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REGIO- AND STEREOSPECIFIC RING-OPENING REACTIONS OF 4-SUBSTITUTED BASKETANES AND SECO-BASKETANES†

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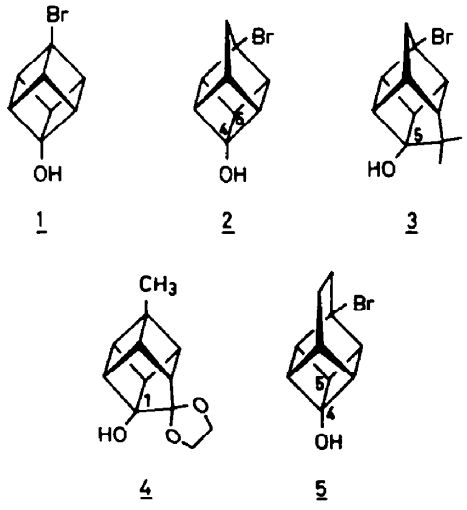
Abstract—Homoketonization of basketane acetates **6** and **10** on brief treatment with NaOMe in MeOH afforded the seco-basketanones **7** and **11**, respectively, in a stereo-and regiospecific cage opening reaction. As shown by deuterium labeling experiments, both for **6** and **10**, this homoketonization proceeds with retention of configuration. Prolonged basic treatment of **10** led to the exclusive formation of bicyclo[2.2.2]octenyl-acetates **12**. Under identical conditions **6** produced a complex mixture of products. Upon treatment of seco-basketanones **7** and **11** with aq HCl in MeOH, a rapid regiospecific cationic rearrangement to homobrendanone **14** was observed. This structure was established by X-ray analysis. The effect of a one carbon cage expansion on the base induced cage opening process by extension of the methylene bridge in the homocubane system into an ethylene bridge in the basketane system, is discussed.

Bridgehead substituted cubane alcohol **1**, homocubane alcohol **2** and 1,3-bishomocubane alcohol **3**, or their acetates are reactive substrates, which under basic conditions give a regio- and stereospecific homoketonization reaction leading to seco-cage systems.[1] The observed reactivity of these polycyclic alcohols in this cage opening process *grosso modo* parallels the total cage strain energy: cubane > homocubane > 1,3-bishomocubane (calc. strain energies: 165,[2] 120[2] and 80[3] kcal mole^{-1}, respectively). Interestingly, however, base treatment of homocuban-1-ol **4** with NaOMe in MeOH at 100° does not lead to any cage opened products[4] whereas homoketonization of the less strained 1,3-bishomocubanol **3**, under the same conditions, proceeds smoothly. Hence, there is no apparent correlation between base lability and the strain energy of the respective polycyclic systems. The presence of an extra methylene unit in **3**, as compared with **4**, causes the C–C bonds around C_5 in **3** to be relatively more strained than the corresponding C–C bonds around C_1 in homocubanol **4**, which apparently results in an increased base lability of **3**. Structural effects on the base induced cage opening may be expected if the one carbon methylene bridge in homocuban-4-ol **2** is extended to a two carbon ethylene bridge as present in basketane-4-ol**5**. Comparison of X-ray data[5] of the homocubane structure with those of the basketane nucleus indicates that the C–C bonds around C_4 and C_5 in basketane are somewhat more compressed than in the homocubane system, mainly due to an outbending effect of the ethylene bridge. In order to evaluate the influence of structural changes such as a one carbon bridge expansion, on the base induced homoketonization of strained bridgehead cage alcohols, we studied the cage opening of basketane 4-acetates.

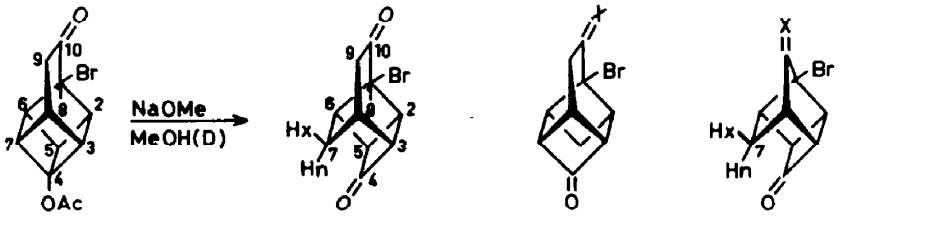


1 **2** **3** **4** **5**

As was shown in the preceding paper[6] basketanone acetate **6** is readily available by cage expansion of an appropriate homocubane derivative.

This bridgehead acetate was extremely base sensitive, upon treatment with NaOMe in MeOH at room temp. for 15 min acetate **6** gave a crystalline ketone in high yield to which half cage structure **7** was assigned (Scheme 1).

†Dedicated to Prof. Dr. R. J. F. Nivard on the occasion of his 60th birthday.



6 **7** **8** **9**

Scheme 1.

The IR spectrum showed carbonyl absorptions at 1720 and 1772 cm^{-1} attributable to a six and four membered ring ketone, respectively. The ^{1}HNMR spectrum ($CDCl_3$) displayed a resonance pattern with at least five unique proton absorptions. Careful analysis using double resonance techniques allowed the assignment of all the signals. A sharp first order sextet ($J_{H_5, H_6/H_2} \sim 6.2$ Hz, $J_{H_5, H_3} \sim 3$ Hz) was observed at δ4.19 for proton H_5. Protons H_2 and H_6 appeared as a broad quartet between δ3.65 and 3.35, whereas proton H_3 was found at δ3.40–3.16 as a broad triplet. The remaining bridgehead proton H_8 appeared at δ3.10 as a broad singlet. The ethylene bridge protons H_9 absorbed at δ2.67 as a narrow multiplet. This absorption completely disappeared when ketone **7** was subjected to treatment with a dilute solution of NaOMe in MeOD, due to a rapid H/D exchange reaction. *Endo*-proton H_{7n} and *exo*-proton H_{7x} showed a typical AB quartet ($J_{H_{7n}, H_{7x}} \sim 13$ Hz), each half of which was split further by additional coupling with vicinal but different protons. Using proton decoupling techniques, the rather broad doublet of doublets at δ2.21 ($J_{H_{7n}, H_8} \sim 5$ Hz) was assigned to H_{7n} while the sharp doublet of doublets at δ1.85 ($J_{H_{7x}, H_6} \sim 3.5$ Hz) was assigned to H_{7x}. A molecular model of **7** showed that the dihedral angles both between H_{7x} and H_8, and between H_{7n} and H_6 are close to 90° which explains the minor coupling between these protons. The occurrence of *exo*-proton H_{7x} at a higher field position than the *endo*-proton H_{7n} is unlike the observation in the corresponding seco-homocubanone system **9** where the opposite order is found. On basis of the NMR spectrum the isomeric structure **8** (X = O) which can be envisaged by cleavage of the central C_4–C_5 bond is ruled out. This ketone has C_s-symmetry and a more degenerated resonance pattern is expected. Substantial proof for structure **7** was provided by its acid catalyzed rearrangement to homobrendanone **14** (*vide infra*).

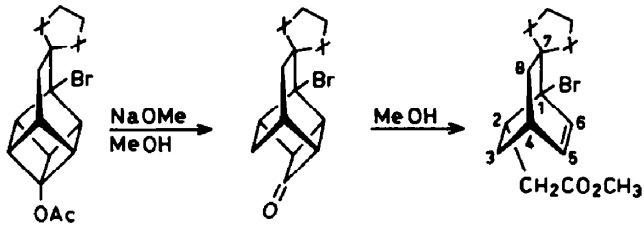
Prolonged basic treatment (16 h at room temp) of acetate **6** did not yield ketone **7** but instead a complex mixture was produced from which no identifiable materials could be isolated. Control experiments showed that half cage ketone **7** is indeed very sensitive to nucleophilic reagents.

To establish the stereochemistry of this homoketonization process, acetate **6** was treated with NaOMe in MeOD. A fast exothermic reaction was observed, leading to a trideuterated ketone **7**. The NMR spectrum ($CDCl_3$) was lacking signals for the ethylene bridge protons H_9 and *endo*-proton H_{7n}, while a simplified pattern was observed for both the H_{7x} and H_8 proton (the signals of the other protons remained unchanged). Evidently, the base induced cage opening of acetate **6** is both a regio- and stereospecific process which proceeds with retention of configuration.

In order to establish possible electronic or strain effects of the bridge ketone function at C_{10} in **6**, the homoketonization reaction was also investigated for the corresponding 10-ethylene ketal and 10-dithioethylene ketal acetates **10a** and **10b**. Unexpectedly, treatment with NaOMe in MeOH under identical conditions as used for **6**, both acetates **10a** and **10b** led to a mixture of two cage opened products, *viz.* **11** and **12** (Scheme 2). Isolation of these compounds from the mixture was a laborious task due to rapid decomposition of one of the products. Fortunately, variation of the reaction time allowed the isolation and characterization of both products. When ketal acetate **10a** was briefly treated with NaOMe in MeOH for just 1 min, followed by timely quenching with acetic acid, half cage ketone **11a** was obtained as a crystalline solid in almost quantitative yield. The IR spectrum showed a typical cyclobutanone absorption at 1770 cm^{-1}. The ^{1}HNMR spectrum ($CDCl_3$) was fully consistent with the proposed tetracyclic structure **11a**, although this spectrum was too complex to allow a definite assignment of all the signals. Attempts to unravel the absorption pattern by use of lanthanide NMR shift reagents failed because of a rapid rearrangement of **11a** into an isomeric ketone, whose structure could not be resolved yet.

In a similar fashion the corresponding thioketalized half-cage ketone **11b** was obtained from acetate **10b**. These seco-basketanes **11** appeared to be quite labile compounds. Both under nucleophilic and electrophilic conditions rapid rearrangement or fragmentation was observed. On refluxing both **11a** and **11b** in CH_3OH, a rapid transformation into the respective unsaturated esters **12a** and **12b** occurred (Scheme 2). These products were identical with those obtained directly from the respective acetates **10a** and **10b** on prolonged treatment with NaOMe in MeOH. These experiments unequivocally demonstrate the intermediacy of half cage ketones **11** in the formation of **12** from the acetates **10**. The transformation of half cage ketones **11** into bicyclic esters **12** can be rationalized straight-forward as depicted in Scheme 3. The driving force of this degradation reaction is the release of a considerable amount of strain. It should be pointed out that no reasonable mechanism can be proposed for the formation of **12** from the isomeric cage ketone **8** (X = ethylene ketal or dithioethylene ketal).

In order to elucidate the stereochemistry of the homoketonization of acetates **10**, these compounds were briefly (1 min only) treated with NaOMe in MeOD. Unfortunately, the position of the deuterium nucleus could

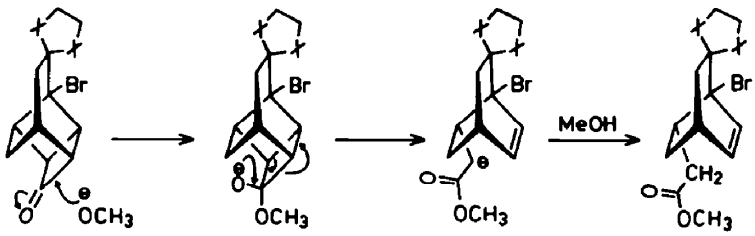


10a X = O
10b X = S

11a X = O
11b X = S

12a X = O
12b X = S

Scheme 2.



11 12

Scheme 3.

not be derived from the ^{1}HNMR spectra of mono-deuterated **11**. Therefore, the homoketonization of acetates **10** was performed for a prolonged period (16 h) to furnish trideuterated esters **12**, exclusively. Comparison of the ^{1}HNMR data clearly showed that both methylene protons adjacent to the ester function had completely been replaced by deuterium, whereas the position of the third deuterium was shown to be C_3-*endo*. Treatment of non-deuterated esters **12** with NaOMe in MeOD only led to complete H/D exchange of the methylene ester protons while no exchange of the C_3-*endo*-proton was observed at all. Accordingly, the stereochemistry of the base induced homoketonization of acetates **10** conforms entirely to the stereochemical pattern observed for the base induced cage opening of basketanone acetate **6** and proceeds with exclusive retention of configuration.

The seco-basketanones **7** and **11** are extremely sensitive to acidic reagents. Attempts to purify these compounds by chromatography over silicagel met no success due to rapid cationic rearrangement. We studied this rearrangement reaction in detail for the seco-basketanones **7** and **11a**.

Treatment of diketone **7** with aqueous HCl in MeOH gave a crystalline material (m.p. 169–170°, from CCl_4) in high yield. Mass spectral analysis showed the presence of one chlorine and one bromine substituent (*m/e* 276, 278, 280 (M^+, $C_{10}H_{10}BrClO_2$). The IR spectrum featured carbonyl absorptions at 1745 and 1735 cm^{-1}. In the ^{1}H NMR spectrum no olefinic signals were found. Its absorption pattern suggested the presence of a tetracyclic structure with a chlorine substituent incorporated stereospecifically. However, the spectrum was too complicated to assign a definite structure. Therefore, an X-ray analysis was carried out. The result of this analysis,[7] as pictured in Fig. 1, shows that the rearranged product has the homobrendanone structure. Furthermore, it confirms the stereospecific incorporation of chlorine at the C_2-position in **14**. The formation of homobrendanone **14** from **7** can be explained by a cyclobutyl-cyclopropylcarbinyl rearrangement that ultimately leads to cyclopropylcarbinyl cation **13** (Scheme 4). Sub-

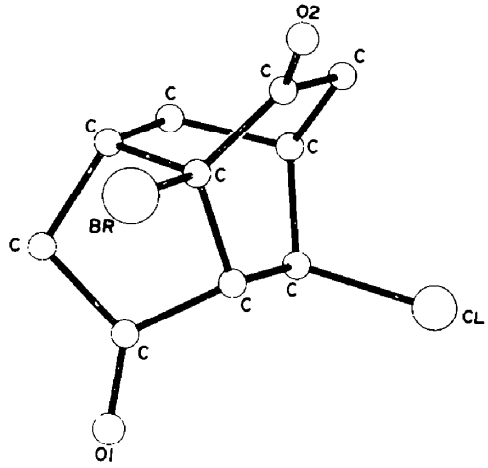
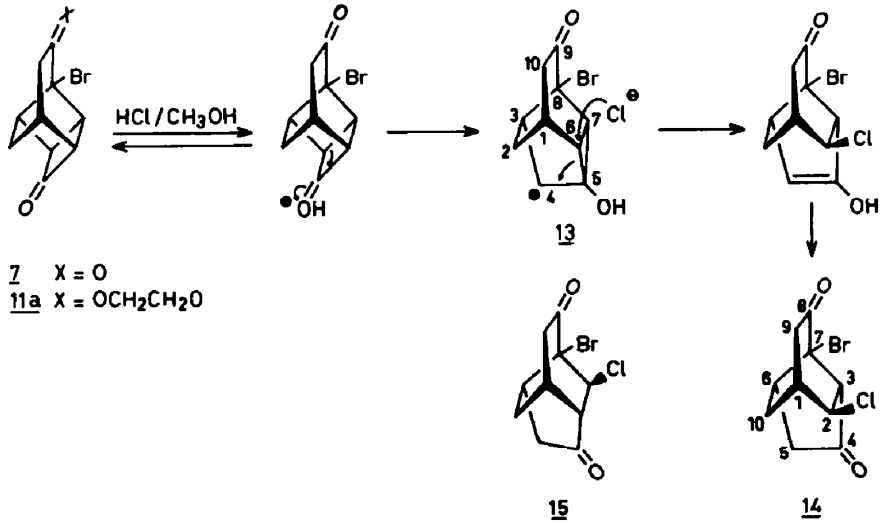


Fig. 1.



Scheme 4.

sequent cyclopropanol ring opening by $Cl^{\ominus}$ gives regio- and stereospecifically homobrendanone **14**. Formation of the isomeric twistanone **15** which can be envisaged by attack of $Cl^{\ominus}$ on C_7 in **13**, is unlikely for thermodynamic reasons, viz **15** being approximately 5 kcal $mole^{-1}$ [8] less stable than **14**. Recently, we observed a similar acid catalyzed rearrangement for seco-homocubanones **9**.[9] This formation of homobrendanone **14** from half-cage ketone **7** unequivocally excludes structure **8** as the alternative homoketonization product. No logical mechanism can explain the formation of **14** from **8**. Acid treatment of ketalized ketone **11a** also produced homobrendanone **14** as the exclusive product. Evidently, under the acid conditions applied, the 10-ethylene ketal function suffers from rapid hydrolysis.

In conclusion, the base induced homoketonization of basketane 4-acetates is a stereo- and regiospecific process proceeding exclusively with retention of configuration. This result conforms to the general pattern observed for this cage opening process in the homocubane and 1,3-bishomocubane systems. Cage expansion by extension of the methylene bridge in the homocubane system into an ethylene bridge in the basketane system does not effect the regio- and stereochemistry of the homoketonization process. However, it does effect the reactivity of the bridgehead acetates. Our results reveal that basketane 4-acetates are considerable more reactive towards base than the corresponding 4-substituted homocubane acetates. Furthermore, the effect of the expanded ethylene bridge is even more pronounced if the relative chemical stability of the half cage ketones is considered. Whereas seco-homocubanones **9** are stable under the homoketonization conditions, the seco-basketanones **7** and **11** rapidly react with NaOMe/MeOH to give an extended degradation to a bicyclo [2.2.2]octene. This difference in reactivity cannot be explained by the difference in total cage strain, because, according to force field calculations, basketane is about 5 kcal $mole^{-1}$ less strained than homocubane.[2] This implies that the observed difference in reactivity is due to an outbending effect of the ethylene bridge which increases the constraint around the C_4 and C_5 carbon atoms in the basketane and seco-bishomocubane systems relative to the homocubane and seco-homocubane analogues. Apparently, this alteration in local strain features is not sufficient to be reflected in the stereo- and regiochemistry of the base induced homoketonization process.

EXPERIMENTAL

IR spectra were taken on a Perkin–Elmer 257 grating spectrometer. NMR spectra were recorded on a Varian HA-100, Varian EM 390 or Bruker WH-90 using TMS as internal standard. Mass spectra were recorded on a Varian SM-1B spectrometer. All m.ps are uncorrected. Elemental analyses were carried out in the micro analytical department of the University of Nijmegen.

1 - *Bromotetracyclo*[4.4.0.$0^{2,5}$.$0^{3,8}$]*decan* - 4,10 - *dione* **7**. To a stirred solution of NaOH (0.3 g, 7.5 mmole) in MeOH (4.8 ml) and H_2O (1.2 ml was added, in one portion, very finely ground basketanone acetate **6** (0.3 g, 1.06 mmole). The mixture immediately turned yellow. After 15 min AcOH (0,45 ml, 7.5 mmole) was added and the resulting mixture concentrated *in vacuo*. The residue was extracted with $CHCl_3$, the organic layers were dried ($MgSO_4$), filtered and concentrated to give a crystalline material (0.3 g). Recrystallization from benzene/CCl_4 (1:1) gave diketone **7** (0.17 g, 67%), m.p. 134–136°; IR ν_{max}^{KBr} 1772, 1740 (sh), 1720 (C=O) cm^{-1}; NMR ($CDCl_3$) δ4.19 (sext, $J_{5,6-2} \sim 6.2$ Hz, $J_{5,3} = 3.4$ Hz, 1H, proton H_5), 3.65–3.35 (m, 2H, protons H_2 and H_6), 3.40–3.16 (m, 1H, proton H_3), 3.22–2.98 (broad s, 1H, proton H_8), 2.73–2.61 (m, 2H, protons H_9), 2.21 (d of d, $J_{7n,7x} \sim 13.0$ Hz, $J_{7n,8} \sim 5$ Hz, one half of an AB-quartet, 1H, proton H_{7n}), 1.85 (d of d, $J_{7x,7n} \sim 13.0$ Hz, $J_{7x,6} \sim 3.5$ Hz, one half of an AB-quartet, proton H_{7x}). *m/e* 242, 240 (M^+), 172, 170 (M^+-[$CH_2CO + CO$]), 161 (M^+–Br). (Found: C, 49.90; H, 3.78. Calc. for $C_{10}H_9BrO_2$: C, 49.82; H, 3.76%). 1 - *Bromo* - 7 - *endo* - 9,9 - *trideuteriotetracyclo* [4.4.0.$0^{2,5}$.$0^{3,8}$]*decan* - 4,10 - *dione* was prepared as described above using MeOD, D_2O and NaOD instead of MeOH, H_2O and NaOH. NMR ($CDCl_3$) δ4.19 (sext, $J_{2,6-5} \sim 6.2$ Hz, $J_{3,5} = 3.4$ Hz, 1H, proton H_5), 3.65–3.35 (m, 2H, protons H_2 and H_6), 3.40–3.16 (m, 1H, proton H_3), 3.20–2.98 (broad s, 1H, proton H_8), 1.84 (broad s, 1H, proton H_{7x}). *m/e* 245, 243 (M^+) 173, 171 (M^+-[$CD_2CO + CO$]), 164 (M^+–BR).

1 - *Bromotetracyclo*[4.4.0.$0^{2,5}$.$0^{3,8}$]*decane* - 4,10 - *dione* 10 - *ethylene ketal* **11a**. A solution of NaOMe (1 mmole) in MeOH (5 ml) was added to a stirred solution of acetate **10a** (0.143 g, 0.437 mmole) in MeOH (5 ml). The mixture immediately turned yellow. After ~1 min. AcOH was added, the colorless solution concentrated and the residue extracted with $HCCl_3$. The organic layer was dried ($MgSO_4$) and the solvent evaporated to give ketone **11a** as an oil (0.122 g, 97%), which slowly solidified. Careful crystallization from cyclohexane gave a pure sample, m.p. 95–97°; IR ν_{max}^{KBr} 1770 (C=O) cm^{-1}; NMR ($CDCl_3$) δ4.48–3.82 (m, 5H, ketal protons and a cage proton), 3.44 – 2.94 (m, 3H), 2.88–2.60 (broad s, 1H), 2.22–1.82 (m, 4H). *m/e* 286, 284 (M^+), 258, 256 (M^+–CO), 177 (M^+–CO), 177 (M^+-[Br + CO]). This tetracyclic ketone **11a** was very unstable. (Found: C, 49.76; H, 4.54. Calc. for $C_{12}H_{13}BrO_3$: C, 50.55; H, 4.60%). 1 - *Bromo* - 7 - *endo* - *deuterio* - *tetracyclo*[4.4.0.$0^{2,5}$.$0^{3,8}$]*decan* - 4,10 *dione* 10 *ethylene ketal* was prepared as described above using MeOD instead of MeOH; NMR ($CDCl_3$) δ4.48–3.82 (m, 5H), 3.44–2.94 (m, 3H), 2.88–2.60 (broad s, 1H), 2.18–1.82 (m, 3H), *m/e* 287, 285 (M^+), 259, 257 (M^+–CO), 178 (M^+-[Br + CO]).

Methyl 2 - (1 - *bromobicyclo*[2.2.2]*oct* - 5 - *enyl* - 7 - *one ethylene ketal*) *acetate* **12a**. NaOMe (0.186 g, 3.45 mmole) was added to a stirred solution of acetate **10a** (0.25 g, 0.76 mmole) in MeOH (15 ml). After stirring at room temp for 16 h, MeOH was removed *in vacuo*, the residue diluted with H_2O and ether extracted. The ether layer was dried ($MgSO_4$) and the solvent evaporated to give a gummy residue which was chromatographed on silica. Elution with $HCCl_3$ afforded methyl ester **12a** (0.09 g, 37%). Crystallization from hexane gave an analytically pure sample, m.p. 164–167°; IR ν_{max}^{KBr} 1730 (C=O) cm^{-1}; NMR ($CDCl_3$) δ6.15 (d, $J \sim 3.5$ Hz, olefinic protons H_5 and H_6), 4.22–3.76 (m, 4H, ethylene ketal protons), 3.56 (s, 3H, OCH_3), 3.10–2.80 (m, 2H, proton H_2 and one of the diastereotopic methylene proton adjacent to $-CO_2CH_3$), 2.70–2.44 (m, 1H, proton H_4), 2.20–1.76 (m, 2H, *exo*-proton H_3 and diastereotopic proton adjacent to $-CO_2CH_3$), 1.81 (d, $J \sim 2.5$ Hz, 2H, bridge-CH_2-), 1.20 (broad d, $J \sim 13$ Hz, 1H, *endo*-proton H_3). *m/e* 318, 316 (M^+), 287, 285 (M^+–OCH_3), 237 (M^+–Br). (Found: C, 49.23; H, 5.50. Calc. for $C_{13}H_{17}BrO_4$: C, 49.23; 5.40%).

Methyl 2 - (1 - *bromobicyclo*[2.2.2]*oct* - 5 - *enyl* - 7 - *one ethylene dithioketal*) *acetate* **12b**. A solution of NaOMe (4 mmole) in MeOH (20 ml) was added to acetate **10b** (0.225 g, 0.626 mmole). The stirred mixture was refluxed for 4 hr and kept at room temp overnight. AcOH was then added to neutralize the mixture, solvents were evaporated and the residue extracted with $HCCl_3$. The organic layer was dried ($MgSO_4$), filtered and concentrated to give a gummy material from which **12b** could be isolated (0.135 g, 62%) by tlc on silica (eluant: cyclohexane/ether (75:25 vol %). Recrystallization from hexane yielded a pure sample, m.p. 70–72°; IR ν_{max}^{KBr} 1725 (C=O) cm^{-1}; NMR ($CDCl_3$) δ6.60–6.40 (d, $J_{6,5} \sim 7$–8 Hz, 1H, proton H_6), 6.44–6.16 (m, $J_{5,6} \sim J_{5,4} \sim 7$–8 Hz, 1H, proton H_5), 3.68 (s, 3H, OCH_3), 3.63–3.29 (m, 4H, thioketal protons), 3.32–2.92 (m, 2H, protons H_2 and one of the diastereotopic protons adjacent to the $-CO_2CH_3$), 2.65 (m, 3H, protons H_4 and H_8), 2.32–1.93 (m, 2H, *exo*-proton H_3 and one of the diastereotopic protons adjacent to the $-CO_2CH_3$), 1.34–1.04 (broad d, $J_{3n,3x} \sim 12$ Hz, one half of an

AB-pattern, 1H, *endo*-proton H_n). *m/e* 350, 348 (M^+), 319, 317 (M^+-OCH_3), 269 (M^+-Br). (Found: C, 44.85; H, 4.86. Calc. for $C_{13}H_{17}BrO_2S_2$: C, 44.70; H, 4.91%). *Methyl α, α - dideuterio - 2 - (1 - bromo - 3 - endo - deuteriobicyclo[2.2.2]oct - 5 - enyl - 7 - one ethylene dithioketal)* acetate was prepared as described above using MeOD instead of MeOH. NMR ($CDCl_3$) δ6.60–6.40 (d, 1H), 6.44–6.16 (m, 1H), 3.68 (s, 3H), 3.63–3.29 (m, 4H), 3.20–3.00 (d, $J_{2,3x} \sim 9.3$ Hz, 1H, proton H_{3x}), 2.65 (m, 3H), 2.26–2.02 (d, $J_{3x,2} \sim 9.3$ Hz, 1H). *m/e* 353, 351 (M^+), 322, 320 (M^+-OCH_3), 272 (M^+-Br).

7 - *Bromo - 2 - chlorotricyclo[4.3.1.0^{3,7}]decan - 4,8 - dione* 14. Diketone 7 (0.217 g, 0.9 mmole) was added to conc HCl (19 ml). This mixture was warmed slightly until all the material was dissolved. Water was added and the solution concentrated *in vacuo* yielding a solid residue. Crystallization from CCl_4 furnished 14 (0.13 g, 56%). Recrystallization from benzene gave analytical pure sample, m.p. 169–170°; IR ν_{max}^{KBr} 1745, 1735 (C=O) cm^{-1}; NMR ($CDCl_3$) δ4.42–4.20 (m, 1H, –CHCl–), 3.52–2.92 (m, 4H), 2.80–2.14 (m, 4H), 2.02–1.68 (broad d, $J \sim 14$ Hz, 1H). *m/e* 280, 278, 276 (M^+). (Found: C, 43.32; H, 3.60. Calc. for $C_{10}H_{10}BrClO_2$: C, 43.28; H, 3.63%).

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