7.99; N, 4.44. Found: C, 87.82; H, 7.78; N, 4.21.

- *1-Ethyl-1,2,2a,5,5a,6,7,8,8a,8b-decahydrobenzo[cd]indole* **10d–11d**

$^1H$ and $^{13}C$ NMR spectral data are presented in tables III and IV.

Anal calc for $C_{13}H_{21}N$: C, 81.60; H, 11.07; N, 7.33. Found **10b**: C, 82.08; H, 11.2; N, 7.10.

- *1-Benzyl-1,2,2a,5,5a,6,7,8,8a,8b-decahydrobenzo[cd]indole* **10e**

$^1H$ NMR $\delta$: 2.62 (1H, H2), 2.44 (1H, H2'), 2.47 (1H, H12), 2.70 (1H, H3), 1.29 (2H, H9), 1.53 (2H, H8), 1.65 (2H, H10), 1.85 (1H, H7), 1.92 (1H, H6), 2.20 (1H, H6'), 2.66 (1H, H11), 3.18 (1H, HBn), 3.95 (1H, H'Bn), 5.73 (1H, H5), 5.85 (1H, H4), 7.33 (5H, Ar).

$^{13}C$ NMR $\delta$: 17.8, 24.3, 28.9, 30.3, 30.8, 34.9, 38.9, 56.9, 60.8, 62.9, 127.6, 128.0, 128.3, 130.9, 140.0, 140.9.

Anal calc for $C_{18}H_{23}N$: C, 85.31; H, 9.16; N, 5.53. Found: C, 85.75; H, 9.16; N, 5.43.

- *1-Benzylhydryl-1,2,2a,5,5a,6,7,8,8a,8b-decahydrobenzo[cd]indole* **10f**

$^1H$ and $^{13}C$ NMR spectral data are presented in tables III and IV.

Anal calc for $C_{24}H_{27}N$: C, 87.48; H, 8.27; N, 4.25. Found: C, 87.72; H, 8.07; N, 4.45.

- *Diethyl 2,2a,3,4,4a,5,7a,7b-octahydro-1H-cyclopenta[cd]indene-2,2-dicarboxylate* **12a**

$^1H$ NMR $\delta$: 1.20 (m, 6H), 1.60 (m, 6H), 2.20 (m, 4H), 2.70 (m, 1H), 3.20 (m, 1H), 4.18 (m, 14H), 5.68 (s, 2H).

$^{13}C$ NMR $\delta$: 13.9, 14.0, 26.1, 28.3, 32.0, 34.4, 37.2, 39.6, 43.4, 47.2, 49.2, 60.8, 61.1, 64.5, 124.2, 127.8, 170.5, 171.9.

IR (film): 1 670, 1 730 $cm^{-1}$.

- *Diethyl 2,2a,3,4,4a,5,7a,7b-octahydro-1H-cyclopenta[cd]indene-2,2-dicarboxylate* **13a**

$^1H$ and $^{13}C$ NMR spectral data are presented in tables III and IV.

- *Diethyl 1,2,2a,5,5a,6,7,8,8a,8b-decahydroacenaphthylene-1,1-dicarboxylate* **12b**

$^1H$ and $^{13}C$ NMR spectral data are presented in tables III and IV.

- *Diethyl 1,2,2a,5,5a,6,7,8,8a,8b-decahydroacenaphthylene-1,1-dicarboxylate* **13b**

$^1H$ and $^{13}C$ NMR spectral data are presented in tables III and IV.

- *Dimethyl 1,2,2a,5,5a,6,7,8,8a,8b-decahydroacenaphthylene-1,1-dicarboxylate* **12c**

$^1H$ NMR $\delta$: 1.50 (m, 10H), 2.30 (m, 2H), 2.80 (m, 2H), 3.69 (s, 6H), 5.50 (m, 1H), 5.68 (m, 1H).

IR (film): 1 640, 1 730 $cm^{-1}$.

- *Dibenzyl 1,2,2a,5,5a,6,7,8,8a,8b-decahydroacenaphthylene-1,1-dicarboxylate* **12d**

$^1H$ NMR $\delta$: 1.20 (m, 5H), 2.00 (m, 7H), 2.80 (m, 2H), 5.10 (m, 4H), 5.65 (m, 1H), 5.71 (m, 1H), 7.29 (m, 10H).

IR (film): 1 640, 1 730 $cm^{-1}$.

- *1,2,2a,5,5a,6,7,8,8a,8b-Decahydroacenaphthylene-1,1-dimethanol* **12e**

$^1H$ NMR $\delta$: 1.20 (m, 4H), 1.70 (m, 4H), 2.00 (m, 4H), 2.50 (m, 2H), 2.85 (m, 2H), 3.70 (m, 4H), 5.50–5.75 (m, 1H), 5.69 (s, 1H).

F: 145 °C.

Anal calc for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.02; H, 9.85.

- *1,2,2a,5,5a,6,7,8,8a,8b-Decahydroacenaphthylene-1,1-dimethanol* **13e**

$^1H$ NMR $\delta$: 1.30 (m, 4H), 1.70 (m, 6H), 1.95 (m, 2H), 2.40 (m, 2H), 2.95 (m, 2H), 3.69 (m, 4H), 5.55 (m, 1H), 5.75 (m, 1H).

$^{13}C$ NMR $\delta$: 23.6, 26.0, 28.7, 31.9, 32.1, 32.8, 35.7, 41.1, 44.4, 49.2, 68.3, 71.4, 126.5, 128.8.

F: 161 °C.

Anal calc for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.28; H, 9.77.

- *2,2-Bis{[(3,5-dinitrobenzoyl)oxy]methyl}-2,2a,3,4,4a,5,7a,7b-octahydro-1H-cyclopenta[cd]indene* **14a**

F: 104 °C.

Anal calc for $C_{27}H_{24}N_4O_{12}$: C, 54.37; H, 4.05; N, 9.39. Found: C, 54.53; H, 4.34; N, 9.33.

- *1,1-Bis{[(3,5-dinitrobenzoyl)oxy]methyl}-1,2,2a,5,5a,6,7,8,8a,8b-decahydroacenaphthylene* **14b**

F: 210 °C.

Anal calc for $C_{28}H_{26}N_4O_{12}$: C, 55.08; H, 4.29; N, 9.18. Found: C, 55.24; H, 4.32; N, 9.07.

## Acknowledgment

C Bois (Laboratoire de chimie des métaux de transition, UPMC) is acknowledged for the determination of the crystal structure.

## Supplementary material available

X-ray characterization data for **12b**, including tables of distances and angles, fractional atomic coordinates, thermal parameters, (tables S1–S4), calculated and observed structural factors have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° = SUP 90413 and are available on request from the Document Supply Center.

## References

1 For reviews of the IMDA reaction, see:
  a) Carlson RG, *Ann Rep Med Chem* (1974) 9, 270
  b) Oppolzer W, *Angew Chem Int Ed Engl* (1977) 16, 10
  c) Oppolzer W, *Synthesis* (1978) 793
  d) Brieger G, Bennett JN, *Chem Rev* (1980) 80, 63
  e) Funk R, Vollhardt KPC, *Chem Soc Rev* (1980) 9, 41
  f) Ciganek E, *Org React* (1984) 32, 1

g) Fallis AG, *Can J Chem* (1984) 62, 183
h) Taber DF, *Intramolecular Diels–Alder Reactions and Alder Ene Reactions*, Springer, Berlin, 1984
i) Craig D, *Chem Soc Rev* (1987) 16, 187
j) Roush WR, In: *Advances in Cycloaddition*, Curran DP, Ed, JAI Greenwich, CT, 1990, Vol 2, p 91
h) Roush WR, In: *Comprehensive Organic Synthesis*; Trost BM, Ed, Pergamon, Oxford, 1991, Vol 5, p 513

2 a) Guy A, Lemaire ML, Nègre M, Guetté JP, *Tetrahedron Lett* (1985) 3575
b) Guy A, Lemaire ML, Graillot Y, Nègre M, Guetté JP, *Tetrahedron Lett* (1987) 2969
c) Guy A, Graillot Y, *Tetrahedron Lett* (1990) 7315
d) Guy A, Serva L, *Synlett* (1994) 647

3 Murashi SI, Taniguchi Y, Imada Y, Tanigawa Y, *J Org Chem* (1989) 54, 3292

4 Guy A, Barbetti JF, *Synth Commun* (1992) 22, 853

5 Corey EJ, Estreicher H, *J Am Chem Soc* (1978) 100, 6294

6 Moffett RB, Hart CA, Hoehn WM, *J Am Chem Soc* (1947) 69, 1854

7 Armarego WLF, Perrin DD, *Purification of Laboratory Chemicals*, 3rd ed, Pergamon, Oxford, 1988

8 Page PCB, Jennens DC, Porter RA, Baldock AN, *Synlett* (1991) 472

9 Vogel AI, *Practical Organic Chemistry*, Longman, London, 1961, p 262

10 Neuhaus D, Williamson M, *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, VCH, New York, 1989

11 Bax A, Griffey RH, Hawkins BL, *J Magn Res* (1983) 55, 301

12 a) Aue WP, Bartholdie E, Ernst RR, *J Chem Phys* (1976) 64, 2229
b) Nagayama K, *J Magn Res* (1980) 40, 321 cosy

13 Ono N, Miyake H, Kaji A, *J Chem Soc, Chem Commun* (1982) 33