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Halogen Addition to endo- and exo-Tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-ones

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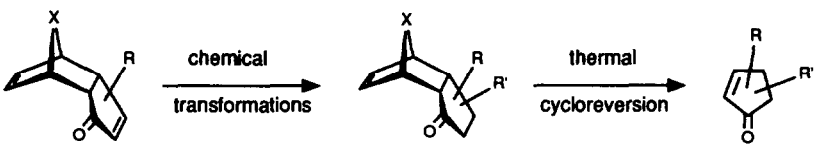
Abstract: *The reactions of* endo- *and* exo-*tricyclodecadienones* **2a-c** *and* **3a-c** *with bromine and iodine are described. The chemo- and regioselectivity of these additions depend on the nature of both reagent and substrate and are explained in terms of the configuration of the tricyclic compounds and the general mechanism for electrophilic halogenation. From a synthetic point of view only the bromination of* endo-*tricyclodecadienone* **2a** *is useful. Other reactions fail (***2a-c** *with* I_2*), result in addition to the norbornene double bond (***3a-c** *with* I_2*) or give rise to complex mixtures (***2b-c** *and* **3a-c** *with* Br_2*).*

INTRODUCTION

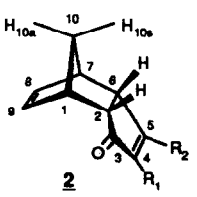
Tricyclodecadienones **1** are synthetic equivalents of cyclopentadienone and can be applied as such for the synthesis of cyclopentenoid natural products[1]. The basic strategy underlying this approach is depicted in scheme 1[2]. It generally involves stereoselective nucleophilic addition to the enone moiety, followed by

Scheme 1



endo-**1** (X= CH_2)
exo-**1** (X= CH_2, O)

chemical transformations to introduce the desired functionalities. Thermal cycloreversion utilizing the technique of flash vacuum thermolysis ultimately leads to the appropriately substituted cyclopentenones. Chemical modifications and/or selective transformations of the tricyclodecadienone system are essential to broaden the scope of this strategy. In the preceding paper, we reported on the regio- and stereochemistry of nucleophilic additions of some organometallic reagents to *endo-* and *exo*-tricyclodecadienones **2a** and **3a** and a related tricyclic ester. In this paper we describe our results concerning the seemingly trivial problem of



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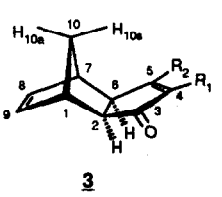

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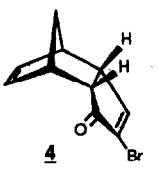

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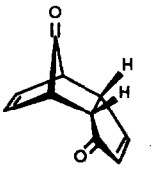

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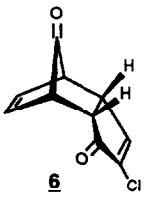

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a: $R_1 = R_2 = H$ **b**: $R_1 = Me$, $R_2 = H$ **c**: $R_1 = H$, $R_2 = Me$

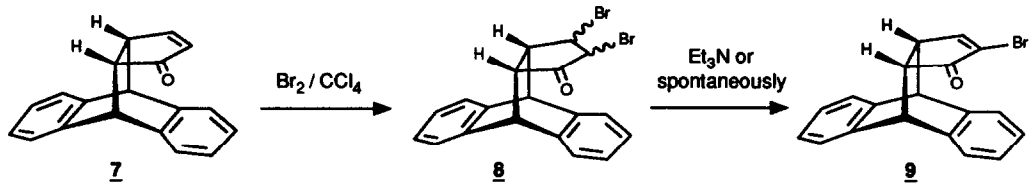
competing carbon-carbon double bonds in the addition of halogens to tricyclic dienones **2** and **3**. Normally, the electron-richer C_8-C_9 double bond would be expected to be halogenated by preference, were it not, that steric constraints present in **2** and **3** may hamper such a simple addition to this bond. It should be emphasized, that electrophilic reactions of *endo*- or *exo*-tricyclodecadienones received scarce attention in the literature, in contrast to nucleophilic reactions. The only halogenation reaction involving *endo*-tricyclodecadienone **2a** has been described by Paquette and Ward[3], who reported the formation of tricyclic α-bromoenone **4** by bromination of **2a** in the presence of triethylamine. A related example is chlorination of the dimer of cyclopentadienone, *viz.* **5**, which gave α-chloroenone **6**[4]. In both cases the α-haloenones were isolated as the only products, in excellent yields. This rather surprising product formation suggests that reaction with halogen has taken place exclusively with the electron-poor double bond of the enone moiety and that no halogen addition has occurred to the C_8-C_9 double bond of the norbornene unit, which generally exhibits high reactivity towards electrophilic reagents[5]. Scherer and Scerbo[4b] suggested that the unexpected formation of α-chloroenone **6** is due to some electronic influence of the C_{10}-carbonyl group in **5**, while Paquette and Ward did not comment at all on the deviating chemoselectivity. In our opinion the above formation of α-haloenones may be attributed to steric and electronic constraints present in *endo*-tricyclodecadienones. To shed more light on the behavior of tricyclodecadienones toward halogens, a thorough investigation of the halogen addition to *endo*-tricyclodecadienones **2a-c** and their *exo*-analogs **3a-c** was initiated.

BROMINATIONS

The bromination of *endo*-tricyclodecadienone **2a**, following Paquette and Ward's procedure[3], involves addition of one equivalent of bromine, immediately followed by the addition of excess triethylamine. α-Bromoenone **4** was obtained in 80% yield. Surprisingly, the reaction also proceeds in the absence of triethylamine, even at -20 °C, producing, after work-up, also α-bromoenone **4** as the sole product in 75% yield. The reaction is however less clean than in the presence of triethylamine, probably due to the formation of hydrogen bromide. Attempts to identify intermediates or by-products by spectral means were not met with success.

In remarkable contrast to the clean reaction observed for parent **2a**, complex mixtures of products were obtained when 4- and 5-methyl substituted *endo*-tricyclodecadienones **2b** and **2c** were subjected to bromination under a variety of conditions. No products could be isolated or identified from these brominations, neither in the presence nor in the absence of triethylamine. The starting materials could however, not be recovered, suggesting that bromination of **2b,c** is more complicated than that of the parent system **2a**. Bromination of *exo*-compounds **3a-c** under various conditions in all three cases also led to

Scheme 2



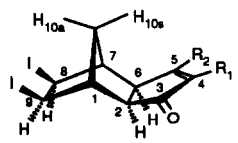
7 8 9

complex product mixtures, which could not be unraveled. For the sake of comparison bromination of anthracene adduct 7, lacking a competing C_8-C_9 double bond was investigated (Scheme 2). In this substrate bromination is only feasible at the enone system and consequently a rather clean formation of the corresponding α-bromoenone is expected when 7 is subjected to bromination under almost identical conditions as applied for parent *endo*-tricyclodecadienone 2a. Indeed, when bromine was added to 7, followed by the addition of triethylamine, α-bromoenone 9 was formed in almost quantitative yield. The rate of addition however, was slower than for 2a, as was shown by the slow disappearance of the brown color of added bromine at 0 °C (*cf.* experimental section). In the absence of triethylamine, dibromide(s) 8 was (were) formed which rapidly lost hydrogen bromide to give again 9 as the only product. Unfortunately, as crude 8 was very unstable, its ^{1}H-NMR spectrum was too complicated to distinguish between *cis*- and/or *trans*-isomers.

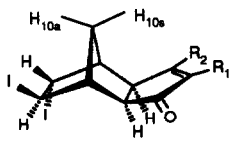
IODINATIONS

In order to study the effects of the reagent on the halogenation of 2a-c and 3a-c the electrophilic iodination of these tricyclic compounds was also studied.

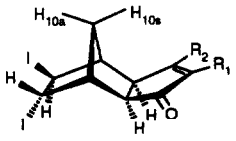
Since addition of iodine to alkenes may occur by an ionic as well as a free radical mechanism[6,7], 2a-c and 3a-c were reacted in the dark and in an inert atmosphere using a solution of iodine in tetrachloromethane. For *endo*-tricyclodecadienones 2a-c no reaction was observed at all under these conditions. The starting material was recovered completely, showing the inertness of these structures towards iodine. The corresponding *exo*-isomers 3a-c showed a completely different behavior towards iodine. They all reacted relatively fast, producing a mixture of three isomeric diiodides in varying ratios, in a moderate (3b) to excellent (3a,c) total yield (50-85%). By flash chromatography one of the products could be separated from the reaction mixture, while the remaining two components were obtained as a 1:1 mixture. NMR and IR spectral data showed that the addition products obtained for all three substrates 3a-c were structurally very similar and that in all products the enone moiety was retained. Therefore, addition of iodine must have taken place at the C_8-C_9 double bond in each case. All three diiodides showed very distinct patterns for the C_8 and C_9 methine protons in the ^{1}H-NMR spectrum. The two diiodides constituting the 1:1 mixture displayed a triplet ($J_{8,9}\approx J_{1,9}$ resp. $J_{7,8}\approx 4.0$ Hz) around 4.6 ppm and a double doublet ($J_{8,9}=4.0$ Hz and $J_{1,9}$ resp. $J_{7,8}\approx 2.8$ Hz) around 4.0 ppm, respectively. The isolated single addition products exhibited a double AB-pattern ($J_{AB}\approx 7.1$ Hz and $J_{1,9}\approx J_{7,8}\approx 2.1$ Hz) around 4.4 ppm. In order to assign these NMR signals to specific configurations around C_8 and C_9 in all diiodides, an X-ray diffraction study of the single compound isolated from the reaction of 3c with iodine was undertaken[8]. The analysis showed this product to be *cis-exo*-diiodide 10c. On the basis of this structure elucidation and a detailed analysis of the ^{1}H-NMR spectral data[9] of all three products, the other two



10a-c



11a-c



12a-c

a: R_1= R_2= H **b**: R_1= Me, R_2= H **c**: R_1= H, R_2= Me

compounds were identified as *trans*-diiodides **11c** and **12c**[11].

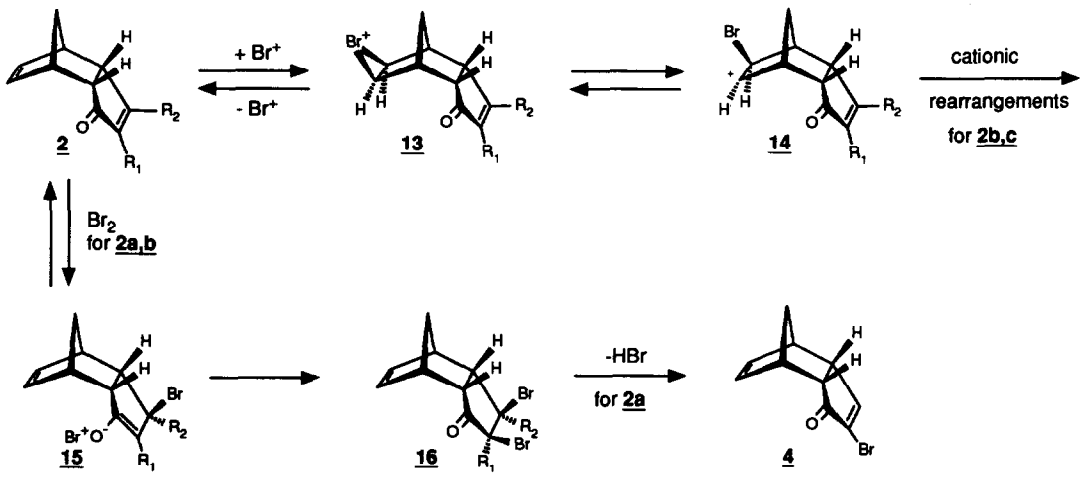
The *trans*-diiodides **11a-c** and **12a-c** are stable in solution at room temperature when exposed to visible light, in contrast however, the *cis-exo*-isomers **10a-c** are not. Exposure of a solution of *cis*-diiodides **10a-c** in chloroform to light, rapidly produced a slightly purple color, indicating the formation of some free iodine. Removal of the solvent after one day and spectral analysis of the residue showed that hardly any *cis*-diiodides **10a-c** had remained. Instead, a 1:1 mixture of *trans*-isomers **11a-c** and **12a-c** had been formed. Control experiments showed that the isomerization was slowed down considerably by addition of a radical-inhibitor[12] and did not take place at all when the solution was stored in the dark.

DISCUSSION

The results described in the preceding sections will be analyzed in terms of the general mechanism of halogenation of alkenes and enones, respectively, by taking into account the special constraints of both tricyclodecadienone systems.

At first sight bromination of **2a-c** is expected to occur preferentially at the electron-rich C_8-C_9 double bond by initial formation of a bromonium ion **13** at the *convex* face of the substrate (Scheme 3). However, the normal next step, *viz.* reaction of the bromonium ion with a bromide anion by attack from the rear side, is sterically strongly hampered in **13**, due to the *endo*-annelated cyclopentenone ring. Therefore, the further reaction of the bromonium ion may follow an escape route via its α-bromo cationic form (*i.e.* **14** or its isomer) and skeletal rearrangement thereof. This pathway resembles the reaction of norbornene with bromine, which is reported to produce a complex mixture of at least seven products, some resulting from skeletal rearrangement of the Wagner-Meerwein type[13]. The bromination results for substrates **2b,c** can be explained in this manner. However, with compound **2a** a deviating reaction path is followed, *viz.* bromination of the enone moiety to produce compound **4**. As for enones in general[14], it is assumed that initial interaction of the carbonyl group with bromine, followed by 1,4-addition of bromine leads to enolic compound **15a**. During this reaction bromide will approach C_5 from the *convex* side for steric reasons. Subsequent reaction of the enolic unit with bromine now produces *cis*-dibromide **16a** as a likely intermediate, because bromine attack from the *endo*-face is again sterically not feasible. The formation of dibromide(s) **8** in the bromination of **7** (Scheme 2) strongly supports the intermediacy of dibromide **16a** in the bromination of **2a**, although its occurrence could not be substantiated. Finally, rapid elimination of hydrogen bromide, either spontaneously or aided by triethylamine, yields the ultimate product **4**. Such a bromination process is not very likely for substrate **2c** as this would lead to enolic intermediate **15c** with the methyl group forced into the severely congested *endo*-region of the enolic molecule. For the same reason, formation of dibromide **16b** in the bromination of

Scheme 3



a: $R_1 = R_2 = H$ **b**: $R_1 = Me$, $R_2 = H$ **c**: $R_1 = H$, $R_2 = Me$

2b is sterically not very feasible. The kinetic balance between reaction of bromine with the C_8-C_9 bond and the enone moiety in compound **2a** is apparently very subtle. Because of the steric constraints of the normal bromination reaction of the C_8-C_9 double bond, the alternative pathway involving the enone moiety becomes energetically feasible. Apparently this is not the case for compounds **2b,c**, for reasons indicated above.

From an electronic point of view, both π-systems in **2a-c** interact because of their close spatial proximity. This is clearly illustrated by the fact that (sterically congested) *endo*-dicyclopentadiene derivatives undergo a Cope rearrangement when heated[4b,15]. Therefore, there is a shift in electron density from the C_8-C_9 double bond to that of the enone moiety, making the latter double bond more competitive in the electrophilic bromination of **2a-c**. In *exo*-congeners **3a-c**, however, such an interaction between both π-systems is not possible. Therefore, the enone double bond is less competitive and bromination of these compounds gives a complex mixture, probably by skeletal rearrangement of the α-bromo cationic form of the initial *exo*-bromonium ion.

Iodinations of **3a-c** lead exclusively to reaction at the C_8-C_9 double bond. The formation of *trans*-diiodides **11** and **12** can be explained by rear side attack of an iodine anion on the initially formed *exo* iodonium ion, whereas formation of *cis-exo*-diiodides **10** can be rationalized by either a four-center mechanism[16] or radical addition[17]. As the addition of iodine to alkenes is accompanied by a small change in free energy it is generally an equilibrium, sensitive to the structure of alkene and diiodide, the solvent and the temperature[18]. The above mentioned interaction between the C_8-C_9 double bond and the enone double bond in **2a-c** leads to a levelling of the difference in electron density in both double bonds, leaving both unreactive towards addition of iodine.

The instability of diiodo-compounds *cis-exo*-**10a-c** is demonstrated by their conversion to a mixture of *trans*-**11a-c** and **12a-c**, when subjected to daylight at room temperature. The C-I bonds in the sterically congested *cis-exo*-diiodides **10a-c** are readily cleaved to give a tight radical pair, which recombines to yield the more stable *trans*-isomers **11a-c** and **12a-c**. The purple color observed during this process confirms the

formation of iodine radicals.

CONCLUDING REMARKS

The halogen-additions to tricyclodecadienones **2a-c** and **3a-c** are very dependent on structural features of the substrates, as well as the nature of the reagent. Small structural changes such as the introduction of a methyl group at the enone moiety in *endo*-tricyclodecadienones **2** affect the product formation dramatically. The halogenation of **2** and **3** therefore, has a limited synthetic applicability. So far, only bromination of **2a** leads to a useful product, *viz.* **4**.

EXPERIMENTAL SECTION

General remarks

Melting points were measured with a Reichert Thermopan microscope and are uncorrected. IR spectra were taken on a Perkin Elmer 298 infrared spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AM-400, using TMS as an internal standard. For mass spectra a Bruker double focussing VG 7070E mass spectrometer was used. Elemental analyses were performed on a Carlo Eban Instruments CHNS-O 1108 Elemental Analyzer. Flash chromatography was 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. All solvents used were dried and distilled according to standard procedures.

4-*Bromo*-endo-*tricyclo*[5.2.1.0^{2,6}]*deca*-4,8-*dien*-3-*one* **4**[3]

A solution of **2a** (585 mg, 4.0 mmol) in CCl_4 (15 ml) was cooled to -25 °C and then 40 ml of a 0.11 M solution of Br_2 in CCl_4 (4.4 mmol) was rapidly added, while stirring. Immediately thereafter a solution of triethylamine (805 mg, 8.0 mmol) in CCl_4 (5 ml) was quickly added. The cooling-bath was removed after 30 min. and the mixture was stirred for another 4 hours. The crude mixture was filtered to remove precipitated ammonium salts, the filtrate washed with water and the aqueous phase extracted with ether. The combined organic fractions were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography (hexane:ethyl acetate = 5:1) gave 726 mg (80%) **4** as a white solid. An analytical sample was obtained by sublimation.

4: white powder (subl.). m.p.: 55.4-56.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$)[3]: δ 7.50 (d, $J_{5,6}$=2.9 Hz, 1H, H_5), 5.96 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), 5.85 B of AB (dd, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.36 (ddd, $J_{2,6}$=5.2 Hz, $J_{6,7}$=4.2 Hz, 1H, H_6), 3.29 (bs, 1H, H_1), 3.03 (bs, 1H, H_7), 2.92 (t, $J_{1,2}$≈5.1 Hz, 1H, H_2), 1.79 A of AB (d, $J_{10a,10s}$=8.7 Hz, 1H, H_{10a} or H_{10s}), 1.62 B of AB (d, 1H, H_{10a} or H_{10s}). IR (CH_2Cl_2): υ 3000-2820 (C-H, sat.), 1715 (C=O, conj.), 1580 (C=C, conj.) cm^{-1}. CI/MS: *m/e* (%) 225/227 (73/71,M^++1), 197/199 (8/8,-CO), 159/161 (12/12,-C_5H_6), 145 (100,-HBr), 117 (23,-HBr,-CO), 66 (29,$C_5H_6^+$).

4-*Bromo*-8,10-*dibenzotricyclo*[5.2.2.0^{2,6}]*undeca*-4,8,10-*trien*-3-*one* **9**

A solution of **7**[19] (302 mg, 1.2 mmol) in dry $CHCl_3$ (15 ml) was cooled to 0 °C and then 12 ml of a 0.11 M solution of Br_2 in dry $CHCl_3$ (1.3 mmol) was added over a period of 5 min., while stirring. The color of the

reaction mixture remained orange-brown. After 15 min. the mixture was allowed to attain room temperature and the color slowly changed to yellow, in 1 h. Additional Br_2 in $CHCl_3$ was added after 1 h. (1 ml) and 3 hrs. (1.2 ml) to complete the reaction. After 6 hrs. the reaction was complete according to cap. GC and the crude mixture was concentrated under reduced pressure to give a fuming, dark-brown oil, mainly consisting of dibromide(s) **8**, according to the ^{1}H-NMR spectrum. After addition of triethylamine (500 mg, 5.0 mmol) in dry CH_2Cl_2 (25 ml) the resulting mixture was stirred overnight at room temperature. The crude mixture was washed successively with 3% aqueous HCl, a saturated aqueous solution of $NaHCO_3$ and brine and finally, the aqueous fractions were extracted once with CH_2Cl_2 (30 ml). The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography (hexane:ethyl acetate = 3:1) gave 390 mg (quant.) **9** as a white solid (91% pure by cap. GC). An analytical sample was obtained by crystallization.

9: white powder (methanol). m.p.: 196-198 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48 (d, $J_{5,6}$=2.7 Hz, 1H, H_5), 7.37-7.34 and 7.20-7.08 (2m, 2H and 6H, H_{arom}), 4.68 (d, $J_{1,2}$=3.5 Hz, 1H, H_1), 4.48 (d, $J_{6,7}$=3.0 Hz, 1H, H_7), 3.32-3.29 (m, 1H, H_6), 2.87 (dd, $J_{2,6}$=6.2 Hz, 1H, H_2). IR ($CHCl_3$): υ 3100-2980 (C-H, unsat.), 2980-2890 (C-H, sat.), 1720 (C=O, conj.), 1580 (C=C, conj.) cm^{-1}. EI/MS: *m/e* (%) 336/338 (1/1,M^+), 257 (1,-Br), 202 (13,-C_3H_3OBr), 178 (100,$C_{14}H_{10}^+$), 79 (19,$C_5H_3O^+$). EI/HRMS *m/e*: 202.0783 (calc. for $C_{16}H_{10}$ (M^+-C_3H_3OBr): 202.0782).

General procedure for the reaction of endo- *and* exo-*tricyclodecadienones* **2a-c** *and* **3a-c** *with iodine.*

In a round bottom flask, protected from light by aluminum foil, a 0.05 M solution of I_2 in CCl_4 (1.1 equiv.) is added to the tricyclodecadienone. After stirring the reaction mixture at room temperature for 4-6 days, unreacted iodine is destroyed by stirring the crude solution vigorously with an aqueous solution of $NaHSO_3$, until the purple color has disappeared. The organic and aqueous phase are separated, the organic phase washed with water and the aqueous phases extracted with CCl_4. The combined organic fractions are washed with water, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Separation and purification of the products was achieved by flash chromatography (hexane:ethyl acetate = 2:1). Samples thus obtained were purified further by crystallization.

Reaction of endo-*tricyclodecadienones* **2a-c** *with iodine.*

The reaction of *endo*-tricyclodecadienones **2a-c** with iodine according to the general procedure gave recovered starting material only.

exo,exo-8,9-*Diiodo*-exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-4-*en*-3-*one* **10a**, endo-8-exo-9-*diiodo*-exo-*tricyclo*-[5.2.1.0^{2,6}]*dec*-4-*en*-3-*one* **11a** *and* exo-8-endo-9-*diiodo*-exo-*tricyclo*[5.2.1.0^{2,6}]*dec*-4-*en*-3-*one* **12a**

Following the general procedure [0.05 M I_2 in CCl_4 (63 ml, 3.2 mmol), 6 days], **3a** (438 mg, 3.0 mmol) gave, after work-up, 1.1 g crude material. Flash chromatography yielded 76 mg (6%) **10a** and 943 mg (80%) of a mixture of **11a** and **12a** (ratio 1.3:1). Both the mixture and the single compound were crystallized from methanol.

10a: yellow powder (methanol). m.p.: 140 °C (decomp.). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, $J_{4,5}$=5.6 Hz, $J_{5,6}$=2.8 Hz, 1H, H_5), 6.30 (dd, $J_{4,6}$=1.6 Hz, 1H, H_4), 4.42 A of AB (dd, $J_{8,9}$=7.1 Hz, $J_{8,10s}$ resp. $J_{9,10s}$=2.1 Hz, 1H, H_8 or H_9), 4.39 B of AB (dd, $J_{8,10s}$ resp. $J_{9,10s}$=2.1 Hz, 1H, H_8 or H_9), 2.91 (s, 1H, H_1), 2.88 (bs, 1H,

H_6), 2.76 (s, 1H, H_7), 2.32 (d, $J_{2,6}$=5.3 Hz, 1H, H_2), 2.08 A of AB (dt, $J_{10a,10s}$=11.7 Hz, $J_{2,10a}\approx J_{6,10a}\approx$1.5 Hz, 1H, H_{10a}), 1.27 B of AB (dm, 1H, H_{10s}). IR (CH_2Cl_2): υ 3000-2860 (C-H, sat.), 1705 (C=O, conj.), 1585 (C=C, conj.) cm^{-1}. CI/MS: *m/e* (%) 401 (27,M^++1), 273 (50,-HI), 245 (14,-HI,-CO), 147 (100,-2I), 146 (29,-HI,-I), 119 (24,-2I,-CO), 117 (23,-2HI,-CO), 81 (14,$C_5H_5O^+$), 66 (11,$C_5H_6^+$). CI/HRMS *m/e*: 400.8906 (calc. for $C_{10}H_{11}I_2O$ (M^++1): 400.8899).

11a and **12a** (ratio 1.3:1, major isomer **x**, minor isomer **y**): yellow powder (methanol). m.p.: 130.1-132.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, $J_{4,5}$=5.7 Hz, $J_{5,6}$=2.6 Hz, 1H, H_5 of **x**), 7.52 (dd, $J_{4,5}$=5.4 Hz, $J_{5,6}$=2.8 Hz, 1H, H_5 of **y**), 6.35 (dd, $J_{4,6}$=1.8 Hz, 1H, H_4 of **x**), 6.33 (dd, $J_{4,6}$=1.6 Hz, 1H, H_4 of **y**), 4.61 (t, $J_{1,9}$ resp. $J_{7,8}\approx J_{8,9}\approx$4.2 Hz, 1H, *exo*-H of H_8 resp. H_9 of **x**), 4.54 (t, $J_{1,9}$ resp. $J_{7,8}\approx J_{8,9}\approx$4.0 Hz, 1H, *exo*-H of H_8 resp. H_9 of **y**), 4.02 (dd, $J_{8,10s}$ resp. $J_{9,10s}$=2.8 Hz, 1H, *endo*-H of H_8 resp. H_9 of **y**), 3.98 (dd, $J_{8,10s}$ resp. $J_{9,10s}$=2.8 Hz, 1H, *endo*-H of H_8 resp. H_9 of **x**), 3.41-3.39 (m, 1H, H_1 or H_7 of **x**), 2.90-2.89 (m, 1H, H_1 or H_7 of **y**), 2.75 (ddd, $J_{2,6}$=5.3 Hz, $J_?$=1.9 Hz, $J_?$=0.9 Hz, 1H, H_2 or H_6 of **y**), 2.60 (bs, 1H, H_1 or H_7 of **x**), 2.52 (bd, 1H, H_2 or H_6 of **y**), 2.50 (bs, 1H, H_1 or H_7 of **y**), 2.39 (bd, 1H, H_2 or H_6 of **x**), 2.31 (ddd, $J_{2,6}$=5.3 Hz, $J_?$=1.6 Hz, $J_?$=1.0 Hz, 1H, H_2 or H_6 of **x**), 1.85 A of AB (dm, $J_{10a,10s}$=11.6 Hz, 2H, H_{10a} of **x** and **y**), 1.21-1.15 B of AB (m, 2H, H_{10s} of **x** and **y**). IR (CH_2Cl_2): υ 3000-2880 (C-H, sat.), 1705 (C=O, conj.), 1585 (C=C, conj.) cm^{-1}. CI/MS: *m/e* (%) 401 (100,M^++1), 273 (100,-HI), 245 (40,-HI,-CO), 147 (50,-2I), 146 (50,-HI,-I), 118 (39,-HI,-I,-CO), 117 (45,-2HI,-CO), 81 (15,$C_5H_5O^+$), 66 (11,$C_5H_6^+$). CI/HRMS *m/e*: 400.8898 (calc. for $C_{10}H_{11}I_2O$ (M^++1): 400.8899).

exo,exo-8,9-*Diiodo*-4-*methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*en*-3-*one* **10b**, endo-8-exo-9-*diiodo*-4-*methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*en*-3-*one* **11b** *and* exo-8-endo-9-*diiodo*-4-*methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*en*-3-*one* **12b**

Following the general procedure [0.05 M I_2 in CCl_4 (88 ml, 4.4 mmol), 4 days], **3b** (650 mg, 4.1 mmol) gave, after work-up, 1.0 g crude material, containing *ca.* 50% **3b**. Flash chromatography gave 57 mg (3%) **10b**, as well as an inseparable mixture of **11b**, **12b** and starting material **3b**. The single compound **10b** was crystallized from methanol.

10b: yellow plates (methanol). m.p.: 136 °C (decomp.). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.09 (bs, 1H, H_5), 4.41 A of AB (dd, $J_{8,9}$=7.1 Hz, $J_{8,10s}$ resp. $J_{9,10s}$=2.1 Hz, 1H, H_8 or H_9), 4.38 B of AB (dd, $J_{8,10s}$ resp. $J_{9,10s}$=2.1 Hz, 1H, H_8 or H_9), 2.89 (s, 1H, H_1), 2.71 (bs, 1H, H_6), 2.70 (s, 1H, H_7), 2.33 (d, $J_{2,6}$=5.2 Hz, 1H, H_2), 2.03 A of AB (dt, $J_{10a,10s}$=11.6 Hz, $J_{2,10a}\approx J_{6,10a}\approx$1.4 Hz, 1H, H_{10a}), 1.79 (s, 3H, -CH_3), 1.19 B of AB (dm, 1H, H_{10s}). IR (CH_2Cl_2): υ 3000-2830 (C-H, sat.), 1700 (C=O, conj.), 1635 (C=C, conj.) cm^{-1}. EI/MS: *m/e* (%) 286 (85,M^+-HI), 160 (100,M^+-2I), 132 (11,M^+-2I,-CO), 131 (10,M^+-HI,-I,-CO), 117 (24,M^+-2I,-CO,-CH_3), 66 (81,$C_5H_6^+$).

exo,exo-8,9-*Diiodo*-5-*methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*en*-3-*one* **10c**, endo-8-exo-9-*diiodo*-5-*methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*en*-3-*one* **11c** *and* exo-8-endo-9-*diiodo*-5-*methyl*-exo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*en*-3-*one* **12c**

Following the general procedure [0.05 M I_2 in CCl_4 (88 ml, 4.4 mmol), 4 days], **3c** (642 mg, 4.0 mmol) gave, after a short time, a brown precipitate which was filtered off after three days to yield crude **10c** (440 mg, 28%). This product was purified further by crystallization from 2-propanol. The filtrate was stirred for another day, during which no more product precipitated. Flash chromatography of the crude material isolated

from the filtrate gave 795 mg (48%) of a mixture of **11c** and **12c**, which was crystallized from methanol to obtain an analytically pure sample.

10c: yellow plates (2-propanol). m.p.: 151 °C (decomp.). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 6.02 (qn, $J_{4,6}\approx J_{4,CH3}\approx$1.3 Hz, 1H, H_4), 4.42 A of AB (dd, $J_{8,9}$=7.2 Hz, $J_{8,10s}$ resp. $J_{9,10s}$=2.2 Hz, 1H, H_8 or H_9), 4.39 B of AB (dd, $J_{8,10s}$ resp. $J_{9,10s}$=2.2 Hz, 1H, H_8 or H_9), 2.90 (s, 1H, H_1), 2.79 (s, 1H, H_7), 2.68 A of AB (d, $J_{2,6}$=5.1 Hz, 1H, H_6), 2.36 B of AB (d, 1H, H_2), 2.11 (s, 3H, $-CH_3$), 2.08 A of AB (dt, $J_{10a,10s}$=11.6 Hz, $J_{2,10a}\approx J_{6,10a}\approx$1.5 Hz, 1H, H_{10a}), 1.29-1.25 B of AB (m, 1H, H_{10s}). IR (CH_2Cl_2): υ 3000-2820 (C-H, sat.), 1695 (C=O, conj.), 1620 (C=C, conj.) cm^{-1}. CI/MS: *m/e* (%) 415 (19,M^++1), 287 (25,-HI), 259 (5,-HI,-CO), 161 (100,-2I), 132 (9,-HI,-I,-CO), 117 (5,-HI,-I,-CO,-CH_3), 95 (11,$C_6H_7O^+$), 66 (9,$C_5H_6^+$). CI/HRMS *m/e*: 414.9056 (calc. for $C_{11}H_{13}I_2O$ (M^++1): 414.9056).

11c and **12c** (ratio 1:1): yellow plates (methanol). m.p.: 99.9-101.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.12 (qn, $J_{4,6}\approx J_{4,CH3}\approx$1.3 Hz, 1H, H_4), 6.10 (qn, $J_{4,6}\approx J_{4,CH3}\approx$1.3 Hz, 1H, H_4), 4.61 (t, $J_{1,9}$ resp. $J_{7,8}\approx J_{8,9}\approx$4.0 Hz, 1H, *exo*-H of H_8 resp. H_9), 4.53 (t, $J_{1,9}$ resp. $J_{7,8}\approx J_{8,9}\approx$4.0 Hz, 1H, *exo*-H of H_8 resp. H_9), 4.00 (dd, $J_{8,10s}$ resp. $J_{9,10s}$=2.9 Hz, 1H, *endo*-H of H_8 resp. H_9), 3.95 (dd, $J_{8,10s}$ resp. $J_{9,10s}$=2.8 Hz, 1H, *endo*-H of H_8 resp. H_9), 3.23 (d, J=5.3 Hz, 1H), 2.88 A of AB (d, J=5.1 Hz, 1H), 2.72 B of AB (d, J=5.4 Hz, 1H), 2.65 (s, 1H), 2.58 (bd, J=4.1 Hz, 1H), 2.54 (s, 1H), 2.42 (bd, J=4.1 Hz, 1H), 2.38 (d, J=5.3 Hz, 1H), 2.13 (s, 3H, $-CH_3$), 2.12 (s, 3H, $-CH_3$) 1.88 A of AB (bd, $J_{10a,10s}$=11.6 Hz, 2H, 2xH_{10a}), 1.23-1.16 B of AB (m, 2H, 2xH_{10s}). IR (CH_2Cl_2): υ 3000-2830 (C-H, sat.), 1695 (C=O, conj.), 1620 (C=C, conj.) cm^{-1}. CI/MS: *m/e* (%) 415 (100,M^++1), 287 (100,-HI), 259 (19,-HI,-CO), 161 (71,-2I), 160 (40,-HI,-I), 132 (18,-HI,-I,-CO), 131 (18,-2HI,-CO), 117 (6,-HI,-I,-CO,-CH_3), 95 (10,$C_6H_7O^+$), 66 (10,$C_5H_6^+$).

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19. Details of the synthesis of **7**, which was obtained by a Diels-Alder reaction of 4-acetoxy-cyclopent-2-en-1-one with anthracene in the presence of $AlCl_3$ will be published in a forthcoming paper.

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