A Facile Approach to Norbornene-annulated Cyclopentenones,
A Novel Class of Tricyclodecadienones

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Abstract: An efficient synthesis of norbornene annulated cyclopentenones 5 and 18 starting from readily available tricyclodecadienone carboxylic acid 2a is described. Parent tricyclo[5.2.1.02,6]decadi-2(6),8-ene 5, an hitherto unknown compound, has been obtained in good yield by subjecting bromide 7b to base induced elimination or by oxidative deselenylation of 7c. 5-Substituted analogues 18 are conveniently obtained from phenylselenide 3c by stereoselective conjugate cuprate addition followed by oxidative elimination of the seleno group. Dehydrobromination of epoxy bromide 21 affords norbornene-annulated cyclopentadienone 22 which immediately undergoes stereoselective 1,4-addition at the strained C_2-C_6 enone moiety to give 23. These novel norbornene annulated cyclopentenones can be considered as the synthetic equivalent of 2-cyclopentynones.

Introduction

The tricyclo[5.2.1.02,6]decadienone system 1 constitutes a versatile synthetic equivalent of cyclopentadienone. Its rigid structure, the presence of a reactive α,β-enone system and the ability of the tricyclic skeleton to undergo [4+2]-cycloreversion are instrumental in the synthesis of a variety of functionalized cyclopentenones with defined stereochemistry and chirality. The endo-tricyclodecadienone system, racemic as well as enantiopure, is conveniently accessible via carboxylic acid 2a, which in turn is readily available from the Diels-Alder adduct of benzoquinone and cyclopentadiene.

In the preceding paper, the synthesis of a series of 6-substituted tricyclodecadienones 3 starting from 2a employing Barton’s radical chain decarboxylation methodology is described. Bromodecarboxylation of 2a appeared to be particularly suitable for a high yield synthesis of bridgehead bromide 3a. Dehydrobromination of 3a using selected basic conditions is an efficient process to give elusive...
norbornene-annulated cyclopentadienone 4 as a transient intermediate in nearly quantitative yield. Although this cyclopentadienone is still too reactive to be isolated its bicyclic structure retards its [4+2]-dimerization to such an extent that nucleophilic conjugate addition and crossed Diels-Alder reactions can compete efficiently. This is exemplified by the alkaline methanolysis of bromide 3a which produces bridghead methyl ether 3b in excellent yield (>80%). The exclusive formation of 3b shows that 4 can be effectively intercepted by a nucleophile in a regio- and stereospecific conjugate addition involving the central C2-C6 enone moiety which is evidently more strained than the peripheral C4-C5 enone function. The efficient two step synthesis of 4 from acid 2a suggests that this sequence of steps may also be applicable to the synthesis of the interesting hitherto unknown positional isomer of 1 viz. tricyclo[5.2.1.02.6]deca-2(6),8-dien-3-one 5. The absence of the peripheral enone moiety as present in 4 will probably lead to considerable chemical stability and accordingly it may be expected that this tricyclodecadienone 5 is isolable despite its constrained C2-C6 enone system. In this paper the successful synthesis of 5 and some of its derivatives is described.

Results and discussion

Norbornene-annulated cyclopentenone 5 is essentially the Diels-Alder adduct of cyclopentadiene and 2-cyclopentynone. Although this direct route to 5 is obviously blocked by the non-availability of 2-cyclopentynone, even as a transient intermediate, the use of an appropriate synthetic equivalent may, however, circumvent this synthetic problem. Kienzle and Minder applied β-arylsulfonylcyclopentenones 6 for this purpose. With cyclopentadiene the corresponding tricyclodecadienones 7aa were obtained as an endolexox-mixture (2:1 ratio) in 60-80% yield (Scheme 1). Attempts to eliminate the arylsulfonyl group in 7a by a variety of basic reagents did not produce the desired ketone 5 but only led to its isomer 1 (R=H). Although the authors suggest that 1 is the result of β,γ-, and not of α,β-elimination, involving the initial formation of 8, this seems highly unlikely as the γ-hydrogen at C5 is not activated at all. Most interestingly, reducing the C8-C9 double bond in 7a and repeating the elimination procedure now smoothly converted 9 into the C2-C6 enone 10 in 60-80% yield. (Scheme 1). This result indicates that the C8-C9 double bond in the β-elimination of sulfone 7a plays a decisive role in the product formation.

An effective route to 6-substituted tricyclodecenones 7 is Barton's radical chain decarboxylation of the corresponding carboxylic acid 11 (Scheme 2). As was demonstrated for 3 in the preceding paper, both the 6-bromo and 6-selenyl compounds 7b and 7c are available using this methodology. Both compounds may then undergo α,β-elimination to form 5 either by base induced dehydrobromination or oxidative syn-deselenylation. These conversions may be much more effective than the elimination of sulfinic acid.
from sulfone 7a.

The bromodecarboxylation of tricyclic acid 11 which is readily available by lithium aluminum hydride reduction of tricyclic ester 2b (R=C2H5) and subsequent basic hydrolysis, was accomplished using essentially the same procedure as reported for the transformation of carboxylic acid 2a into enone bromide 3a. Conversion of 11 into the corresponding acid chloride with oxalyl chloride, followed by treatment with the sodium salt of N-hydroxypyridine-2-thione afforded the N-acyloxypyridine-2-thione ester 12 which was immediately exposed to bromotrichloromethane at reflux temperature to give 6-bromo compound 7b in an excellent overall yield of 91% (Scheme 2).

Scheme 2

Phenylselenyldecarboxylation of 11 also proceeded smoothly with diphenyl selenide in toluene as the radical trapping agent. 6-Phenylselenyltricyclodecadienone 7c was obtained in 84% yield as a nice crystalline material.

6-Bromotricyclodecenone 7b showed similar reactivity towards triethylamine in methanol (1:4) as did as tricyclodecadienone bromide 3a. At room temperature hardly any elimination of bromide was observed whereas at reflux temperature the reaction was complete within 30 minutes. Capillary gas chromatography revealed the formation of three products in a ratio 12:4:1, which, on basis of their 1HNMR-spectra were identified as the desired enone 5, and endo- and exo-tricyclodecadienone 1 (R=H) and 13, respectively (Scheme 3). Pure 5 was readily obtained in 60% yield by flash chromatography over silica gel. The formation of endo- and exo-tricyclodecadienone (1 and 13) in this bromo-elimination of 7b is readily explained by rearrangement of the initially formed 5 involving the base induced enolization process depicted in Scheme 4. Deprotonation at C4 leads to the cyclopentadienolate intermediate which by
a series of 1,5 proton shifts eventually forms either endo-14 or exo-14. Subsequent stereospecific protonation of these enolates at C2 then leads to observed mixture of endo- and exo-tricyclodecadienones (1 and 13). The occurrence of such a base catalyzed process was conveniently demonstrated by treating 5 under identical conditions as applied by Kienzle and Minder5 using diazabicyclo[5.4.0]undecene (DBU) in tetrahydrofuran. After stirring for 3 days quantitative conversion of 5 into a mixture of endo-1 and exo-13 in a ratio of 8:3 was observed. This result not only explains the failure of the Swiss group to isolate 5 but also shows that the choice of the base used in the preparation of 5 is crucial. The thermodynamic bias which is the reason for the rapid base induced isomerization of 5 was substantiated by both force field (MM2) and semi-empirical (AM1) calculations 8 (Table 1).

Table 1. Calculated heat of formation(AM1) and strain energy(MM2)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>5</th>
<th>13</th>
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<tbody>
<tr>
<td>Heat of formation (AM1) Kcal/mol</td>
<td>27.62</td>
<td>41.13</td>
<td>25.85</td>
</tr>
<tr>
<td>Strain energy (MM2) Kcal/mol</td>
<td>30.49</td>
<td>39.76</td>
<td>28.92</td>
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</table>

After the successful synthesis of tricyclic enone 5 using the non-nucleophilic base triethylamine, the question arose whether a more nucleophilic base system, such as potassium hydroxide in methanol could be used for the preparation of 6-methoxy-endo-tricyclodecenone 7d. At room temperature bromide 7b rapidly reacted with this reagent to give 7d in 90% yield (Scheme 5)11. No enone 5 was detected in the product mixture. The formation of 7d is clearly the result of rapid conjugate addition of methoxide to relatively strained C2-C6 enone moiety of initially formed 5. This result already indicates the high reactivity of this central enone system in 5 toward nucleophiles. Interestingly, no tricyclodecadienones 1 and 13 were observed showing that nucleophilic addition to 5 is much more rapid than the enolization shown in Scheme 4.

The oxidative deselenylation is a syn-elimination reaction which generally proceeds at moderate
temperatures and in high yields. Oxidation of selenide \( 7\text{c} \) with sodium periodate at 5 °C using standard conditions fully conformed to this general picture. After 20 min, the reaction was already complete to give tricyclodecadienone 5 as a single product in 75% isolated yield (Scheme 6). No tricyclodecadienones \( 7\) and \( 13 \) were detected in the reaction mixture, confirming that base is needed for the isomerization of 5 to these compounds.

It should be possible to extend the scope of the above methodology to the synthesis of derivatives of 5. One way to do so would be to use the enone system in either carboxylic acid \( 2\text{a} \) or 6-substituted tricyclodecadienones \( 3 \) as a handle for derivatization. After the desired enone transformation, elimination of an appropriate leaving group at \( C_6 \) would then give the desired \( C_2-C_6 \) enone moiety.

Tricyclic phenylselenide \( 3\text{c} \) was selected to verify this approach as this compound is readily available in high yield from acid \( 2\text{a} \) (Scheme 7). In view of the previous experiences with conjugate cuprate additions to tricyclodecadienones \( 1 \), this reaction was investigated for \( 3\text{c} \) using four different cuprates.
The addition of dimethyl- and di-n-butylcuprate to 3e proceeded smoothly and in both cases afforded a single addition product in excellent yield. Based on their spectral data which will be discussed below, structures 15a and 15b were assigned to these addition products (Scheme 7). Increasing the steric bulk of the nucleophile by using di-t-butylcuprate led again to a single addition product viz. 15c in a modest yield which is most likely due to the instability of the cuprate reagent. Subjecting 3e to diphenylcuprate gave again a single 1,4-addition product, 15d, and also a small amount of the 1,2-addition product.

The gross structures of the products 15a-d were all deduced from their mass, IR, and NMR data. However, the unequivocal assignment of the configuration (endo or exo) of the newly introduced substituent at C5 in 15 required a more detailed 1H-NMR analysis. Comparison of the 1H-NMR spectra of structures 15a-d with related tricyclodecenones viz. 16 and 17 revealed unambiguously the stereochemistry at C5 in 15 (Table 2). All tricyclodecenones 16 and 17 having C5 endo-protons exhibit proton signals at a considerably higher field (lower shift value) than the C5 exo-protons in the related structures. This phenomenon is the result of effective shielding of the endo-C5 protons by the C8-C9 double bond. The observation that for 15a-d the C5 protons are found at relatively lower field (higher shift value) proves their endo-stereochemistry (endo-R). Additional evidence for the correctness of this assignment is derived from the strong shielding effect exhibited by the C5 endo-phenyl group on the C8 and C9 olefinic.

Table 2. Chemical shift of selected protons in 15, 16 and 17

<table>
<thead>
<tr>
<th>compound</th>
<th>H_5,exo</th>
<th>H_5,endo</th>
<th>H_8 and H_9</th>
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<td>15a R=endo-Me</td>
<td>2.76</td>
<td>6.11</td>
<td>6.31</td>
</tr>
<tr>
<td>b endo-n-Bu</td>
<td>2.60</td>
<td>6.09</td>
<td>6.27</td>
</tr>
<tr>
<td>c endo-t-Bu</td>
<td>2.77</td>
<td>6.13</td>
<td>6.35</td>
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<tr>
<td>d endo-Ph</td>
<td>3.99</td>
<td>5.69</td>
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<td>6.20</td>
<td>6.30</td>
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<tr>
<td>b exo-n-Bu</td>
<td>1.86</td>
<td>6.18</td>
<td>6.30</td>
</tr>
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<tr>
<td>e endo-n-Bu</td>
<td>2.31</td>
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<tr>
<td>f endo-Ph</td>
<td>3.97</td>
<td>5.79</td>
<td>6.12</td>
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</table>
protons in 17f and 15d. In 17c which contains an C₅-exo-phenyl substituent these olefinic protons absorb at considerably lower field (higher shift value). At a later stage of this project definite proof of the correctness of this ¹H NMR analysis was obtained from an X-ray diffraction analysis of 15a the result of which is depicted in figure 1.

![Figure 1. X-ray structure of 15a](image)

The complete endo-selectivity in combination with the high yields and relatively fast reaction rates observed for the cuprate addition to 3c is quite surprising as the endo-face of the endo-tricyclodecadienone system is severely hindered by the C₅-C₆ ethene bridge which generally results in predominant exo-addition. It is evident that the bulky phenylselenyl group at C₆ may severely hinder or even block conjugate addition from the exo-face of 3c but this should at least be reflected in lower reaction rates and lower yields. Detailed studies to uncover the true nature of this cuprate addition to 3c are currently underway and will be reported in due course. From a synthetic point of view this directing effect of the phenylselenyl group is highly rewarding.

The oxidative deselenation of 15 was carried out as described above for the synthesis of 5 from 7c. By stirring 15a-d with sodium periodate in methanol a smooth elimination was observed in all cases to afford the corresponding tricyclodecadienones 18a-d in yields of ca. 80% (Scheme 8).

![Scheme 8](image)

The successful synthesis of norbornene-annulated cyclopentenones 5 and 18 was a reason to consider this methodology for the preparation of norbornene-annulated cyclopentenone epoxide 22 (Scheme 9). Cyclopentenone epoxide 22 is a fascinating compound for which an unusual chemical reactivity is expected on basis of the unique combination of an epoxide ring, a vinyl system and a ketone function within in a compact, small ring system. In recent papers, a first general synthesis of some simply substituted cyclopentadienone epoxides and their reactions with nucleophilic reagents was reported. The
synthetic potential of these epoxides for natural product synthesis was demonstrated by the preparation of *epi*-pentenomycin\textsuperscript{14,13}.

A direct route to \( 22 \) would be the regioselective epoxidation of the enone moiety in tricyclic bromide \( 3a \) to give epoxy bromide \( 21 \) followed by dehydrobromination. However, attempts to obtain \( 21 \) by alkaline epoxidation of tricyclic bromide \( 3a \) using standard methods did not give satisfactory results. Epoxide \( 21 \) was obtained in only 40\% yield due to the base sensitivity of bromide \( 3a \). As oxidation of selenium by hydrogen peroxide is a fast process we did not try such an epoxidation for \( 3c \).

An alternative route to epoxy bromide \( 21 \) starts from tricyclic epoxide ester \( 19 \) which is produced from ester \( 2b \) in more than 90\% yield by alkaline epoxidation\textsuperscript{1a,8} (Scheme 9). Basic hydrolysis using sodium hydroxide in methanol afforded epoxy acid \( 20 \) in quantitative yield. Barton halodecarboxylation of \( 20 \) using essentially the same procedure as described earlier for the synthesis of \( 7b \), gave \( 21 \) in 84\% yield. Applying triethylamine as the base to effect dehydrobromination of \( 21 \) under a variety of conditions led only to complex mixtures. No cyclopentadienone epoxide \( 22 \) was detected among the products. When a more nucleophilic reagent was applied, such as potassium hydroxide in methanol, a methoxy substituted epoxide was isolated in 71\% yield. Again there were no indications of the presence of \( 22 \) in the reaction mixture showing that this annulated cyclopentadienone epoxide is apparently too reactive to be isolated under these nucleophilic conditions\textsuperscript{14}. Analysis of the \(^1\text{H}NMR\) spectra suggested structure \( 23 \) for the newly formed epoxy ketone. The formation of this *endo*-6-methoxy-exo-tricyclodecenone epoxide from *exo*-6-bromo-endo-tricyclodecenone epoxide \( 21 \) proves the intermediacy of norbornene-annulated cyclopentenone epoxide \( 22 \) which under the reaction conditions rapidly undergoes stereospecific conjugate addition of methanol at its *endo*-face. In the preceding paper, it was reported that methanol addition to norbornene-annulated cyclopentenone \( 4 \) is also a stereospecific process to give exclusively *exo*-6-methoxy-endo-tricyclodecenone \( 24 \) (Scheme 10)\textsuperscript{4}. This observation shows that in \( 4 \) the methylene bridge exerts less steric hindrance to the incoming nucleophile than the C\(_8\)-C\(_9\) ethylene bridge. The complete inversion of stereochemistry observed for the methoxylation to epoxide \( 22 \) illustrates the subtlety of this 'bridge effect' on the facial stereoselectivity of conjugate addition reactions to these
A novel class of tricyclodecadienones. The presence of a relative small epoxide function at the exo-face as in 22 exerts enough steric bulk to completely outweigh the directing effect of the bridges.

Unambiguous proof for the correctness of structure 23 was obtained from the alkaline epoxidation of 24 which gave \textit{exo}-6-methoxy-\textit{endo}-tricyclodecadienone epoxide 25 in almost quantitative yield (Scheme 10). This epoxide, which structure was unequivocally established by comparison of its $^1$H NMR-data with those of tricyclic \textit{exo}-epoxides 19, 20 and 21, was not identical with tricyclic epoxide 23.

The results described above indicate that the synthesis of norbornene annulated cyclopentenones including parent tricyclodeca-2(6),8-dien-3-one 5 can be accomplished starting from readily available carboxylic acid 2a.

**Experimental**

**General remarks**

Melting points were measured with a Reichert Thermopan microscope and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. $^1$H and $^{13}$C-NMR spectra were recorded on a Bruker AM-400 spectrophotometer, using TMS as an internal standard. For mass spectra a double focussing VG 7070E mass spectrometer was used. Capillary GC analyses were performed using a Hewlett-Packard 5890A gas chromatograph, containing a cross-linked methyl silicone column (25m). Flash chromatography were carried out at a pressure of ca. 1.5 bar, a column length of 15-25 cm and a column diameter of 1-4 cm, using Merck Kieselgel 60H. Elemental analyses were performed on a Carlo Erba Instruments CHNS-O 1108 Elemental analyzer. All solvents used were dried and distilled according to the standard procedures.

**6-Bromo-endo-tricyclo[5.2.1.0$^{2,6}$]deca-8-en-3-one 7b**

A solution of acid 11 (192 mg, 1 mmole) in benzene (5 ml) was treated with oxalyl chloride (0.3 ml) and a drop of dimethylformamide. After stirring for 2 hrs at room temp. with protection from moisture, the solvent and excess oxalyl chloride were evaporated and the residual acid chloride was used as such.

A solution of acid chloride (1 mmole) in benzene (5 ml) was added dropwise (15 min.) to a dried, stirred suspension of N-hydroxypyridin-2-thione sodium salt (190 mg, 1.2 mmole) in refluxing bromotrichloromethane while irradiating with a 250 w tungsten lamp in an inert atmosphere. After completion of the addition, the reaction mixture was cooled to room temp. and evaporated to dryness. The crude product was purified by flash chromatography over silica gel to give pure 7b (200 mg, 90%) as a

![Scheme 10](attachment:scheme10.png)
colorless oil.

7b: 1H-NMR (400 MHz, CDCl₃): δ 6.25-6.20 (m, 2H, H₈ and H₉), 3.41 (brs, 1H, H₁ or H₇), 3.32 (d, J₁₂=4.5 Hz, 1H, H₂), 3.25 (brs, 1H, H₁ or H₇), 2.73-2.65, 2.61-2.52, 2.35-2.25 and 2.15-1.91 (4 x m, 4H, H₄ and H₅), 2.26 A of AB (d, J₁₀a⁺₁₀b=8.9 Hz, 1H, H₁₀a), 1.91 B A of AB (d, J₁₀a⁺₁₀b=8.9 Hz, 1H, H₁₀a).

13C-NMR (100 MHz, H-dec., CDCl₃): δ 216.5 (quat.), 138.0/134.5 (tert.), 71.1 (quat.), 66.0/57.9 (tert.), 52.7 (sec.), 47.0 (tert.), 41.8/37.4 (sec.). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1730 (C=O) cm⁻¹. CI/MS: m/e (%) 229/227 (0.1/0.1, M⁺+1), 163/161 (12/13, M⁺+1-Br), 147 (12, M⁺-C₅H₆), 66 (29, C₅H₆⁺).

EI/HRMS m/e: 227.0071 [calc. for C₁₀H₁₂O₂Br(M⁺+1): 227.0072].

6-Phenylselenyl-endotricycl[5.2.1.0²⁶]deca-8-en-3-one 7c

A solution of acid 11 (192 mg, 1 mmole) in benzene (5 ml) was treated with oxalyl chloride (0.3 ml) and a drop of dimethylformamide. After stirring for 2 hrs at room temp. with protection from moisture, the solvent and excess oxalyl chloride were evaporated and the residual acid chloride used as such.

A solution of acid chloride (1 mmole) in toluene (5 ml) was added dropwise (15 min.) to a dried, stirred suspension of N-hydroxypyridin-2-thione sodium salt (190 mg, 1.2 mmole) in refluxing toluene (10 ml) containing 2 mmol of diphenyl diselenide while irradiating with a 250 w tungsten lamp in an inert atmosphere. After completion of the addition, the reaction mixture was cooled to room temp. and evaporated to dryness. The crude product was purified by flash chromatography (n-hexane/EtOAc = 9/1) over silica gel to give pure 7c (260 mg, 84 %) as a white solid.

7c: m.p.: 101-103 °C (diisopropyl ether). 1H-NMR (400 MHz, CDCl₃): δ 7.68-7.32 (m, 5H, Ph-H), 6.20-6.16 (m, 2H, H₈ and H₉), 3.24 and 3.19 (2 x brs, 2H, H₁ and H₇), 2.91 (d, J₁.²=4.5 Hz, 1H, H₂), 2.46-2.26 (m, 2H, H₄), 2.24 A of AB (d, J₁₀a⁺₁₀b=8.7 Hz, 1H, H₁₀a), 2.08-2.00 and 1.94-1.76 (2 x m, 2H, H₅), 1.77 B A of AB (d, J₁₀a⁺₁₀b=8.7 Hz, 1H, H₁₀a). 13C-NMR (100 MHz, H-dec., CDCl₃): δ 218.5 (quat.), 137.0/113.6/136.6/135.9/129.2 (tert.), 128.9 (quat.), 128.7/62.4 (tert.), 58.0 (quat.), 53.8 (tert.), 52.4 (sec.), 47.0 (tert.), 41.5/33.3 (sec.). IR (CH₂Cl₂): ν 3100-3020 (C-H, sat.), 1725 (C=O) cm⁻¹. Cl/MS: m/e (%) 304 (0.5, M⁺), 238 (44, M⁺-C₅H₆), 66 (10, C₅H₆⁺). EI/HRMS m/e: 304.0366 [calc. for C₁₆H₁₆O₈²⁶Se(M⁺): 304.0366].

endo-Tricyclo[5.2.1.0²⁶]deca-2(6),8-dien-3-one 5 and endo- and exo-tricyclo[5.2.1.0²⁶]deca-4,8-dien-3-one 1 and 17

A solution of 7b (60 mg) in methanol (8 ml) and Et₃N (2 ml) was refluxed for 30 min. Removal of the solvent followed by dissolution of the residue in n-hexane/ethyl acetate (3/1) and subsequent filtration gave, after drying (MgSO₄) and concentration, a mixture (40 mg) of 5, 1 and 13 in 12:4:1 ratio (according to GC and NMR). Pure 5 was obtained by flash chromatography (n-hexane/EtOAc = 9/1).

5: 1H-NMR (400 MHz, CDCl₃): δ 6.88 A of AB (dd, J₈.₉=5.0 Hz, H₈, resp. J₇.₈=3.2 Hz, 1H, H₈ or H₉), 6.79 B of AB (dd, J₈.₉=5.0 Hz, J₁.₉ resp. J₇.₈=3.3 Hz, 1H, H₈ or H₉), 3.76 and 3.61 (2 x brs, 2H, H₁ and H₁), 2.84-2.50 (m, 4H, H₄ and H₅), 2.47 and 2.39 AB x 2 (2 x d, J₁₀a⁺₁₀b=6.8 Hz, 2H, H₁₀a). 13C-NMR (100 MHz, CDCl₃): δ 203.2/199.4/159.4 (quat.), 144.6/141.6 (tert.), 74.6 (sec.), 51.1/44.9 (tert.), 41.2/26.3 (sec.). IR (CH₂Cl₂): ν 3010-2860 (C-H, sat.), 1675 (C=O) cm⁻¹. El/MS: m/e (%) 146 (100, M⁺), 66 (21, C₃H₆⁺). EI/HRMS m/e: 146.0732 [calc. for C₁₀H₁₀O(M⁺): 146.0732].
A novel class of tricyclodecadienones

H_{4}), 5.94 A of AB (dd, J_{8,9}=5.6 Hz, J_{1,9} resp. J_{7,8}=2.9 Hz, 1H, H_{8} or H_{9}), 5.78 B of AB (dd, J_{8,9}=5.6 Hz, J_{1,9} resp. J_{7,8}=3.0 Hz, 1H, H_{8} or H_{9}), 3.42 and 3.22 and 2.97 (3 x brs, 3H, H_{1}, H_{6} and H_{7}), 2.80 (dd, J_{1,2}= J_{2,6}=5.1 Hz, 1H, H_{2}), 1.74 and 1.63 AB x 2 (2 x d, J_{10a,10b}=8.4 Hz, 2H, H_{10a} and H_{10b}). GCEI/MS: m/e (%)

146 (84, M^+), 118 (33, M^+-CO), 81 (13, M^{+}+1-C_{3}H_{6}), 66 (100, C_{3}H_{6}^+).

end-5-Methyl-exo-6-phenylselenyl-endotricyclo[5.2.1.0^2^6]deca-8-en-3-one 15a

Following the general procedure A [MeLi (1 ml of 1.6 M solution in hexane, 1.6 mmol), CuI (200 mg, 1 mmol), 3c (150 mg, 0.5 mmol)], gave, after work-up and flash chromatography (n-hexane /EtOAc = 20/1), 140 mg (89 %) of 15a as a white solid.

15a: m.p.: 61-62 °C (disisopropylether). ^1H-NMR (400 MHz, CDCl_{3}): 8 7.66-7.29 (m, 5H, Ph-H), 6.31 A of AB (dd, J_{8,9}=5.6 Hz, J_{1,9} resp. J_{7,8}=3.0 Hz, 1H, H_{8} or H_{9}), 6.12 B of AB (dd, J_{8,9}=5.6 Hz, J_{1,9} resp. J_{7,8}=2.9 Hz, 1H, H_{8} or H_{9}), 3.27 and 3.12 (2 x brs, 3H, H_{1}, H_{2} and H_{3}), 2.81-2.71 (m, 1H, H_{3}), 2.39 A of AB (d, J_{10a,10b}=8.6 Hz, 1H, H_{10a}), 2.08 A of AB (dd, J_{4a,4n}=18.4 Hz, J_{4a,5}=9.5 Hz, 1H, H_{4a}), 1.78 B of AB.
endo-5-n-Butyl-exo-6-phenylselenyl-endo-tricyclo[5.2.1.0\(^1\)]deca-8-en-3-one \(\text{15b}\)

Following the general procedure A [n-BuLi (1 ml of 1.6 M solution in hexane, 1.6 mmol), CuI (200 mg, 1 mmol), \(\text{3c} (150 \text{ mg, 0.5 mmol})\), gave, after work-up and flash chromatography (n-hexane /EtOAc= 20/1), 155 mg (86 %) of \(\text{15b}\).

\(\text{15b}: \) \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 7.66-7.29 \text{ (m, 5H, Ph-H)}\), 6.27 A of AB (dd, \(J_{8,9}=5.6 \text{ Hz}, J_{1,9} \text{ resp. } J_{7,8}=3.1 \text{ Hz, 1H, H}_8 \text{ or H}_9\)), 6.09 B of AB (dd, \(J_{8,9}=5.6 \text{ Hz}, J_{1,9} \text{ resp. } J_{7,8}=2.9 \text{ Hz, 1H, H}_8 \text{ or H}_9\)), 3.25 and 3.14 (2 x brs, 2H, \(H_1 \text{ or H}_7\)), 3.11 (d, \(J_{1,2}=4.9 \text{ Hz, 1H, H}_2\)), 2.63-2.55 (m, 1H, \(H_2\)), 2.37 A of AB (d, \(J_{10a,s}=8.6 \text{ Hz, 1H, H}_{10a}\)), 2.11 A of AB (dd, \(J_{4x,4n}=18.4 \text{ Hz, } J_{4x,5}=12.0 \text{ Hz, 1H, H}_{4n}\)), 1.70 B of AB (dd, \(J_{4x,4n}=18.4 \text{ Hz, } J_{4n,5}=12.0 \text{ Hz, 1H, H}_{4n}\)), 1.75 B of AB (d, \(J_{10a,s}=8.6 \text{ Hz, 1H, H}_{10a}\)), 1.58-1.00 (m, 6H, -(CH\(_2\))\(_3\)), 0.84 (t, 3H, CH\(_3\)). 13C-NMR (100 MHz, CDCl\(_3\)): \(\delta 218.7 \text{ (quat.)}, 137.7/137.1 \text{ (tert.), } 129.5/129.0 \text{ (quat.), } 62.8 \text{ (quat.), } 54.8 \text{ (sec.), } 54.1/53.6/46.8 \text{ (tert.), } 44.6 \text{ (sec.), } 37.0 \text{ (quat.), } 37.0 \text{ (prim.)}\). IR (CH\(_2\)Cl\(_2\)): \(\nu 3080-3020 \text{ (C-H, unsat.), } 3010-2860 \text{ (C-H, sat.), } 1720 \text{ (C=O) cm}^{-1}\). El/MS: m/e (%) 360 (3, M\(^+\)), 294 (100, M\(^+-\text{CsH}_6\)), 203 (55, M\(^+-\text{SePh}\)), 175 (37, M\(^+-\text{SePh-CO}\)), 137 (68, M\(^+-\text{SePh-C_5H}_6\)), 66 (51, C\(_3\)H\(_6\)^\). El/HRMS m/e: 360.0991 [calc.for C\(_{20}\)H\(_{24}\)O\(^8\)Se (M\(^+\)): 360.0992].

endo-5-t-Butyl-exo-6-phenylselenyl-endo-tricyclo[5.2.1.0\(^2\)]deca-8-en-3-one \(\text{15c}\)

Following the general procedure A [t-BuLi (1 ml of 1.6 M solution in hexane, 1.6 mmol), CuI (200 mg, 1 mmol), \(\text{3c} (150 \text{ mg, 0.5 mmol})\), gave, after work-up and flash chromatography (n-hexane /EtOAc= 20/1), 45 mg (25 %) of \(\text{15c}\).

\(\text{15c}: \) \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 7.66-7.29 \text{ (m, 5H, Ph-H)}\), 6.36 A of AB (dd, \(J_{8,9}=5.6 \text{ Hz}, J_{1,9} \text{ resp. } J_{7,8}=3.0 \text{ Hz, 1H, H}_8 \text{ or H}_9\)), 6.13 B of AB (dd, \(J_{8,9}=5.6 \text{ Hz}, J_{1,9} \text{ resp. } J_{7,8}=2.9 \text{ Hz, 1H, H}_8 \text{ or H}_9\)), 3.34 (brs, 1H, \(H_1 \text{ or H}_7\)), 3.18 (d, \(J_{1,2}=5.1 \text{ Hz, 1H, H}_2\)), 3.12 (brs, 1H, \(H_1 \text{ or H}_7\)), 2.77 (dd, \(J_{4n,5}=12.9 \text{ Hz, } J_{4x,5}=10.3 \text{ Hz, 1H, H}_8\)), 2.63 A of AB (d, \(J_{10a,s}=8.6 \text{ Hz, 1H, H}_{10a}\)), 1.97 (d, \(J_{4x,5}=10.3 \text{ Hz, 1H, H}_4x\)), 1.96 (d, \(J_{4n,5}=12.9 \text{ Hz, 1H, H}_4n\)), 1.79 B of AB (d, \(J_{10a,s}=8.6 \text{ Hz, 1H, H}_{10a}\)), 1.13 (s, 9H, CH\(_3\)). 13C-NMR (100 \text{ MHz, CDCl}\(_3\)): \(\delta 218.7 \text{ (quat.)}, 137.7/137.1 \text{ (tert.), } 129.5 \text{ (quat.), } 129.3/129.0 \text{ (quat.), } 62.8 \text{ (quat.), } 62.2 \text{ (tert.), } 54.8 \text{ (sec.), } 54.1/53.6/46.8 \text{ (tert.), } 44.6 \text{ (sec.), } 37.0 \text{ (quat.), } 37.0 \text{ (prim.)}\). IR (CH\(_2\)Cl\(_2\)): \(\nu 3080-3020 \text{ (C-H, unsat.), } 3010-2860 \text{ (C-H, sat.), } 1720 \text{ (C=O) cm}^{-1}\). El/MS: m/e (%) 360 (4, M\(^+\)), 294 (7, M\(^+-\text{C}_5\)H\(_6\)), 203 (66, M\(^+-\text{SePh}\)), 137 (35, M\(^+-\text{SePh-C}_3\)H\(_6\)), 66 (11, C\(_3\)H\(_6\)^\). El/HRMS m/e: 360.0991 [calc.for C\(_{20}\)H\(_{24}\)O\(^8\)Se (M\(^+\)): 360.0992].

endo-5-Phenyl-exo-6-phenylselenyl-endo-tricyclo[5.2.1.0\(^2\)]deca-8-en-3-one \(\text{15d}\) and exo-3-phenyl-6-phenylselenyl-exo-tricyclo[5.2.1.0\(^2\)]deca-4,8-dien-3-ol

Following the general procedure A [PheLi (1.5 ml of 2 M solution in hexane, 3 mmol), CuI (200 mg, 1
mmol), 3c (150 mg, 0.5 mmol), gave, after work-up and flash chromatography (n-hexane/EtOAc = 20/1), 170 mg (89%) of a mixture of 15d and 1,2-product in 4:1 ratio.

15d: ¹H-NMR (400 MHz, CDCl₃): δ 7.66 - 7.29 (m, Ph-H), 6.05 A of AB (dd, J₈,₉=5.6 Hz, J₁,₂ resp. J₇,₈=2.9 Hz, 1H, H₈ or H₉), 5.69 B of AB (dd, J₈,₉=5.6 Hz, J₁,₂ resp. J₇,₈=3.2 Hz, 1H, H₈ or H₉), 3.99 (dd, J=9.5 Hz, J=12.1 Hz, 1H, H₄), 3.42 (d, J₂=3.6 Hz, 1H, H₂), 3.30 and 3.02 (2 x brs, 2H, H₁ and H₇), 2.54 A of AB (dd, J₄,A=18.1 Hz, J₄,B=12.1 Hz, 1H, H₄), 2.35 A of AB (d, J₉,,₈=8.6 Hz, 1H, H₁₉₉), 2.25 B of AB (dd, J₉,₉=18.1 Hz, J₉,₈=9.5 Hz, 1H, H₉₉), 1.63 B of AB (d, J₁₀,₀₉=8.6 Hz, 1H, H₁₀₉₉).

1,2-product: ¹H-NMR (400 MHz, CDCl₃): δ 7.66 - 7.29 (m, Ph-H), 6.31 A of AB (dd, J₈,₉=5.4 Hz, J₁,₂ resp. J₇,₈=2.9 Hz, 1H, H₈ or H₉), 5.91 B of AB (dd, J₈,₉=5.4 Hz, J₁,₂ resp. J₇,₈=3.4 Hz, 1H, H₈ or H₉), 5.77 and 5.56 AB (2 x d, J₄=A,₅=5.5 Hz, 2H, H₄ and H₅), 3.15 and 3.05 (2 x brs, 2H, H₁ and H₇), 2.97 (d, J₁₂=4.1 Hz, 1H, H₂), 2.21 A of AB (d, J₁₀,₀₉=8.5 Hz, 1H, H₁₀₉₉), 1.77 B of AB (d, J₁₀,₀₉=8.5 Hz, 1H, H₁₀₉₉), 1.61 (s, 1H, OH).

**General procedure B for the synthesis of 18 by oxidative elimination of 15**

A solution of 15 (100 mg, 0.3 mmol) in methanol (5 ml) was treated with a solution of sodium periodate (100 mg, 0.5 mmol in 1 ml water) at ca. 5 °C (ice water) with stirring. After 20 min., the solid was filtered and washed with ethyl acetate. The combined organic phases were evaporated and purified by chromatography.

5-endo-Methyl-tricyclo[5.2.1.0²^6]deca-2(6),8-en-3-one 18a

Following the general procedure B and applying 15a gave, after flash chromatography (n-hexane/EtOAc = 4/1), pure 18a (40 mg, 82%) as a colorless oil.

18a: ¹H-NMR (400 MHz, CDCl₃): δ 6.88 A of AB (dd, J₈,₉=4.9 Hz, J₁,₂ resp. J₇,₈=3.2 Hz, 1H, H₈ or H₉), 6.77 B of AB (dd, J₈,₉=4.9 Hz, J₁,₂ resp. J₇,₈=3.3 Hz, 1H, H₈ or H₉), 3.74 and 3.59 (2 x brs, 2H, H₁ and H₇), 3.17-3.10 (m, 1H, H₅), 2.99 A of AB (dd, J₄,B=18.0 Hz, J₄,A=5.7 Hz, 1H, H₄₉₉), 2.44 and 2.37 AB x 2 (2 x d, J₁₀,₁₀=6.7 Hz, 2H, H₁₀₉₉), 2.20 B of AB (d, J₄,A=18.0 Hz, 1H, H₄₉₉). ¹³C-NMR (100 MHz, CDCl₃): δ 206.9/198.9/158.5 (quat.), 144.8/141.6 (tert.), 74.1/49.9 (sec.), 49.9/45.0/33.3 (tert.), 17.4 (prim.). IR (CH₂Cl₂): ν 3010-2860 (C-H, sat.), 1675 (C=O) cm⁻¹. EI/MS: m/e (%) 160 (64, M⁺), 105 (100), 94 (29, M⁺-C₅H₆), 66 (41, C₅H₆⁺). EI/HRMS m/e: 160.0888 [calc. for C₁₁H₁₂O(M⁺): 160.0882].

5-endo-n-Butyl-tricyclo[5.2.1.0²^6]deca-2(6),8-en-3-one 18b

Following the general procedure B and applying 15b gave, after flash chromatography (n-hexane/EtOAc = 4/1), pure 18b (44 mg, 81%) as a colorless oil.

18b: ¹H-NMR (400 MHz, CDCl₃): δ 6.82 A of AB (dd, J₈,₉=4.9 Hz, J₁,₂ resp. J₇,₈=3.1 Hz, 1H, H₈ or H₉), 6.68 B of AB (dd, J₈,₉=4.9 Hz, J₁,₂ resp. J₇,₈=3.2 Hz, 1H, H₈ or H₉), 3.66 and 3.54 (2 x brs, 2H, H₁ and H₇), 3.0-2.95 (m, 1H, H₅), 2.82 A of AB (dd, J₄,A=18.0 Hz, J₄,B=5.7 Hz, 1H, H₄₉₉), 2.37 and 2.30 AB x 2 (2 x d, J₁₀,₁₀=6.7 Hz, 2H, H₁₀₉₉), 2.21 B of AB (d, J₄,B=18.0 Hz, 1H, H₄₉₉ or H₄₉₉), 1.43 (m, 1H, one of CH₂CH₂CH₂CH₃), 1.29-1.14 (m, 5H), 0.82 (d, J=7.0 Hz, 3H, CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ 206.0/198.9/158.9 (quat.), 144.8/141.6 (tert.), 74.6 (sec.), 50.6 (tert.), 48.0 (sec.), 44.8/39.0 (tert.), 32.5/29.7/22.6 (sec.), 13.9 (prim.). IR (CH₂Cl₂): ν 3010-2860 (C-H, sat.), 1670 (C=O) cm⁻¹. EI/MS: m/e
5-endo-1-Butyl-tricyclo[5.2.1.0²⁶]deca-2(6),8-en-3-one \(18c\)

Following the general procedure B and applying \(15c\) gave, after flash chromatography (n-hexane/EtOAc = 6/1), pure \(18c\) (30 mg, 76 %) as a white solid.

\(18c\): m.p.: 63.5-65.5 °C (diisopropyl ether). \(^1H\)-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.87 A of AB (dd, \(J_{8,9}=5.0\) Hz, \(J_{1,9}\) resp. \(J_{7,8}=3.1\) Hz, 1H, \(H_8\) or \(H_9\)), 6.81 B of AB (dd, \(J_{8,9}=5.0\) Hz, \(J_{1,9}\) resp. \(J_{7,8}=3.1\) Hz, 1H, \(H_8\) or \(H_9\)), 3.73 and 3.69 (2 x brs, 2H, \(H_1\) and \(H_7\)), 2.92 (d, \(J_{4,5}=5.8\) Hz, 1H, \(H_4\)), 2.72 A of AB (dd, \(J_{4,5}=18.2\) Hz, \(J_{4a,5}\) resp. \(J_{4b,5}=5.9\) Hz, 1H, \(H_{4a}\) or \(H_{4b}\)), 2.44 B of AB (dd, \(J_{4a,5}=18.2\) Hz, 1H, \(H_{4a}\) or \(H_{4b}\)), 2.45 and 2.37 AB x 2 (2 x d, \(J_{10a,10b}=6.8\) Hz, 2H, \(H_{10a}\)), 0.87 [s, 9H, \(C(CH_3)_3\)].

\(^{13}C\)-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 204.1/199.0/160.2 (quat.), 144.2/141.2 (tert.), 75.6 (sec.), 52.8/50.6/44.6 (tert.), 44.5 (sec.), 34.4 (quat.), 27.9 (prim.). IR (CH\(_2\)Cl\(_2\)): \(\nu\) 3010-2860 (C-H, sat.), 1670 (C=O) cm\(^{-1}\). El/MS: m/e (%) 203 (26, \(M^{+}\)), 146 (100, \(M^{+}-CMe_3\)), 66 (5, \(C_5H_6^+\)), 57 (56, \(CMe_3^+\)). El/HRMS m/e: 203.1435 [calc.for \(C_{14}H_{19}O(M^{+})\): 203.1436].

5-endo-Phenyl-tricyclo[5.2.1.0²⁶]deca-2(6),8-en-3-one \(18d\)

Following the general procedure B and applying \(15_r\) (150 mg, purity is 80%) gave, after flash chromatography (n-hexane/EtOAc = 4/1), pure \(18d\) (43 mg, 90 %) as a white solid.

\(18d\): m.p.: 107-109 °C (diisopropyl ether). \(^1H\)-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.31-6.88 (2 x m, 5H, Ph-H), 6.86 A of AB (dd, \(J_{8,9}=5.0\) Hz, \(J_{1,9}\) resp. \(J_{7,8}=3.1\) Hz, 1H, \(H_8\) or \(H_9\)), 6.36 B of AB (dd, \(J_{8,9}=5.0\) Hz, \(J_{1,9}\) resp. \(J_{7,8}=3.1\) Hz, 1H, \(H_8\) or \(H_9\)), 4.25 (dd, \(J_{1}=6.3\) Hz, \(J_{1}=1.7\) Hz, 1H, \(H_1\)), 3.85 and 3.39 (2 x brs, 2H, \(H_1\) and \(H_7\)), 3.28 A of AB (dd, \(J_{1}=18.2\) Hz, \(J_{1}=6.3\) Hz, 1H, one of \(H_4\)), 2.58 B of AB (dd, \(J_{1}=18.2\) Hz, \(J_{1}=1.7\) Hz, 1H, one of \(H_4\)), 2.44 (s, 2H, \(H_{10}\)). \(^{13}C\)-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 203.6/198.7/158.9 (quat.), 142.8/142.5 (tert.), 139.9 (quat.), 128.8/127.6/127.0 (tert.), 74.4/51.8 (sec.), 50.3/45.2/44.7 (tert.). IR (CH\(_2\)Cl\(_2\)): \(\nu\) 3010-2860 (C-H, sat.), 1680 (C=O) cm\(^{-1}\). El/MS: m/e (%) 222 (100, \(M^{+}\)), 156 (7, \(M^{+}-C_5H_6\)), 66 (5, \(C_5H_6^+\)). El/HRMS m/e: 222.1044 [calc.for \(C_{16}H_{14}O(M^{+})\): 222.1045].

exo-3,4-Epoxy-endo-tricyclo[5.2.1.0²⁶]deca-8-en-5-one-2-carboxylic acid \(20\)

Ester \(19\) (1.2g, 5mmol) in a solution of NaOH in methanol (10%, 15ml) was stirred at room temp. for 5 hrs. The mixture was neutralized and concentrated to dryness. Water (20ml) was added, followed by extraction with ethyl acetate (3x), then the extracts were washed with water and brine, and dried (Na\(_2\)SO\(_4\)). Concentration in vacuo gave \(20\) (1g, ~100%) as a white solid.

\(20\): m.p. 144.5-146.5 °C (diisopropylether/EtOAc). \(^1H\)-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.5 (bs, 1H, COOH), 6.24 A of AB (dd, \(J_{8,9}=5.6\) Hz, \(J_{1,9}\) resp. \(J_{7,8}=3.1\) Hz, 1H, \(H_8\) or \(H_9\)), 6.19 B of AB (dd, \(J_{8,9}=5.6\) Hz, \(J_{1,9}\) resp. \(J_{7,8}=2.8\) Hz, 1H, \(H_8\) or \(H_9\)), 3.89 (dd, \(J_{3,4}=2.2\) Hz, \(J_{4,5}=1.8\) Hz, 1H, \(H_4\)), 3.40 (bs, 1H, \(H_1\) or \(H_7\)), 3.37 (bs, 1H, \(H_1\) or \(H_7\)), 3.34 (d, \(J_{1,4}=2.2\) Hz, 1H, \(H_1\)), 2.25 (dd, \(J_{1}=4.8\) Hz, \(J_{4,5}=1.8\) Hz, 1H, \(H_4\)), 1.87 A of AB (d, \(J_{10a,10b}=9.1\) Hz, 1H, \(H_{10a}\)), 1.64 B of AB (d, \(J_{10a,10b}=9.1\) Hz, 1H, \(H_{10a}\)). IR (CH\(_2\)Cl\(_2\)): \(\nu\) 3600-2300 (COOH), 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1740 and 1705 (C=O) cm\(^{-1}\). El/MS: m/e (%) 206 (2, \(M^{+}\)), 161 (1, \(M^{+}-CO_2H\)), 141 (72, \(M^{+}+1-C_5H_6\)), 66 (93, \(C_5H_6^+\)). El/HRMS m/e: 206.0580 [calc.for \(C_{11}H_{10}O_4(M^{+})\): 256.0579]. Found: C 64.08, H 4.81 (calc.for \(C_{11}H_{10}O_4\): C 64.08, H 4.89).
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exo-6-Bromo-exo-4,5-epoxy-endo-tricyclo[5.2.1.0²,6]deca-8-en-3-one 21

A solution of acid 20 (208 mg, 1 mmole) in benzene (5 ml) was treated with oxalyl chloride (0.3 ml) and a drop of dimethylformamide. After stirring for 2 hrs at room temp. with protection from moisture, the solvent and excess oxalyl chloride were evaporated and the residual acid chloride was used as such.

A solution of acid chloride (1 mmole) in benzene (5 ml) was added dropwise (15 min.) to a dried, stirred suspension of N-hydroxypyridin-2-thione sodium salt (190 mg, 1.2 mmole) in refluxing bromotrichloromethane while irradiating with a 250 w tungsten lamp in an inert atmosphere. After completion of the addition, the reaction mixture was cooled to room temp. and evaporated to dryness. The crude product was purified by flash chromatography (n-hexane/EtOAc = 9/1) to give 21 (220 mg, 91%) as a white solid.

21: m.p. = 109 °C, decomposition (ether). 1H-NMR (400 MHz, CDCl₃): δ 6.17-6.12 (m, 2H, H₈ and H₉), 3.81 (dd, J₄,₅ = 2.0 Hz, J₂,₄ = 1.6 Hz, 1H, H₅), 3.57 (d, J₄,₅ = 2.0 Hz, 1H, H₆), 3.43 and 3.30 (brs, 2H, H₁ and H₇), 3.05 (dd, J₁,₂ = 4.8 Hz, J₂,₄ = 1.6 Hz, 1H, H₂), 2.30 A of AB (d, J₁₀α,₁₀β = 9.2 Hz, 1H, H₁₀α), 1.95 B of AB (dt, J₁₀α,₁₀β = 9.2 Hz, 1H, H₁₀β). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1740 (C=O) cm⁻¹. CI/MS: m/e (%) 242 (0.33) and 240 (0.35) (M+I), 177 (13) and 175 (13) (M+1-C₅H₆), 66 (100, C₅H₆⁺). CI/HRMS m/e: 239.9786 [calc.for C₁₀H₂O₂⁻Br⁺(M⁺): 239.9786].

endo-4,5-Epoxo-exo-6-methoxy-endo-tricyclo[5.2.1.0²,6]deca-8-en-3-one 23

Crystalline bromide 21 (120 mg, 0.5 mmol) was added to a solution of KOH (20%, 10ml) in methanol with stirring under cooling (ice-water). Stirring was continued until crystalline 21 had dissolved. The mixture was then neutralized and concentrated to dryness. Water (10 ml) was added, the mixture extracted with ether (3x). The extracts were washed repeatedly with water and brine, dried (Na₂SO₄) and concentrated in vacuo to give a viscous oil (95 mg). Subsequent flash chromatography (n-hexane/EtOAc =5/1) gave pure 23 (75mg, 80%) as a colorless oil.

23: 1H-NMR (400 MHz, CDCl₃): δ 6.42 A of AB (dd, J₈,₉ = 5.6 Hz, J₁,₉ resp. J₁,₈ = 3.1 Hz, 1H, H₈ or H₉), 6.25 B of AB (dd, J₈,₉ = 5.6 Hz, J₁,₉ resp. J₁,₈ = 2.9 Hz, 1H, H₈ or H₉), 3.94 (d, J₄,₅ = 2.2 Hz, 1H, H₅), 3.49 (d, J₄,₅ = 2.2 Hz, 1H, H₆), 3.39 (s, 3H, OCH₃), 3.28 and 3.04 (2 x bs, 2H, H₁ and H₇), 2.28 A of AB (d, J₁₀α,₁₀β = 9.3 Hz, 1H, H₁₀α), 2.16 (d, J₁₀α,₁₀β = 2.6 Hz, 1H, H₁₀β), 1.53 B of AB (ddt, J₁₀α,₁₀β = 9.3 Hz, J₁₀α,₁ = J₁₀α,₂ = 1.7 Hz, J₁₀α,₁₀β = 2.6 Hz, 1H, H₁₀α). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1735 (C=O) cm⁻¹. CI/MS: m/e (%) 192 (0.3, M⁺), 161 (1, M⁺-OCH₃), 127 (95, M⁺+1-C₅H₆), 66 (100, C₅H₆⁺). EI/HRMS m/e: 192.0789 [calc.for C₁₁H₁₂O₅⁺(M⁺): 192.0786].

exo-4,5-Epoxo-exo-6-methoxy-exo-tricyclo[5.2.1.0²,6]deca-8-en-3-one 25

A solution of 24 (100 mg, 0.57 mmol) in dichloromethane (4 ml) and methanol (4 ml) was treated with NaOH aq. (0.2 N, 2ml) and H₂O₂ (35%, 2 ml) at room temp. The mixture was stirred for 4 hrs at room temp. Dichloromethane (50 ml) was added and washed with brine. After drying (NaSO₄) and concentration in vacuo, flash chromatography (n-hexane/EtOAc = 3/1) gave 25 (100mg, 90%).

25: 1H-NMR (400 MHz, CDCl₃): δ 6.12-6.10 (m, 2H, H₈ and H₉), 3.76-3.75 (m, 1H, H₄), 3.54 (s, 3H, OCH₃), 3.39 (d, J₄,₅ = 2.4 Hz, 1H, H₅), 3.21-3.19 (m, 2H, H₁ and H₇), 2.57 (dd, J₁,₂ = 5.2 Hz, J₂,₄ = 1.7 Hz, 1H, H₂), 2.02 A of AB (d, J₁₀α,₁₀β = 8.7 Hz, 1H, H₁₀α), 1.78 B of AB (dt, J₁₀α,₁₀β = 8.7 Hz, J₁₀α,₁ = J₁₀α,₇ = 1.6 Hz).
Hz, 1H, H(10a). IR (CH2Cl2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1730 (C=O) cm⁻¹. CI/MS: m/e (%) 127 (100, M+i-C5H6), 66 (100, C5H6+). CI/HRMS m/e: 193.0865 [calc.for C11H13O3(M⁺): 193.0865].

References and notes


8. Use of the services and facilities of the Dutch National NWO/SURF Expertise Center CAOS/CAMM, University of Nijmegen, The Netherlands, under grant numbers SON 326-052 and STW NCH99.1751, is gratefully acknowledged.


14. This result is consistent with an early report in which parent cyclopentadienone epoxide was shown to decompose in acidic or basic media, see: Chapman, O.L.; Hess, T.C., J. Org. Chem., 1979, 44, 962.

15. Comparison of the ¹HNMR-data of epoxide 25 with those of the tricyclic exo-epoxides 19, 20 and 21 immediately revealed the exo-configuration of the epoxide function in 25. In particular, the striking correspondence in chemical shifts observed for the C₄-endo-protons is convincing. If the epoxide function would have been in the endo-position a significant upfield shift (> 0.6 ppm) of the C₄-exo-proton should have been observed.


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