Synthesis of 6-Functionalized Tricyclodecanedienones using Barton's Radical Decarboxylation Reaction. Generation of Tricyclo[5.2.1.0\textsuperscript{2,6}]decatrienone, a Norbornene Annulated Cyclopentadienone

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Abstract: An effective synthesis of 6-functionalized endo-tricyclo[5.2.1.0\textsuperscript{2,6}]deca-4,8-dien-3-ones \(7\) starting from carboxylic acid \(6\) has been accomplished whereby the chemical scope of the tricyclodecanedienone system \(1\) as a synthetic equivalent of cyclopentadienone has been expanded. Bridgehead bromide \(7d\) gives upon treatment with base access to norbornene annulated cyclopentadienone \(10\) which rapidly undergoes either regioselective nucleophilic addition or Diels-Alder cyclization depending on the applied reaction conditions.

Introduction

In recent years, it was demonstrated that the endo-tricyclo[5.2.1.0\textsuperscript{2,6}]decadienone system \(1\) is an extremely useful synthon for a great variety of naturally occurring cyclopentanoids\(^1\). The basic strategy underlying this approach is depicted in Scheme 1. It generally involves stereoselective nucleophilic addition to the enone moiety, followed by chemical transformations to introduce the desired functionalities. Thermal cycloreversion of the appropriately functionalized tricyclodecadienone \(2\) employing the technique of flash vacuum thermolysis ultimately leads to the desired cyclopentenones \(3\). The availability of both antipodes of \(1\) in enantiopure form, either by enzymatic resolution\(^{1a,2}\) or asymmetric synthesis\(^3\) completes this strategy and makes it extremely useful for the enantioselective synthesis of a
variety of cyclopentenoids.

The synthetic merit of the endo-tricyclo[5.2.1.02,6]decadienone 1 is nicely demonstrated by the efficient enantioselective synthesis of 4-hydroxycyclopentenone 4\(^{1b,4}\) which is the essential intermediate in the synthesis of clavulones 5. Key structure in this route to clavulones 5 is tricyclic carboxylic acid 6 which is readily available from cyclopentadiene and benzoquinone\(^5\). Furthermore, it can conveniently be obtained in enantiopure form\(^2a\). Decarboxylation of 6 to parent endo-tricyclodecadienone 7 (X=H) is achieved in dimethylformamide at 100 °C in excellent yield without racemization. Retrosynthetic analysis reveals that the substituent X as present at the 6-position in tricyclodecadienone 7 eventually appears at the C\(_2\)-position in cyclopentenone 4. Hence, by choosing the appropriate substituent at C\(_6\) in 7, \(\alpha\)-substituted cyclopentenones 4 and accordingly the corresponding \(\alpha\)-substituted clavulones are within reach. Interesting examples of such \(\alpha\)-substituted clavulones are the \(\alpha\)-halogenated marine prostanoids, such as halovulones 8 (X= Cl, Br and I)\(^6\) and punaglandines 9\(^7\). Therefore, the halodecarboxylation of carboxylic acid 6 was investigated to broaden the synthetic scope of the tricyclodecadienone system. In this paper, the synthesis of a variety of 6-substituted tricyclodecadienones 7 using Barton’s radical chain decarboxylation process is reported. In addition, the surprisingly facile dehydrohalogenation of 7 (X=Br) to form the elusive tricyclodecatienone 10 will be described\(^8\).

**Results and discussion**

The radical chain decarboxylation process involving the thermal or photochemical decomposition of thiohydroxamic esters, as reported by Barton \textit{et al.}\(^9\), seems a suitable method for the halodecarboxylation of 6. The high yields for this halodecarboxylation reaction observed for primary, secondary and tertiary carboxylic acids\(^9,10\) and the avoidance of molecular halogen as the halogen radical source makes this method very attractive. It is obvious that halodecarboxylation methods using molecular halogen, such as the Hunsdiecker type processes, cannot be applied for the halodecarboxylation of 6 because of the presence of the reactive olefinic norbornene moiety. Also the use of lead tetracetate in the presence of metal halides does not seem a good choice because this aggressive reagent may cause unwanted reactions with the relative labile unsaturated tricyclodecadienone system and, moreover, the work-up is usually
troublesome. The attractive feature of Barton's radical decarboxylation process is its synthetic scope. By varying the radical trapping agent in principle a great variety of different substitution products can be obtained (Scheme 2). During the reaction process, the radical may exhibit considerable stability as on Scheme 2.

6-Functionalized tricyclodecadienones

One hand it constitutes a tertiary radical and on the other hand it is stabilized by the adjoining enone system. Moreover, the rigidity of the strained system probably prevents intramolecular interaction with the C8-C9 norbornene type double bond which could lead to cyclopropane ring formation. The considerations above suggest a rather selective behavior of radical towards radical trapping agents, which may be beneficial for the product formation.

The preparation of the required thiohydroxamic ester was carried out by converting acid into the corresponding acyl chloride using oxalyl chloride, followed by treatment with the sodium salt of N-hydroxypyridine-2-thione (Scheme 2). Attempts to isolate and characterize N-acyloxypyridine-2-thione failed due to its instability under work-up conditions. Therefore, in all experiments described hereafter, the thiohydroxamic ester was not isolated but immediately subjected to the radical decarboxylation process.

In order to gain insight into the efficiency of this radical decarboxylation process the well-documented replacement of the carboxylic acid function by hydrogen was first studied. For this purpose was heated in benzene at 60 °C, while irradiating with a tungsten lamp, in the presence of a large excess of t-butyl mercaptan as the hydrogen donor. A mixture consisting of parent tricyclodecadienone and pyridyl sulfide was obtained in yields of 60% and 15%, respectively (Scheme 2; Table 1). The latter product was formed in almost quantitative yield when no suitable radical trapping agent, such as t-butyl mercaptan, was present. The formation of some pyridyl sulfide despite the presence of a large excess of t-butyl mercaptan is indicative of the relative stability of radical. It should be noted that no products arising from radical rearrangement or ring closure reactions of the tricyclodecadienone system were observed.

The halodecarboxylation of was studied under standard conditions. For the synthesis of 6-chlorotricyclodecadienone a solution of the acid chloride of in tetrachloromethane was added to a suspension of the sodium salt of N-hydroxypyridine-2-thione in refluxing tetrachloromethane while irradiating with a tungsten lamp. A mixture of two products was obtained from which the desired chloride was isolated as the minor product in 10% yield only. The major product, which was obtained in 70% yield, was identified as pyridyl sulfide. The high selectivity of bridgehead radical for reaction with hydroxamic ester can readily be explained by assuming a low energy profile for radical which apparently is too stable to effectively induce C-Cl bond cleavage in tetrachloromethane. The formation of appears to be a rather common side reaction in those cases where rather unreactive radical trapping
Table 1

<table>
<thead>
<tr>
<th>X</th>
<th>trapping reagent</th>
<th>yield (%)</th>
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<tr>
<td>H</td>
<td>t-BuSH</td>
<td>60</td>
</tr>
<tr>
<td>SPy</td>
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<tr>
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<tr>
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<td>93</td>
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<tr>
<td>I</td>
<td>HCl3</td>
<td>62</td>
</tr>
<tr>
<td>CH3S</td>
<td>(MeS)2</td>
<td>22</td>
</tr>
<tr>
<td>PhS</td>
<td>(PhS)2</td>
<td>42</td>
</tr>
<tr>
<td>PhSe</td>
<td>(PhSe)2</td>
<td>94</td>
</tr>
<tr>
<td>OH</td>
<td>(PhS)3Sb</td>
<td>40</td>
</tr>
<tr>
<td>H2O/O2</td>
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</tbody>
</table>

Agents such as tetrachloromethane are used\textsuperscript{10b}. Attempts to promote the formation of 7c by modifying the reaction condition and using other chlorine donors, such as N-chlorosuccinimide and t-butylhypochlorite, led only to slight improvements. Eventually, chloride 7c was obtained in an optimum yield of 30% by applying t-butylhypochlorite in tetrachloromethane.

A much better result was obtained for the bromodecarboxylation of 6. In bromotrichloromethane, which is the commonly used radical trapping agent in this Barton decarboxylation process, an effective bromodecarboxylation of 6 was observed giving 6-bromotricyclodecadienone 7d in an excellent yield of 93%. Only a trace of pyridyl sulfide 7bb had been formed indicating that the C-Br bond in bromotrichloromethane is apparently weak enough to let this solvent successfully compete with the thiohydroxamic ester in capturing the 6-tricyclicdecadienonyl radical 12. A similar satisfactory result was obtained when iodoform was used as the trapping agent. By generating the radical 12 in toluene in the presence of an excess of iodoform 6-iodotricyclodecadienone 7e was isolated in 62% yield as a crystalline compound. No pyridyl sulfide 7bb was formed in this iododecarboxylation of 6. This result further substantiates the selective nature of bridgehead radical 12.

Having successfully accomplished the halodecarboxylation of acid 6 using Barton's procedure, the question arose whether this methodology can be applied for the introduction of other heteroatom containing functionalities at the C6-position in 7. The formation of pyridyl sulfide 7bb from 11 in benzene indicates that the introduction of other sulfur containing substituents at C6 in 7 seems feasible. The radical chalcogenation has already been studied by Barton \textit{et al.}\textsuperscript{13} and was shown to proceed quite well in many cases, provided an efficient trapping agent is selected which can effectively compete with the thiohydroxamic ester.

When using dimethyl disulfide as the trapping agent under standard reaction conditions, carboxylic acid 6 only gave a disappointingly low yield (22%) of tricyclic methyl sulfide 7f. Again the major product isolated was pyridyl sulfide 7bb. Using the somewhat more reactive diphenyl disulfide as the trapping agent only slightly affected the efficiency of this chalcogenation process. The disulfide bond in both dimethyl disulfide and diphenyl disulfide is apparently too strong to effectively compete with the thiohydroxamic ester in trapping the tricyclicdecadienyl radical 12. Decreasing the reaction temperature to 0 °C which, as reported by Barton \textit{et al.}\textsuperscript{13}, should disfavor the formation of the undesired pyridyl sulfide 7bb, did not lead to improvement. Contrary to Barton's observations, the yields of the desired sulfides 7g considerably dropped while pyridyl sulfide 7bb was now obtained in almost quantitative yield. These results indicate that the nature of the intermediate free carbon radical plays an determining role in the product formation. In the
present case lowering the temperature favors the more selective radical addition of 12 to thiohydroxamic ester 11. Although a reversible formation of 12 from the initial addition product cannot be excluded, the subsequent reaction of 12 with the disulfides is apparently too slow to prevent the preferential formation of pyridyl sulfide 7b.

In agreement with the above reasoning, the use of the much more reactive diphenyl diselenide as the radical trapping agent gave efficient capture of carbon radical 12 affording 6-phenylselanyltricyclodecadienone 7h in an excellent yield of 94%.

The transformation of the 2-carboxylic acid function in 6 into 6-oxygen substituted tricyclodecadienones such as alcohol 7i is of great importance as these compounds may eventually give rise to 3-oxycyclopent-2-enones by the sequence of events depicted in Scheme 1. These substructures occur in natural cyclopentenoids, e.g. kjellmanianone14. The transformation of carboxylic acid moiety into an oxy group is usually a multistep operation involving either some oxidation process e.g. a Baeyer-Villiger oxidation of the corresponding ketone, or a decarboxylative conversion to a leaving group e.g. a halide, which then allows oxygen substitution using a metal hydroxide or alkoxide. As radicals are usually efficiently trapped by triplet oxygen, the synthesis of bridgehead alcohol 7i was attempted applying Barton’s decarboxylation procedure in the presence of oxygen9. Unfortunately, no satisfactory results were obtained. Again the formation of the pyridyl sulfide 7b turned out to be much more effective than capture of molecular oxygen. Recently, a new and synthetically more attractive method for the oxydecarboxylation of thiohydroxamic esters was developed15 involving the generation of the carbon radical in the presence of antimony trisphenyl sulfide which leads to the formation of the corresponding carbon substituted bisphenyl antimonate (Scheme 3). Oxidation of this rather unstable antimonate with molecular oxygen, followed by aqueous work up, then produces the desired alcohol. When this procedure was applied to tricyclic carboxylic acid 6 by adding antimony trisphenyl sulfide to thiohydroxamic ester 11 at room temperature, in the dark and under an oxygen atmosphere followed by the addition of water, 6-hydroxytricyclodecadienone 7i was isolated in 40% yield after column chromatography (Scheme 3, Table 1). This result suggests that tricyclic antimonate 13 has indeed been formed. A second tricyclic

Scheme 3

![Scheme 3](image-url)

compound was isolated in 25% yield to which, on basis of spectral evidence, structure 14 was assigned. This product is clearly the result of thiophenolate addition to thiohydroxamic ester 11 which apparently competes with the radical reaction. The occurrence of appreciable amounts of thiophenolate in the reaction mixture is probably the result of decomposition of the antimony trisphenyl sulfide which is known to be water and air sensitive. Although there is certainly room for improving this oxydecarboxylation of 6 into
no further attempts were made as a much more effective route to 6-substituted oxytricyclodecadienone was found starting from tricyclic bromide 7d (vide infra).

In view of our interest in functionalized cage compounds, the synthesis of bridgehead bromide 18a and phenylselenide 18b starting from 1,3-bishomocubanone carboxylic acid 17 was undertaken (Scheme 4). Irradiation of tricyclic ester 15 in toluene gave 1,3-bishomocubanone ester 16 which on alkaline hydrolysis afforded carboxylic acid 17 in a quantitative overall yield. The bromodecarboxylation and the phenylselenodecarboxylation of 17, following the procedure described for the preparation of 7d and 7h, gave 18a and 18b, respectively, in excellent yields.

The results described above show that an excellent route to a variety of 6-substituted tricyclodecadienones 7 starting from readily available tricyclic carboxylic acid 6 has been attained using the thiohydroxamic radical chemistry. The only drawback encountered is the relatively high stability of bridgehead radical 12 which necessitates rather reactive radical trapping reagents in order to suppress the formation of pyridyl sulfide 7b and to obtain acceptable yields of the desired 6-functionalized tricyclodecadienones 7.

The 6-substituted halides 7c,d,e appeared to be rather reactive compounds. At room temperature they slowly decompose as indicated by their darkening. They can however be kept in the refrigerator for months without noticeable change. In order to uncover the chemical properties of these halides 7 in connection with their application in the synthesis of halovulones and punaglandines, the behavior of tricyclic bromide 7d in nucleophilic medium was investigated. A fast reaction was observed when 7d was stirred in methanol in the presence of some potassium hydroxide. At room temperature the bromide disappeared within a few minutes to give a major compound together with a minor amount of a second product. Both compounds could readily be separated by column chromatography. Spectral analysis of both compounds immediately revealed the absence of bromine. The major compound isolated contained a methoxy group while its NMR-spectral features closely resembled that of the original bromide 7d suggesting this product to be 6-methoxy-endo-tricyclodecadienone 19 (Scheme 5). To prove the endo-configuration, photocyclization of 19, which is a well-established process for endo-tricyclodecadienones, was performed by irradiation in toluene, affording 1,3-bishomocubanone 20 in quantitative yield. This reaction unambiguously confirms that structure 19 is correct. The minor compound exhibited a rather complicated ¹H NMR-spectrum whereas the ¹³C NMR-spectrum indicated a high degree of unsaturation which together with the observed number of carbon resonances suggested a product with a dimeric structure. On the basis of these spectral features together with mechanistic considerations dimeric structure 21 was assigned.
Interestingly, a nearly quantitative formation of 21 was achieved by refluxing 7d in methanol containing triethylamine as the base. The unambiguous proof for structure 21 was obtained by an X-ray diffraction analysis (Figure 1)\(^{16}\).

The high yield formation of both 19 and 21 from 7d can conveniently be rationalized by assuming an initial base-induced enolization of 7d followed by rapid elimination of the 6-bromo substituent to give the highly strained norbornene annulated cyclopentadienone 10. This elusive cyclopentadienone then, depending on the reaction conditions, undergoes either conjugate addition of methoxide or dimerization to give 19 and 21, respectively.

The occurrence of such a facile dehydrobromination of 7d to give 10 is surprising in view of the considerable increase in energy that goes along with the formation of such an annulated cyclopentadienone system. Cyclopentadienones are extremely reactive compounds and generally immediately dimerize in a Diels-Alder reaction after their formation\(^{17}\). The isolation of the complicated heptacyclic dione 21 which is one of the conceivable Diels-Alder dimerization adducts of 10 therefore presents firm evidence for its intermediacy in the reaction of bromide 7d with either potassium hydroxide or triethylamine in methanol.
Apparently, the conjugate addition of methoxide to the C2-C6 enone system in 10 to give 19 can effectively compete with the [4+2]-dimerization. To our knowledge this is the first example of a successful trapping of a cyclopentadienone intermediate by nucleophilic conjugate addition. The exclusive formation of 19 shows that this conjugate addition of the methoxide nucleophile to 10 is regio- and stereoselective. The observed regiospecificity agrees with the higher reactivity of the more strained C2-C6 enone moiety as compared with the peripheral C4-C5 enone. The observation of exclusive methoxide attack at C6 in 10 from the exo-face leading to the endo-tricyclodecadienone system is probably of steric origin although stereoelectronic effects may also play a role. Inspection of molecular models shows that addition of a nucleophile from this exo-face may sterically be slightly favored over attack from the endo-face.

For the dimerization of 10, which proceeds via a [4+2]-cyclization, eight possible combinations can be envisaged. However, molecular modeling studies involving all conceivable transition states clearly reveal that only the transition state involving the peripheral enone moiety and leading to endo-dicyclopentadienone 21 is stereochemically feasible. Involvement of the very reactive central C2-C6 double bond in this Diels-Alder dimerization leads to highly unfavourable transition states due to severe van der Waals interactions. The steric constraints encountered in the dimerization of 10 leading to 21 suggest that this process may be relatively slow as compared to the dimerization of monocyclic cyclopentadienones. This would explain the successful trapping of tricyclic cyclopentadienone 10 with potassium methoxide in methanol to give 19.

Additional evidence for the relatively slow dimerization rate of 10 was obtained from its trapping in a crossed Diels-Alder reaction with cyclopentadiene. When the dehydrobromination of 7d was carried out under the conditions used for the preparation of dimer 21, however, now in the presence of a five-fold excess of cyclopentadiene, hardly any dimer 21 was formed. Instead, a mixture of cycloaddition products 22 and 23 was obtained in a ratio of 1:2 and in 80% total yield (Scheme 6). The structures of 22 and 23 were secured by correlation with known compounds. For this purpose the mixture of 22 and 23 was reduced with lithium in ammonia and subsequently oxidized with pyridinium chlorochromate to give 24.
6-Functionalized tricyclodecadienones

and 25 (ratio 1:2). After separation by column chromatography the $^1$H- and $^{13}$CNMR spectra of both compounds indicated that these structures were highly symmetric. In principle, there are four possible structures which fulfill this requirement for either D or C$_2$-symmetry viz. 24, 25, 28 and 29 (Schemes 6, 7 and 8). Since the NMR-spectra of the isolated adducts did not allow an unambiguous structure assignment, independent synthesis of some of the possible candidates was pursued. Compounds 25 and 28 were readily available by the Diels-Alder reaction of parent endo- and exo-tricyclodecadienones 7a and 26, respectively, with cyclopentadiene under Lewis acid catalysis (Scheme 7)$.^{18}$ After separation from the non-symmetrical adduct 27, which was formed in both reactions, comparison of the spectral data of these C$_2$-symmetrical adducts 25 and 28 immediately identified one of the unknown products obtained in the reactions depicted in Scheme 6 as 25. The other unknown compound must therefore possess either structure 24 or 29 (Scheme 8). Differentiation between these structures is in principle conceivable by their difference in photochemical behavior. Only for 24 irradiation is expected to give rapid intramolecular [2+2]-cycloaddition to cage ketone 30 due to the close proximity of the two olefinic bonds. Since ketone 30 is a known compound$^{19}$ comparison of spectral data will allow unequivocal assignment of this second unknown structure. Indeed, when this adduct was subjected to irradiation in benzene containing 10% of acetone cage ketone 30 was obtained in 60% yield and accordingly identifying its photoprecursor as 24. It
should be mentioned that ketone 30 can also be obtained from related benzoquinone 31 in 7 steps and in an overall yield of 3.9%.

The formation of adducts 22 and 23 in the crossed Diels-Alder with cyclopentadiene demonstrates that the [4+2] cycloaddition does not occur at the central C2-C6 enone system despite its higher reactivity. Even with a reactive diene such as cyclopentadiene, the steric barrier imposed by either the methylene or ethene bridge can not be overcome and the cycloaddition reaction takes place exclusively at the peripheral enone system in 10 and in the endo-fashion.

It is of interesting to note that tricyclodecatrienone 10 constitutes a chiral cyclopentadienone and therefore will allow the synthesis of enantiopure products. This is nicely demonstrated by the synthesis of enantiopure dimer (-)-21 from enantiopure bromide (-)-7d by treatment with triethyl amine in methanol. The chemistry of tricyclic bromide 7d described above opens interesting new manners for the synthesis of natural products and cage compounds via the intermediacy of norbornene annulated cyclopentadienone 10.

Experimental section

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. 1H and 13C-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. Optical rotations were determined on a Perkin-Elmer 241 polarimeter. All solvents used were dried and distilled according to the standard procedures.

General procedure for Barton's radical decarboxylation reaction

A: Preparation of acid chlorides
The acid chlorides were prepared immediately before use and were not purified. Thus, a solution of the corresponding carboxylic acid (1 mmole) in benzene (5 ml) was treated with oxalyl chloride (0.3 ml) and a drop of dimethyl formamide. After stirring for 2 hrs at room temp. with protection from moisture, the solvent and the excess of oxalyl chloride were evaporated in vacuo and the residual acid chloride was used as such.

B: Barton's radical reaction
Acid chloride (1 mmole) in appropriate solvent (5 ml) was added dropwise (adding rates depend on the reaction) to a dried, stirred suspension of N-hydroxypyridin-2-thione sodium salt (1.2 mmole) in the same solvent and containing the radical trapping reagent. During the addition the mixture was heated at reflux and irradiated with a 250 w tungsten lamp under 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 and/or recrystallization.

**endo-Tricyclo[5.2.1.0²⁶]deca-4,8-dien-3-one 7a**

Following the general procedure (addition time: 15 min., benzene as solvent and t-butyl thiol as trapping reagent), flash chromatography (n-hexane:ethyl acetate = 9/1) gave 7a (90 mg, 60%) as a white crystalline material together with 7b (38 mg, 15%).

**7a**: 1H-NMR (400 MHz, CDCl₃): δ 7.38 (dd, J₄,5=5.7 Hz, 1H, H₅), 5.95 (m, 2H, H₄, H₈ or H₉), 5.78 (dd, J₈,9=5.6 Hz, J₁₉ resp. J₇,₈=2.9 Hz, 1H, H₈ or H₉), 3.42 (m, 1H, H₆), 3.22 and 2.97 (2 x brs, 2H, H₁ and H₂). 2.80 (dd, J₁₂=J₂,₆=5.1 Hz, 1H, H₂), 1.76 A of AB (d, J₁₀₈,₁₀₉=8.4 Hz, 1H, H₁₀₈ or H₁₀₉). 1.62 B of AB (d, J₁₀₈,₁₀₉=8.4 Hz, 1H, H₁₀₈ or H₁₀₉).

**6-Pyridylthio-endo-tricyclo[5.2.1.0²⁶]deca-4,8-dien-3-one 7b**

Following the general procedure (addition time: 15 min., benzene as solvent), flash chromatography (n-hexane/ethyl acetate = 1/1) gave 7b (230 mg, 90%) as an oil.

**7b**: 1H-NMR (400 MHz, CDCl₃): δ 8.45, 7.50, 7.22 and 7.04 (m, 4H, Py-H), 7.83 (d, J₄,₅=5.6 Hz, 1H, H₅), 6.05-5.99 (m, 2H, H₈ and H₉), 5.91 (d, J₄,₅=5.6 Hz, 1H, H₄), 3.40 and 3.32 (2 x brs, 2H, H₁ and H₂), 3.00 (d, J₁,₂=4.6 Hz, 1H, H₂), 2.50 A of AB (d, J₁₀₈,₁₀₉=8.9 Hz, 1H, H₁₀₈). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1705 (C=O), 1575 (C=C, conj.) cm⁻¹. CI/MS: m/e (%) 256 (100, M⁺+1), 228 (25, M⁺-CO), 190 (35, M⁺-C₅H₆-CO), 145 (24, M⁺-SPy), 112 (92, SPy⁺+1), 66 (7, C₅H₆⁺). EI/HRMS m/e: 256.0796 [calc.for C₁₅H₁₃NOS(M⁺): 256.0795].

**6-Chloro-endo-tricyclo[5.2.1.0²⁶]deca-4,8-dien-3-one 7c**

Following the general procedure (addition time: 30 min., carbon tetrachloride as solvent and trapping reagent), flash chromatography (n-hexane/ethyl acetate = 9/1) gave 7c (25 mg, 14%) and 7b (180 mg, 70%).

**7c**: 1H-NMR (400 MHz, CDCl₃): δ 7.30 (d, J₄,₅=5.6 Hz, 1H, H₅), 6.02-5.96 (m, 3H, H₄, H₈ and H₉), 3.32 and 3.10 (2 x brs, 2H, H₁ and H₂), 3.10 (d, J₁,₂=4.7 Hz, 1H, H₂), 2.38 A of AB (d, J₁₀₈,₁₀₉=9.0 Hz, 1H, H₁₀₈). 2.00 B of AB (d, J₁₀₈,₁₀₉=9.0 Hz, 1H, H₁₀₈). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1705 (C=O), 1580 (C=C, conj.) cm⁻¹. CI/MS: m/e (%) 182 (6, M⁺+1), 180 (18, M⁺), 145 (21, M⁺-Cl), 117 (18, M⁺-Cl-CO). 66 (100, C₅H₆⁺). EI/HRMS m/e: 180.0343 [calc.for C₁₀H₉OCl(M⁺): 180.0342].

**An improved procedure for the preparation of chloride 7c**

The reaction was carried out as above but now without irradiation. (The reaction vessel was covered with aluminium foil). After adding the acid chloride, chlorine t-butyloxide (0.5 ml) in CCl₄ (1 ml) was added immediately. The stirring was continued for 20 min. at room temp. The yield of 7c was improved to ~30% (55 mg).
Following the general procedure (enantiopure 6; [α]D25 = -84.3°, c=0.65, CH3OH; addition time: 15 minutes, bromotrichloromethane as solvent and trapping reagent), flash chromatography (n-hexane/ethyl acetate =9/1) gave 150 mg (67%) white crystalline bromide 7d and 155 mg of a mixture of bromide 7d and pyridyl sulfide 7b (containing 38% bromide 7d according to GC). (Complete isolation of 7d is possible by repeating flash chromatography and recrystallization). So, the total yield of bromide 7d is 93%.

7d: m.p.: >80 °C, decomposition (n-hexane), [α]D25 = -222° (c=0.69, CH3OH). 1H-NMR (400 MHz, CDCl3): δ 7.41 (d, J4,5=5.6 Hz, 1H, Hs), 6.00 A of AB (dd, J8,9=5.6 Hz, J1,9 resp. J7,8=2.8 Hz, 1H, Hs or H9), 5.95 B of AB (dd, J8,9=5.6 Hz, J1,9 resp. J7,8=3.2 Hz, 1H, Hs or H9), 5.94 (d, J4,5=5.6 Hz, 1H, H4), 3.31 and 3.25 (2 x brs, 2H, H 1 and HT), 3.21 (d, J1.2---4.6 Hz, 1H, H2), 2.44 A of AB (d, Jloa,A0s=9.0 Hz, 1H, Hloa), 2.04 B of AB (dt, J10a,10s=9.0 Hz, J10a,1 = J10a,7=1.6 Hz, 1H, H10a). IR (CH2Cl2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O), 1575 (C=C, conj.) cm -1. CI/MS: m/e (%) 227 (9, M++2), 225 (10, M*), 145 (100, M*+Br), 117 (55, M*+Br-CO), 66 (100, C3H6*). Found: C 52.72, H 3.94 (calc.for C10H9OBr: C 53.36, H 4.03).

Following the general procedure [addition time: 15 minutes, toluene as solvent and iodoform (800 mg, 2 eq.) as trapping reagent], flash chromatography (n-hexane:ethyl acetate =9:1) gave 7e (170 mg, 62.5%) as a white crystalline material. An analytical sample was obtained by crystallization.

7e: m.p.: 83.5-85.5 °C (diisopropylether). 1H-NMR (400 MHz, CDCl3): δ 7.55 (d, J4,5=5.6 Hz, 1H, Hs), 5.97 A of AB (dd, J8,9=5.5 Hz, J1,9 resp. J7,8=2.8 Hz, 1H, Hs or H9), 5.89 B of AB (dd, J8,9=5.5 Hz, J1,9 resp. J7,8=3.1 Hz, 1H, Hs or H9), 5.83 (d, J4,5=5.6 Hz, 1H, H4), 3.39 and 3.27 (2 x brs, 2H, H 1 and HT), 3.24 (d, J1.2---4.6 Hz, 1H, H2), 2.49 A of AB (d, Jloa,A0s=9.0 Hz, 1H, Hloa), 2.07 B of AB (dt, J10a,10s=9.0 Hz, J10a,1 = J10a,7=1.6 Hz, 1H, H10a). IR (CH2Cl2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O), 1570 (C=C, conj.) cm -1. CI/MS: m/e (%) 273 (3, M*+I), 145 (100, -I), 117 (17, -I-CO), 79 (9, I*), 66 (19, C3H6*). EI/HRMS m/e: 272.9776 [calc.for C10H9OI(M+I): 272.9776].

Following the general procedure (addition time: >30 min., dimethyl disulfide as solvent and trapping reagent), flash chromatography (n-hexane/ethyl acetate =9:1) gave 7f (90 mg, 22%) as a colourless oil. An analytical sample was obtained by crystallization.

7f: m.p.: 72.3 A of AB (d, J4,5=5.6 Hz, 1H, Hs), 6.01-5.97 (m, 2H, Hg and H9), 5.95 B of AB (d, J4,5=5.6 Hz, 1H, H4), 3.32 and 2.84(2 x brs, 2H, H 1 and HT), 2.81 (d, J1.2---4.6 Hz, 1H, H2), 2.34 A of AB (d, Jloa,A0s=8.7 Hz, 1H, Hloa), 1.85 B of AB (dt, J10a,10s=8.7 Hz, J10a,1 = J10a,7=1.6 Hz, 1H, H10a). IR (CH2Cl2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O), 1570 (C=C, conj.) cm -1. EI/MS: m/e (%) 192 (9, M*+), 164 (79, M*+CO), 126 (86, M*+C3H6), 144 (57, M*+CH3SH), 98 (28, M*+C5H10-CO), 117 (62, M*+CH3S-CO), 66 (100, C3H6*). EI/HRMS m/e: 192.0608 [calc.for C11H12OS(M+): 192.0609].

Following the general procedure (addition time: 15 minutes, toluene as solvent and diphenyl disulfide (10 eq.) as trapping reagent), flash chromatography (n-hexane:ethyl acetate = 9:1) gave 7g (105 mg, 42%) as a white solid.

7g: m.p.: 58 °C. 1H-NMR (400 MHz, CDCl3): δ 7.50 and 7.29-7.40 (m, 5H, Ph-H), 7.26 A of AB (d,
6-Functionalized tricyclodecadienones 51

14.5±5.6 Hz, 1H, Hs, 5.97 A of AB (dd, J8,9=5.5 Hz, 1H, H9 or H9), 5.80 B of AB (d, J4,5=5.6 Hz, 1H, H4), 3.31 and 2.94 (2 x brs, 2H, H1 and H2), 2.80 (d, J1,2=4.6 Hz, 1H, H2), 2.49 A of AB (d, J10a,10s=8.7 Hz, 1H, H10a), 1.90 B of AB (d, J10a,10s=8.7 Hz, J10a,7=1.6 Hz, 1H, H10a). IR (CH2Cl2): u 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O), 1570 (C=C, conj.) cm⁻¹. CI/MS: m/e (%) 254 (22, M⁺), 226 (100, M⁻-CO), 188 (41, M⁺-C₅H₆), 145 (74, M⁺-PhCO), 117 (71, M⁺-Ph-CO), 66 (11, C₅H₆⁺). EI/HRMS m/e: 254.0765 [calc.for C₁₆H₁₄O₂(M⁺): 254.0765].

6-Phenylselenyl-endo-tricyclo[5.2.1.O₂'6]deca-4,8-dien-3-one 7h

Following the general procedure [addition time: 15 minutes, toluene as solvent and diphenyl diselenide (2 eq.) as trapping reagent], flash chromatography (n-hexane:ethyl = 19:1) gave 7h (282 mg, 94%) as a white solid.

7h: m.p.: 69-71 °C (10% diisopropylether in n-hexane). ¹H-NMR (400 MHz, CDCl₃): δ 7.60 and 7.40-7.25 (m, 6H, Ph-H and Hs), 5.94 A of AB (dd, J8,9=5.5 Hz, J1,9 resp. J7,8=2.9 Hz, 1H, H9 or H9), 5.89 B of AB (dd, J8,9=5.5 Hz, J1,9 resp. J7,8=3.0 Hz, 1H, H9 or H9), 5.75 (d, J4,5=5.6 Hz, 1H, H4), 3.31 and 2.98 (2 x brs, 2H, H1 and H2), 2.83 (d, J1,2=4.6 Hz, 1H, H2), 2.47 A of AB (d, J10a,10s=8.7 Hz, 1H, H10a), 1.92 B of AB (d, J10a,10s=8.7 Hz, J10a,7=1.6 Hz, 1H, H10s). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1695 (C=O), 1570 (C=C, conj.) cm⁻¹. EI/MS: m/e (%) 302 (17, M⁺), 274 (49, M⁺-CO), 157 (17, PhSe⁺), 145 (98, M⁺-PhSe), 117 (100, M⁺-PhSe-CO), 79 (84, M⁺-C₅H₆-PhSe), 66 (17, C₅H₆⁺). EI/HRMS m/e: 302.0200±0.0009 [calc.for C₁₆H₁₄O₂Se(M⁺): 302.0210].


The acid chloride of 6 (1 mmole) in dichloromethane (5 ml) was added (5 minutes) to a dried, stirred suspension of N-hydroxypyridin-2-thione sodium salt (1.2 mmole) in dichloromethane (5 ml) at room temp. under an air atmosphere. The reaction vessel was covered with aluminium foil. After completion of the addition (PhS)₃Sb (900 mg, 2 mmole) in dichloromethane was added and stirring continued for 10 rain. at room temp. while protecting from light!. Then water (0.5 ml) was added and the aluminum foil removed. The mixture was stirred at room temp. for another 2 hrs. Solid material was removed by filtering and the liquid layer concentrated in vacuo. The crude product was purified by flash chromatography (n-hexane/ethyl acetate = 4/1) on silica gel to give 7i (65 mg, 40%) and 14 (70 mg, 25%). An analytical sample was obtained by crystallization.

7i: m.p. 73-75 °C (diisopropylether). ¹H-NMR (400 MHz, CDCl₃): δ 7.28 (d, J4,5=5.7 Hz, 1H, Hs), 6.00 A of AB (dd, J8,9=5.6 Hz, J1,9 resp. J7,8=3.1 Hz, 1H, H9 or H9), 5.97 B of AB (dd, J8,9=5.6 Hz, J1,9 resp. J7,8=2.8 Hz, 1H, H9 or H9), 5.95 (d, J4,5=5.7 Hz, 1H, H4), 3.24 and 2.80 (2 x brs, 2H, H1 and H2), 2.66 (d, J1,2=4.5 Hz, 1H, H2), 2.71 (s, 1H, OH), 2.30 A of AB (d, J10a,10s=8.7 Hz, 1H, H10s), 1.95 B of AB (d, J10a,10s=8.7 Hz, J10a,7=1.5 Hz, 1H, H10a). IR (CH₂Cl₂): ν 3600-3500 (free OH), 3600-3100 (H-bonded OH), 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O), 1570 (C=C, conj.), 1030 (C-O) cm⁻¹. CI/MS: m/e (%) 163 (100, M⁺+1), 145 (36, -H₂O), 134 (76, M⁺-CO), 97 (45, M⁺+1-C₅H₆), 66 (94, C₅H₆⁺). EI/HRMS m/e: 162.0680 [calc.for C₁₀H₁₀O₂(M⁺): 162.0681], 163.0759 [calc.for C₁₀H₁₁O₂(M⁺+1): 163.0759].
**Pentacyclo[5.3.0.0²,5.0³,9.0⁴,11]deca-10-one-2-carboxylic acid 17**

A solution of ester 15 (1.5 g) in toluene (140 ml) was irradiated for 5 hrs using a high-pressure mercury arc and a Pyrex filter. Concentration in vacuo gave rather pure 16 as a oil.

16: 1H-NMR (400 MHz, CDCl₃): δ 4.16 and 4.11 AB x 2 (2 x d, J₆,₇=7.1 Hz, 2H, CH₂CH₃), 3.39, 3.12, 3.02, 2.96, 2.62 and 2.52 (6 x m, 7H), 1.93 and 1.65 AB system (2 x d, J₈,₉=11.7 Hz, 2H, CH₂).

Above ester 16 was dissolved in methanol/water (25 ml, 1:1) containing sodium hydroxide (10%) and stirred at room temp. for 2 hrs to give a 17 (1.5g) as a white solid. Chromatography (a little amount of silica gel, n-hexane/EtOAc = 1/1) gave pure 17 (1.12g, 95%) as a white crystalline solid.

17: m.p.: 83-85°C. 1H-NMR (400 MHz, CDCl₃): δ 9.29 (brs, 1H, COOH), 3.42, 3.17, 3.06, 2.97, 2.64 and 2.59 (6 x m, 7H, all of tert.H), 1.94 and 1.68 ABx2 (2 x d, J₈,₉=11.7 Hz, 2H, CH₂). 13C-NMR (100 MHz, CDCl₃): ~ 214.2/178.6/54.0 (quat.), 53.2/47.5/43.5 (ten.), 41.4 (sec.), 41.0/40.6/38.6/36.9 (ten.). IR (CH₂Cl₂): ν 3500-2700 (COOH), 3010-2820 (C-H, sat.), 1760 and 1700 (C=O) cm⁻¹. El/MS: m/e (%) 190 (14, M⁺), 162 (17, M⁺-CO), 145 (15, M⁺-COOH), 117 (100, M⁺-COOH-CO), 66 (21, C₅H₆⁺). El/HRMS m/e: 190.0631 [calc.for C₁₁H₁₀O₃(M⁺): 190.0630].

**8-Bromo-pentacyclo[5.3.0.0²,5.0³,9.0⁴,11]deca-6-one 18a**

Following the general procedure (addition time: 30 minutes, bromotrichloromethane as solvent and trapping reagent), flash chromatography (n-hexane/ethyl acetate = 9/1) gave a mixture (310mg) of 18a and the corresponding pyridyl sulfide. The yield of 18a is 87% (content of 18a is 63% by GC).

18a: 1H-NMR (90 MHz, CDCl₃): δ 3.41, 3.25, 2.99 and 2.60 (m, 7H, tert-H), 2.15 and 1.61 AB (2 x d, J₆,₇=11.7 Hz, 2H, CH₂). GC-EI/MS: m/e (%) 226 (2, M⁺+I), 224 (2, M⁺-I), 198 (13, M⁺+I-CO), 196 (13, M⁺-I-CO), 145 (52, M⁺-Br), 117 (100, M⁺-Br-CO), 66 (44, C₅H₆⁺).

**8-Phenylselenyl-pentacyclo[5.3.0.0²,5.0³,9.0⁴,11]deca-6-one 18b**

Following the general procedure [addition time: 15 minutes, toluene as solvent and diphenyl selenide (470mg, 1.5mmol) as trapping reagent], flash chromatography (n-hexane/EtOAc = 9/1) gave a mixture (375mg) of 18b and the corresponding pyridyl sulfide. The yield of 18b is 94%. Pure 18b was obtained by recrystallization.

18b: m.p.: 76-77.5°C (ether). 1H-NMR (400 MHz, CDCl₃): δ 1H-NMR (400 MHz, CDCl₃): δ 7.58, 7.37-7.26 (m, 5H, Ph-H), 3.22, 3.08, 3.94, 2.56 and 2.32 (5 x m, 7H), 1.76 and 1.54 ABx2 (2 x d, J₆,₇=11.5 Hz, 2H, CH₂). 13C-NMR (100 MHz, CDCl₃): δ 214.2 (quart.), 136.5/129.0/128.6 (tert.), 127.2 (quart.), 77.5-79 °C (diisopropylether). 1H-NMR (400 MHz, CDCl₃): δ 7.48 (d, J₃,₄=5.7 Hz, 1H, H₃), 7.45-7.38 (m, 5H, Ph-H), 6.09 (d, J₃,₄=5.7 Hz, 1H, H₄), 6.07 A of AB (dd, J₈,₉=5.5 Hz, J₁,₉ resp. J₇,₈=2.7 Hz, 1H, H₈ or H₉), 6.00 B of AB (dd, J₈,₉=5.5 Hz, J₁,₉ resp. J₇,₈=3.1 Hz, 1H, H₈ or H₉), 3.38 (d, J₈,₉=4.7 Hz, 1H, H₉), 3.36 and 3.33 (2 x bs, 2H, H₁ and H₇), 1.99 A of AB (d, J₁₀₈,₁₀₉=9.0 Hz, 1H, H₁₀), 1.79 B of AB (d, J₁₀₈,₁₀₉=9.0 Hz, 1H, H₁₀), IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O), 1580 (C=C, conj.) cm⁻¹. Cl/MS: m/e (%) 283 (28, M⁺+I), 255 (50, -CO), 217 (6, M⁺+I-C₅H₆), 173 (86, M⁺-SPh), 145 (100, M⁺-COPh), 66 (34, C₅H₆⁺). El/HRMS m/e: 283.0791 [calc.for C₁₇H₁₅O₂S(M⁺+I): 283.0793]. Found: C 72.06, H 4.95, S 11.40 (calc.for C₁₇H₁₄O₂S: C 72.31, H 5.00, S 11.36).
6-Functionalized tricyclodecadienones

56.7/52.8 (tert.), 52.3 (quat.), 44.6/42.2/41.7 (tert.), 40.9 (sec.), 40.7/39.3 (tert.). IR (CH\_2Cl\_2): ð 3010-2820 (C-H, sat.), 1755 (C=O), 1580 (C=C, conj.) cm\(^{-1}\). El/MS: m/e (%) 302 (3, M\(^+\)), 274 (25, M\(^+\)-CO), 236 (14, M\(^+\)-C\_5H\_6), 145 (38, M\(^+\)-SePh), 117 (100, M\(^+\)-SePh-CO), 66 (3, C\_3H\_6\(^+\)). El/HRMS m/e: 302.0209 [calc for C\(_{14}\)H\(_{14}\)O\(^{80}\)Se(M\(^+\))]: 302.0210.

6-Methoxy-endo-tricyclo[5.2.1.0\(^2\)6]deca-4,8-dien-3-one 19

Crystalline bromide 7d (100 mg, 0.44 mmol) was added to a solution of potassium hydroxide (20%, 10 ml) in methanol with stirring while cooling (ice-water). Stirring was continued until crystalline 7d had completely disappeared. The mixture was neutralized and concentrated. Water (10 ml) was added followed by extraction with ether (3 x), several washing with brine and water, drying (Na\(_2\)SO\(_4\)) and concentration in vacuo to give 19 as a viscous oil (80 mg, yield is 84% by GC). Pure 19 can be obtained by flash chromatography (n-hexane/EtOAc = 5/1) as a colorless oil.

19: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): ð 7.29 (d, J\(_{4,5}=5.8\) Hz, 1H, H\(_5\)), 6.06 (d, J\(_{4,5}=5.8\) Hz, 1H, H\(_4\)), 6.00 A of AB (dd, J\(_{7,8}=2.8\) Hz, 1H, H\(_8\) or H\(_9\)), 5.96 B of AB (dd, J\(_{7,8}=2.8\) Hz, 1H, H\(_8\) or H\(_9\)), 3.31 (s, 3H, OCH\(_3\)), 3.22 and 2.86 (2 x brs, 2H, H\(_1\) and H\(_7\)), 2.77 (d, J\(_{1,2}=4.7\) Hz, 1H, H\(_2\)), 2.20 A of AB (d, J\(_{10a,10b}=8.5\) Hz, 1H, H\(_{10a}\)), 1.88 B of AB (dt, J\(_{10a,10b}=8.5\) Hz, J\(_{10a,1}=1.6\) Hz, 1H, H\(_{10a}\)). IR (CH\(_2Cl\_2\)): ð 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O) cm\(^{-1}\). EI/MS: m/e (%) 176 (14, M\(^+\)), 148 (44, M\(^+\)-CO), 111 (100, M\(^+\)-I-C\(_5\)H\(_6\)), 81 (74, M\(^+\)-C\(_5\)H\(_6\)-OCH\(_3\)), 66 (93, C\(_5\)H\(_6\)^+). El/HRMS m/e: 176.0837 [calc for C\(_{11}\)H\(_{12}\)O\(_2\)(M\(^+\)): 176.0837].

8-Methoxy-pentacvclo[5.3.0.0\(^2\)5,0\(^3\)9,0\(^4\)9,0\(^11\)9,0\(^16\)9]deca-6-one 20

A solution of 19 (25 mg) in toluene (2.5 ml) was irradiated for 4 hrs using a high-pressure mercury arc and a Pyrex filter. Concentration in vacuo gave 20 (25mg, 100%) as a pure white solid.

20: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): ð 3.20 (s, 3H, OCH\(_3\)), 3.15-2.80 (m, 5H, H\(_4\).H\(_6\).H\(_9\)), 2.58 (m, 1H, H\(_2\)), 2.35 (m, 1H, H\(_5\)), 1.99 and 1.59 AB (2 x d, J\(_{10a,10b}=11.6\) Hz, 1H, H\(_{10a}\)). IR (CH\(_2\)Cl\(_2\)): ð 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1700 (C=O) cm\(^{-1}\). El/MS: m/e (%) 176 (3, M\(^+\)), 148 (53, M\(^+\)-CO), 111 (100, M\(^+\)-I-C\(_5\)H\(_6\)), 81 (74, M\(^+\)-C\(_5\)H\(_6\)-OCH\(_3\)), 66 (93, C\(_5\)H\(_6\)^+). El/HRMS m/e: 176.0835 [calc for C\(_{11}\)H\(_{12}\)O\(_2\)(M\(^+\)): 176.0837].

Heptacyclo[9.6.1.1\(^5\)8.1\(^{12}\)15.0\(^2\)10.0\(^4\)9,0\(^6\)8,0\(^11\)16]eicosa-4(9),6,13,16-tetraene-3,18-dione 21

A solution of 7d (115 mg, 0.5 mmol, [\(\alpha\)]\(_D\)\(^{25}\)= -222°, c=0.69, CH\(_3\)OH) in CH\(_3\)OH (12 ml) and Et\(_3\)N (3 ml) was refluxed for 24h. Concentration in vacuo and subsequent flash chromatography (n-hexane/EtOAc = 3/1) gave 21 (70 mg, >95%) as a white solid.

21: m.p.: 179°C, decomposition (ethyl acetate), [\(\alpha\)]\(_D\)\(^{25}\)= -90.6°, c=1.14, CHCl\(_3\)). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): ð 6.91 A of AB (dd, J\(_{6,7}=5.1\) Hz, J\(_{5,6}\) resp. J\(_{7,8}=3.1\) Hz, 1H, H\(_6\) or H\(_7\)), 6.82 B of AB (dd, J\(_{6,7}=5.1\) Hz, J\(_{5,6}\) resp. J\(_{7,8}=3.2\) Hz, 1H, H\(_6\) or H\(_7\)), 6.61 A of AB (dd, J\(_{13,14}=5.4\) Hz, J\(_{12,13}\) resp. J\(_{14,15}=3.0\) Hz, 1H, H\(_{13}\) or H\(_{14}\)), 5.94 B of AB (dd, J\(_{13,14}=5.4\) Hz, J\(_{12,13}\) resp. J\(_{14,15}=3.2\) Hz, 1H, H\(_{13}\) or H\(_{14}\)), 5.64 (dd, J\(_{1,17}=3.5\) Hz, 1H, H\(_{17}\)), 3.78 and 3.61 (2 x brs, 2H, H\(_5\) and H\(_9\)), 3.42-3.61 (2 x brs, 2H, H\(_5\) and H\(_9\)), 3.42-3.36 (m, 3H), 3.14 (d, J\(_{2,10}=5.7\) Hz, 1H), 3.07 (brs, 1H), 2.49 A of AB (dt, J\(_{20a,20b}=6.8\) Hz, J\(_{1,5}\) Hz, 1H, one of H\(_{20a}\)), 2.30 B of AB (d, J\(_{20a,20b}=6.8\) Hz, 1H, one of H\(_{20}\), 2.01 A of AB (d, J\(_{19a,19b}=8.8\) Hz, 1H, one of H\(_{19}\)), 1.98 B of AB (dt, J\(_{19a,19b}=8.8\) Hz, J\(_{1,6}\) Hz, 1H, One of H\(_{19}\)). \(^13\)C-NMR (100 MHz, H-dec., CDCl\(_3\)): ð 199.2/196.3/195.2/167.5/150.2 (quat.), 145.0/142.2/135.5/133.9/113.7 (tert.), 74.0 (sec.), 68.3 (quat.), 55.7/53.8 (tert.), 53.1 (sec.),
cis-endo-Pentacyclo[9.2.1.1^8,8.0^2,1°.O4,9]pentadeca-2(10),6,12-trien-3-one 22 and anti-endo- pentacyclo-
[9.2.1.1^8,8.0^2,1°.O4,9]pentadeca-2(10),6,12-trien-3-one 23

A mixture of 7d (115 mg, 0.5 mmol) and cyclopentadiene (0.5 ml) in methanol (12 ml) and Et₃N (3 ml)
was refluxed for 24 hrs. Concentration in vacuo and subsequent flash chromatography (n-hexane/EtOAc =
3/1) gave a mixture (85mg, 81%) of 22 and 23 as a white solid in 1:2 ratio.

22: ¹H-NMR (400 MHz, CDCl₃): δ 6.73 A of AB (dd, J=5.0 Hz, J=3.1 Hz, 1H), 6.67 B of AB (dd, J=5.0 Hz,
J=3.2 Hz, 1H), 5.74 A of AB (dd, J=5.6 Hz, J=2.9 Hz, 1H), 5.37 B of AB (dd, J=5.6 Hz, J=2.9 Hz,
1H), 3.61 and 3.48 (2 x brs, 2H), 3.46 and 3.19 AB (2 x t, J=4.6 Hz, 2H), 3.09 and 2.95 (2 x brs, 2H), 2.37
and 2.31 AB (2 x d, J=6.6 Hz, 2H), 1.72 A of AB (dt, J=8.4 Hz, J=1.8 Hz, 1H), 1.59 B of AB (dt, J=8.4 Hz,
1H). CI/MS: m/e (%) 211 (100, M⁺), 182 (76, M⁺-CO), 145 (39, M⁺-C₅H₆), 116 (98, M⁺-C₅H₆-CO),
66(9, C₅H₆⁺).

23: ¹H-NMR (400 MHz, CDCl₃): δ 6.86 A of AB (dd, J=5.1 Hz, J=3.1 Hz, 1H), 6.75 B of AB (dd, J=5.1 Hz,
J=3.2 Hz, 1H), 5.99 A of AB (dd, J=5.6 Hz, J=2.9 Hz, 1H), 5.81 B of AB (dd, J=5.6 Hz, J=2.9 Hz,
1H), 3.61 and 3.49 (2 x brs, 2H), 3.22 and 3.14 AB (2 x t, J=4.6 Hz, 2H), 3.18 and 3.01 (2 x brs, 2H), 2.38 A
of AB (dt, J=6.6 Hz, J=1.5 Hz, 1H, H₁₀a), 2.22 B of AB (dt, J=6.6 Hz, 1H, H₁₀a), 1.82 A of AB (dt, J=8.4 Hz,
J=1.5 Hz, 1H), 1.61 B of AB (dt, J=8.4 Hz, 1H). CI/MS: m/e (%) 211 (65, M⁺), 182 (71, M⁺-CO), 145
(31, M⁺+1-C₅H₆), 116 (100, M⁺-C₅H₆-CO), 66(12, C₅H₆⁺). IR of mixture (CH₂Cl₂): ν 3120-3030 (C-H,
unsat.), 3020-2820 (C-H, sat.), 1670 (C=O) cm⁻¹.

endo-cis-endo-Pentacyclo[9.2.1.1^8,8.0^2,1°.O4,9]pentadeca-6,12-dien-3-one 24 and endo-anti-endo- pentacyclo-
[9.2.1.1^8,8.0^2,1°.O4,9]pentadeca-6,12-dien-3-one 25

A mixture of 22 and 23 (210 mg, 1 mmol) in dry THF (5 ml) was added to a deep blue solution of lithium
in ammonia [made from lithium metal (50 mg) and liquid ammonia (10 ml)] at -78°C with stirring. The
reaction was continued for 10 min. and stopped by adding solid NH₄Cl until the blue colour disappeared.
After evaporation of the ammonia, water (5ml) was added and the mixture was extracted with ether (3x),
washed with brine and water, dried (over Na₂SO₄) and concentrated to give an oil (205mg).
This oil was redissolved in dichloromethane (10 ml) and treated with pyridinium chlorochromate (320 mg,
1.5 mmol) for 2 hrs at room temp. Ether (30ml) was added, the mixture filtered and dried (over MgSO₄)
and concentrated in vacuo. Subsequent flash chromatography (n-hexane/EtOAc = 10/1) gave 24 (60 mg,
29%) and 25 (105 mg, 50%).

24: ¹H-NMR (400 MHz, CDCl₃): δ 5.97 A of AB (dd, J=5.7 Hz, J=3.1 Hz, 2H), 5.90 B of AB (dd, J=5.7 Hz, J=3.0 Hz, 2H), 3.28-3.17 (m, 4H), 2.97 and 2.88 (2 x brs, 4H), 1.52 and 1.38 AB (2 x d, J=7.9 Hz, 4H). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1720 (C=O) cm⁻¹. CI/MS: m/e (%)
212 (6, M⁺), 184 (12, M⁺-CO), 147 (23, M⁺+1-C₅H₆), 66(100, C₅H₆⁺). EI/HRMS m/e: 212.1199
[calc. for C₁₅H₁₆O(M⁺): 212.1201].

25: ¹H-NMR (400 MHz, CDCl₃): δ 6.20 A of AB (dd, J=5.7 Hz, J=3.1 Hz, 2H), 6.07 B of AB (dd, J=5.7 Hz, J=3.1 Hz, 2H), 3.07 (2 x brs, 4H), 2.60 A of AB (dd, J=8.5 Hz, J=4.8 Hz, 2H), 2.42 B of AB (dd, J=8.5 Hz, J=4.8 Hz, 2H), 2.30 A of AB (dd, J=8.5 Hz, J=4.8 Hz, 2H), 2.05 B of AB (dd, J=8.5 Hz, J=4.8 Hz, 2H).
6-Functionalized tricyclodecadienones

Hz, J=3.6 Hz, 2H), 1.45 A of AB (dt, J=8.2 Hz, J=1.6 Hz, 2H), 1.27 B of AB (d, J=8.2 Hz, 2H). IR
(CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1720 (C=O) cm⁻¹. CI/MS: m/e (%) 212 (0.7,
M⁺), 147 (100, M⁺+1-C₅H₆), 66(88, C₅H₆⁺). EI/HRMS m/e: 212.1199 [calc for C₁₅H₁₆O(M⁺): 212.1201].

endo-anti-exo-Pentacyclo[9.2.1.1₅'s.O₂,1°.O₄'9]pentadeca-6,12-dien-3-one 27 and exo-anti-exo-pentacyclo-
[9.2.1.1₅'s.O₂,1°.O₄'9]pentadeca-6,12-dien-3-one 28

A mixture of exo-tricyclodecadienone 26 (440 mg, 3 mmol), cyclopentadiene (400 mg, 6 mmol) and AlCl₃
(80 mg, 0.6 mmol) in dried benzene (15 ml) was stirred for 4h at room temp. Concentration in vacuo
and subsequent flash chromatography (n-hexane/EtOAc = 19/1) gave 27 (185 mg, 29%) and 28 (365 mg,
57%).

27: ¹H-NMR (400 MHz, CDCl₃): δ 6.17 A of AB (dd, J=5.7 Hz and 3.1 Hz, 1H), 6.14 A of AB (dd, J=5.7
Hz and 3.1 Hz, 1H), 6.09-6.05 B of AB (m, 2H), 3.22-3.20 (m, 1H), 3.11-3.07 (m, 2H), 2.97 and 2.83 (2 x
bs, 2H), 2.51 (ddd, J=2.1, 4.1 and 8.6 Hz, 1H), 1.94 A of AB (d, J=7.7 Hz, 1H), 1.78 B of AB (d, J=7.7 Hz,
1H), 1.51 A of AB (d, J=8.4 Hz, 1H), 1.37-1.33 (m, 2H), 1.27 B of AB (d, J=8.4 Hz, 1H).

28: ¹H-NMR (400 MHz, CDCl₃): δ 6.19 A of AB (dd, J=5.6 Hz, J=3.0 Hz, 2H), 6.14 B of AB (dd, J=5.6
Hz, J=2.9 Hz, 2H), 3.07 and 2.86 (2 x brs, 2 x 2H), 2.43 and 1.90 AB (dd, J₁=J₂=8.5 Hz, 2 x 2H), 1.39 and
1.30 AB (d, J=9.0 Hz, 2 x 2H). IR (CH₂Cl₂): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1710
(C=O) cm⁻¹. CI/MS: m/e (%) 212 (2, M⁺), 147 (79, M⁺+1-C₅H₆), 66(100, C₅H₆⁺). EI/HRMS m/e:
212.1202 [calc for C₁₅H₁₆O(M⁺): 212.1201].

Heptacyclo[7.5.1.0₃'8.0₄'7.0₆'1².0₁'4]pentadeca-l l-one 30

A solution of 24 (45 mg, 0.22 mmol) in a mixture of 10% acetone in benzene (10 ml) was irradiated
overnight using a high-pressure mercury arc and a Pyrex filter. Concentration in vacuo
and subsequent chromatography (n-hexane/EtOAc = 20/1) gave 30 (27 mg, 60%) as a pure white solid.

30: m.p.: 137-139 °C (EtOAc in n-hexane)[Lit m.p. 123-125 °C]. ¹H-NMR (400 MHz, CDCl₃): δ 2.76
(m, 6H), 2.43 (d, J=7.1 Hz, 2H), 2.37, 2.27 and 1.60 (3 x bs, 3 x 2H), 1.61 A of AB (dd, J=9.3 Hz, J=1.4
Hz, 2H), 1.41 B of AB (dd, J=9.2 Hz, J=1.3 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 219.7 (quat.), 62.0
(tert.), 45.6 (sec.), 43.4/38.8/38.0/35.1/34.4 (tert.). IR (CH₂Cl₂): ν 3010-2820 (C-H, sat.), 1715 (C=O)
cm⁻¹. CI/MS: m/e (%) 212 (61, M⁺), 184 (55, M⁺-CO), 66(23, C₅H₆⁺). EI/HRMS m/e:
212.1202 [calc for C₁₅H₁₆O(M⁺): 212.1201].

References and Notes

1. For some recent representative examples, see: (a) Klunder, A.J.H.; Huizinga, W.B.; Sessink, P.J.M.;
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