138. A New Synthesis of Triasteranedione[1])

by **Ian A. McDonald**[2]) and **André S. Dreiding**
Organisch-chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich
and **Hans-Martin Hutmacher** and **Hans Musso**
Institut für Organische Chemie der Universität Karlsruhe, Richard-Willstädter-Allee,
7500 Karlsruhe 1

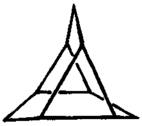
(7. III. 73)

Zusammenfassung. Bromierungen von Bicyclo[3.3.1]nonan-3,7-dion (**6**) mit vier Äquivalenten Brom oder Phenyltrimethylammonium-tribromid lieferten zwei Tetrabromide, deren Zusammensetzung (Hydrat) und IR.-Spektren (keine C=O, dafür OH-Banden) zeigten, dass neben der Bromierung noch eine Cyclisierung unter Anlagerung von Wasser an die beiden Carbonylgruppen zu einem Oxa-adamantan-System stattgefunden hatte. Die Ausbildung der eher seltenen α,α'-Dihydroxyäther-Funktion wird der kooperativen Wirkung des induktiven Effekts der vier Bromatome, der räumlichen Nähe der beiden Carbonylgruppen und der Stabilität des Adamantangerüstes zugeschrieben. Die NMR.-spektren mit den zahlreichen Fernkopplungen bestätigen, dass es sich um zwei stereomere 4,8,9,10-Tetrabrom-1,3-dihydroxy-2-oxa-adamantane handelt. Die Zahl der H—C(Br)-Signale sowie deren Fernkopplungsmuster erlauben die Ableitung der 4β,8β,9β,10α-Konfiguration für das eine Isomere (**8**), Smp. 177°, und der 4α,8α,9β,10β-Konfiguration für das andere (**9**), Smp. 180°.

Dehydrobromierung der rohen Tetrabromierungsprodukte von **6** mit Triäthylamin ergab in 80% Ausbeute ein 1:1-Gemisch von 2,6- und 2,4-Dibrom-triasteran-3,7-dion (**10** und **11**), aus dem sich nur das erstere (**10**) in reiner Form, Smp. 212°, isolieren liess. Die Lagen der Bromatome wurden aus den NMR.-Spektren abgeleitet. Als Nebenprodukt entstand auch ein wenig 2-Brom-triasteran-3,7-dion (**12**), Smp. 172°.

Die drei Brom-triasteran-3,7-dione (**10**, **11** und **12**) liessen sich mit Tri-*n*-butyl-zinnhydrid in 50% Ausbeute zu Triasterandion (**7**), Smp. 154°, reduktiv debromieren. Triasterandion (**7**) wurde auch direkt aus dem rohen Tetrabromierungsgemisch von Bicyclo[3.3.1]nonan-3,7-dion (**6**) durch Erhitzen mit Kupferpulver in 31% Ausbeute hergestellt.

Introduction. – Triasterane (**1**) and some derivatives have previously been prepared: 1. by intramolecular carbene addition in a 7-*endo*-substituted norcar-3-ene [1], 2. by intramolecular carbene insertions in the bicyclo[3.3.1]nonane- [1] and in



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the tricyclo[3.3.1.$0^{2,8}$]nonane-systems [2], 3. by the bromination of barbaralone [3] and 4. by photochemical 1,2-acyl shifts in bicyclo[3.3.1]nona-3,7-diene-2,6-diones [4]. The recently reported [5] synthesis of *anti*- and *syn*-bishomoquinone (**4** and **5**) *via* 2,4,6,8-tetrabromo-cyclooctane-1,5-dione (**3**) suggested another entry into the

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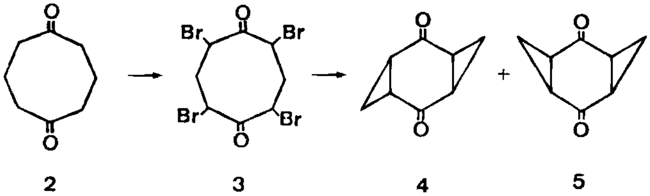
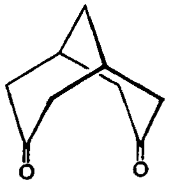
[1]) In part from the planned dissertation of *H. M. H.*, University of Karlsruhe.

[2]) Post-doctoral fellow, University of Zürich, 1972.

triasterane series by starting from bicyclo[3.3.1]nonane-3,7-dione (**6**), which is readily available [6] in large amounts from adamantane. We report here the synthesis of triasteranedione (**7**) in about 40% yield by this approach.





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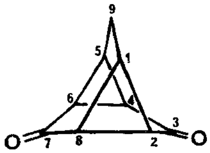

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Bromination of Bicyclo[3.3.1]nonane-3,7-dione. – The bromination of bicyclo[3.3.1]nonane-3,7-dione (**6**) with 4 equivalents of bromine in acetic acid yielded 40% of 4β,8β,9β,10α-tetrabromo-1,3-dihydroxy-2-oxa-adamantane[3]) (**8**), mp. 177°, which crystallized out of the reaction mixture after dilution with water. When, on the other hand, this bromination was performed with 4.5 equivalents of phenyl-trimethyl-ammonium tribromide in CH_2Cl_2, followed by aqueous work-up, it was necessary to chromatograph the product on silica gel to obtain 23% of 4α,8α,9β,10β-tetrabromo-1,3-dihydroxy-2-oxa-adamantane[3]) (**9**), mp. 180°, along with 10% of 2,6-dibromo-triasterane-3,7-dione (**10**) (see below). It is not known whether the difference in brominating agent or in isolation procedure caused the difference in configuration of the tetrabromide products. It is also not known whether the dehydrobromination to the diketone **10** in the second procedure had occured during the bromination, the work-up or the chromatography.

The two major products were shown to be tetrabromides of compositions $C_9H_{10}Br_4O_3$ by elemental analyses and mass spectra. Neither isomer showed a

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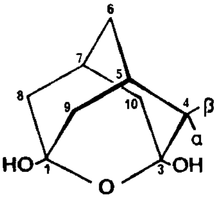
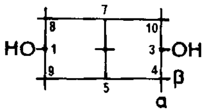
[3]) In this paper we use the positional numbering and configurational symbols in the 2-oxa-adamantane system

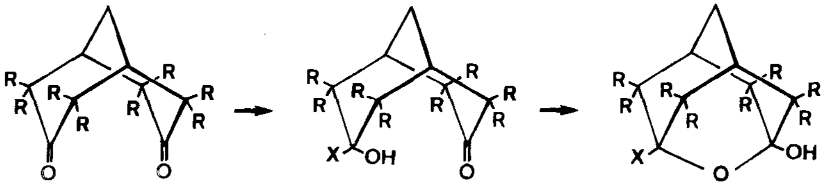


perspective formula



incomplete projection formula (oxygen bridge from C(1) to C(3) omitted) carbonyl stretching absorption in the infrared spectrum, but both had a strong hydroxyl band. By analogy with the cyclooctane-1,5-dione results [5] it was expected that each position next to the carbonyl group would be substituted by one bromine atom. This expectation was correct as can be seen in the NMR.-spectrum, where four protons in each isomer resonate at low field (δ = 4.5 to 5.1 ppm) and four at high field (δ = 2.4–3.0 ppm).

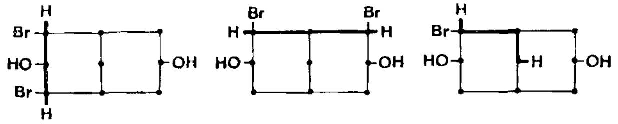
The presence of the bromine atoms in both positions adjacent to the carbonyl groups may enhance the electrophilicity of the carbonyl carbons in the intermediate tetrabromo-diketones (Ia) sufficiently to stabilize the hydrated forms (IIa), which would cyclize spontaneously to the oxa-adamantane system (IIIa). It is known [11] that the product of hydrogenation (IIb) of bicyclo[3.3.1]nonane-3,7-dione (Ib) is isolated as 1-hydroxy-2-oxa-adamantane (IIIb). The isolated tetrabromo-oxa-adamantanes (IIIa = **8** and **9**) contain a α,α'-dihydroxy-ether function, of which only few cases are known: Most of these are hemiacetals of hydrated dialdehydes (also known as hemidials) [12]. Hemiketals of hydrated aldehydo ketones or of hydrated diketones, as in the present examples, are even rarer [13].



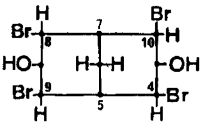
I II III

a *gem.*-R,R = H,Br; X = OH
b *gem.*-R,R = H,H; X = H

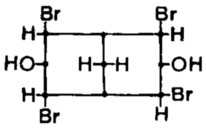
The supposition that both isomers possess an oxa-adamantane skeleton is supported by the observation of the long range couplings in the NMR.-spectra. Several clear (H–C–C–C–H)-W-conformations can be recognized in models of such a skeleton. Three are of interest in this connection: one involves two α-configurated3) H–C(Br) protons on the same cyclohexane ring, the second involves two β-configurated3) H–C(Br) protons on the same oxane ring and the third involves one α-configurated3) H–C(Br) proton and the *anti* bridge-methylene proton. They are shown schematically in the following diagrams:



The configuration of the bromine atoms in the isomer **8** has been determined from the NMR.-spectral evidence. Since all the H–C(Br) protons resonate at different frequencies and the two methylene protons are non-equivalent the bromine atoms must be arranged non-symmetrically. Thus, of the seven possible stereomers of 4,8,9,10-tetrabromo-1,3-dihydroxy-2-oxa-adamantane only the two with C_1-symmetry, namely **A** and **B** need to be considered for this isomer.

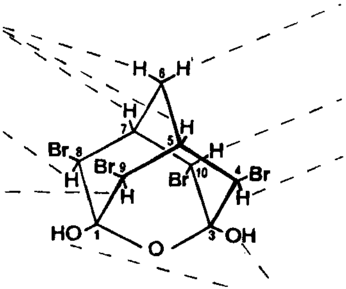


A (C_1)



B (C_1)

A decision between the two is possible on the basis of the multiplicities of the NMR.-signals due to the four H–C(Br) protons: Two of them (δ = 4.95 and 4.52 ppm) appear as triple doublets, the third (δ = 4.76 ppm) as a double doublet and the fourth (δ = 5.10 ppm) just as a single doublet, all doublets with coupling constants between 1 and 3 Hz. Considering that each H–C(Br) proton shows a vicinal coupling with H–C(5) or H–C(7), this means that two H–C(Br) protons (H–C(8) and H–C(9)) are involved in two W-couplings, one H–C(Br) proton (H–C(4)) is involved in one and the fourth (H–C(10)) in none. This fits for structure **A** but not for **B**, where three H–C(Br) protons should participate in only one W-coupling each and the fourth in none. The assignment of H–C(8) to δ = 4.95 ppm and H–C(9) to δ = 4.52 ppm is in accord with the observation that H–C(8) is *syn*-diaxial with one bromine atom (Br–C(10)) and H–C(9) with none. Spin decouplings (see experimental part) are in agreement with the coupling pattern expected for **A**. Thus structure **A** is assigned to isomer **8**. Its spectral properties are interpreted as follows:



δ = 2.66–2.96/m

δ = 4.95/$d \times d \times d$ (J = 1.2 & 1.2 & 1.7)

δ = 4.52/$d \times d \times d$ (J = 1.2 & 1.2 & 1.7)

δ = 2.44/$d \times m$ (J = 14)

δ = 5.10/d (J = 3.2)

δ = 4.76/$d \times d$ (J = 2 & 2)

IR. 3410 (broad)

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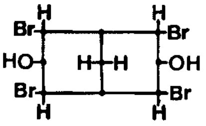
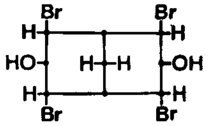
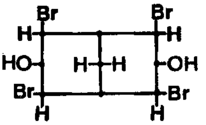
The configuration of the bromine atoms in isomer **9** can also be derived from its NMR.-spectrum: The observation of two signals for the four H–C(Br) protons (δ = 5.08 and 5.02 ppm) eliminates from consideration the stereomers of 4,8,9,10-tetrabromo-1,3-dihydroxy-2-oxa-adamantane (**A** and **B**) with symmetry C_1 (four signals expected, see above) and also those (**C** and **D**) with symmetry C_{2v} (one signal expected). This leaves three stereomers to be considered, namely the two (**E** and **F**) with symmetry C_s and the one (**G**) with symmetry C_2. Since the signal due to the bridge methylene protons (δ = 2.60 ppm) shows no geminal coupling (expected J = 14 Hz, see above) these two protons (2 × H–C(6)) must be equivalent, which excludes that C_s-stereomer (**F**) which has the plane of symmetry through the three oxygens. The second C_s-stereomer (**E**, with the plane of symmetry through C(5), C(6) and C(7)) is eliminated because its two bridgehead protons (H–C(5) and H–C(7)) should give rise to different signals, whereas only one signal (δ = 2.80 ppm) is observed



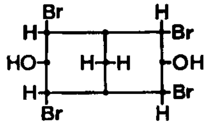
C (C_{2v})



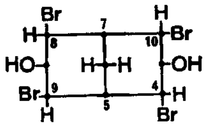
D (C_{2v})



E (C_s)

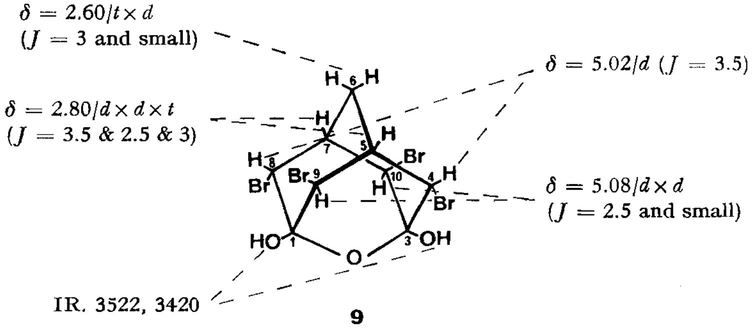


F (C_s)



G (C_2)

which can reasonably be attributed to these protons. Thus only the C_2-stereomer of 4,8,9,10-tetrabromo-1,3-dihydroxy-2-oxa-adamantane (**G**) is left for isomer **9**. In agreement with this structure is the low field absorption of all four H–C(Br) protons ($\delta = 5.08$ and 5.02 ppm, compare with isomer **8** above), each of which is *syn*-diaxial with one bromine atom. The multiplicities observed in the NMR.-signals of **9** are also in agreement with structure **G**: Two of the H–C(Br) protons (H–C(4) and H–C(8)) show only vicinal coupling and the other two (H–C(9) and H–C(10)) show both vicinal and long-range W-coupling. The spectral properties of **9** are interpreted as follows:



$\delta = 2.60/t \times d$ ($J = 3$ and small)

$\delta = 2.80/d \times d \times t$ ($J = 3.5$ & 2.5 & 3)

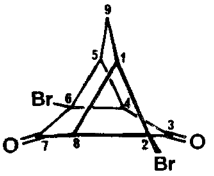
$\delta = 5.02/d$ ($J = 3.5$)

$\delta = 5.08/d \times d$ ($J = 2.5$ and small)

IR. 3522, 3420

9

Triasteranediones. – Bromination of bicyclo[3.3.1]nonane-3,7-dione (**6**) with phenyl-trimethyl-ammonium tribromide [7] in methylene chloride followed by dehydrobromination of the crude product mixture with triethylamine led to a 1:1 mixture of 2,6-dibromo-triasterane-3,7-dione (**10**) and 2,4-dibromo-triasterane-3,7-dione (**11**) in a total yield of 80%. Recrystallization permitted the purification (12%) of only one isomer, mp. 212°, to which the 2,6-dibromo-triasterane-3,7-dione (**10**) structure was assigned on the following basis:



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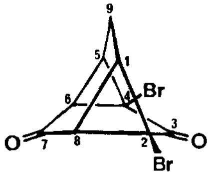

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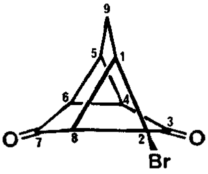
The mass spectrum with molecular peaks at *m/e* 308, 306 and 304 confirms the composition $C_9H_6Br_2O_2$, particularly the presence of two bromine atoms. In the remainder of the mass spectrum peaks are assigned to consecutive losses of Br and CO. A decision between the two reasonable reaction products (structures **10** and **11**) in favor of the 2,6-dibromo-isomer (**10**) can be made on the basis of the NMR.-spectrum: The methylene protons (2 × H–C(9)) appear as a well defined triplet ($J = 2.4$ Hz) at $\delta = 2.60$ ppm and the two cyclopropyl proton pairs (H–C(1), H–C(5) and H–C(4), H–C(8)) as an AB-quartet ($\Delta\delta \sim 0.16$ ppm and $J \sim 8$ Hz) with fine structure at $\delta = 3.00$ ppm. Thus the two methylene hydrogens and the two cyclopropyl groups are equivalent; these conditions are satisfied only when the molecule has C_2-symmetry, as in isomer **10**.

The other isomer, 2,4-dibromo-triasterane-3,7-dione (**11**), could not be obtained in pure form. It was recognized in the mixture, however, by the NMR.-signal due to H–C(9) *anti* to the bromine atoms, which appears at higher field ($\delta = 2.40$ ppm) than the signal due to both H–C(9) protons of the isomer **10** ($\delta = 2.60$ ppm).

The two dibromo-triasterane-3,7-diones (**10** and **11**) are reasonable products if it is considered that the second dehydrobromination step of the intermediate tetrabromo-bicyclo[3.3.1]nonane-3,7-dione can occur in two directions. Since the presence of other isomeric tetrabromides, aside from **9**, in the phenyl-trimethyl-ammonium tribromide bromination has not been excluded (see above), it is not impossible that this direction may be a function of the configuration of the bromine atoms.

When this sequence of bromination and dehydrobromination was repeated on a larger scale a 7% yield of a third product, $C_9H_7BrO_2$, mp. 172°, was isolated in addition to **10** and **11**. The available data suggest 2-bromo-triasterane-3,7-dione (**12**) as the probable structure. These are the peaks in the MS. at *m/e* 228 and 226, which confirm the molecular weight and the presence of just one bromine, as well as the NMR.-spectrum which shows a multiplet at $\delta = 2.3$–3.0 ppm and contains no signals inconsistent with structure **12**.



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Triasteranedione (**7**) was obtained by reductive debromination of either 2-bromo-triasterane-3,7-dione (**12**) or dibromo-triasterane-3,7-dione (**10** or a mixture of **10** and **11**). Attempts to achieve this with zinc in acetic acid, a method applied in the related bis-homoquinone work [5], were unsuccessful in as much as the removal of the two bromines was accompanied by opening of both cyclopropane rings to yield 60% bicyclo[3.3.1]nonane-3,7-dione (**6**). Under more vigorous conditions reduction of the carbonyl groups occurred. However, the treatment of either **10** or **12** with tri-*n*-butyl-tin hydride [8], in the absence of solvent, afforded triasteranedione (**7**) in yields of about 50%. For this reductive debromination it was convenient to use the crude product (containing **10, 11** and **12**) of the bromination and dehydrobromination.

The melting point and spectral data of triasteranedione (**7**) agreed with those reported in the literature [3] [4]. The NMR.-spectrum, even at 100 MHz, was not informative, all signals overlapping in the δ-range of 2.2–2.6 ppm. With Eu(fod)$_3$ [9], the signal due to the four protons adjacent to the carbonyl groups (H–C(2), H–C(4), H–C(6) and H–C(8)) was shifted downfield ($\delta = 7.23$ ppm) more than the rest of the spectrum ($\delta = 4.6$–4.3 ppm) which is due to H–C(1), H–C(5) and 2 × H–C(9). The downfield signal group ($\delta = 7.23$ ppm) was a doublet of triplets, thus showing the vicinal coupling ($J = 8.0$ Hz) of the H–C(2)/H–C(8)- and H–C(4)/H–C(6)-pairs with H–C(1) and H–C(5), respectively, as well as the long-range coupling ($J = 2.0$ Hz) of all four protons adjacent to the carbonyl groups with the two protons at C(9). These couplings disappeared on irradiation at the downfield signal ($\delta = 7.23$ ppm) and thus changed the upfield signal ($\delta = 4.6$–4.3 ppm) from a multiplet to two broadened singlets, one ($\delta = 4.57$ ppm) due to H–C(1) and H–C(5) and the other ($\delta = 4.49$ ppm) due to 2 × H–C(9).

Bromination of bicyclo[3.3.1]nonane-3,7-dione (**6**) with four equivalents of bromine in acetic acid and heating the crude product together with activated [10] copper powder at reduced pressure and 160° produced a 31% yield of triasteranedione (**7**), accompanied by 3% of 2-bromo-triasterane-3,7-dione (**12**).

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung*.

Experimental Part

General. All melting points were taken in a sealed capillary tube in a heated oil bath apparatus; the temperatures are not corrected. The IR.-spectra were measured on a *Perkin-Elmer* 21 and 421 spectrometer. They are recorded as follows: *IR.* (solvent or support): frequency in cm^{-1}, intensity as w = weak, m = medium and s = strong. The MS.-spectra were measured on a *CEC* 21-110B or an *Atlas* CH-5 instrument. They are recorded as follows: *MS.* (energy in eV): molecular ions and/or fragment ions in *m/e* (intensities relative to base peak in %). With the exception of the molecular, the bromine isotope and the loss of water peaks, only the peaks above *m/e* = 90 and above 5% are recorded. The *H^1-NMR.*-spectra were measured with an *HA*-100 instrument. They are recorded as follows: NMR. (frequency and solvent): chemical shifts in ppm on the δ-scale (TMS internal = 0)/multiplicity with *s* = singlet, *d* = doublet, *t* = triplet, AB = AB-quartet and *m* = multiplet (splitting *J* in Hz), relative integration in pr units (interpretation). We thank Dr. *U. I. Zahorszky* (Karlsruhe) and the MS.-laboratory (Zürich, direction Prof. *M. Hesse*) for the mass-spectra, the microlaboratory (Zürich, direction *H. Frohofer*) for the elemental analyses and the IR.-spectra, and Mr. *M. Karpf* as well as the NMR.-laboratory (Zürich, direction Prof. *W. v. Philipsborn*) for the NMR.-spectra.

Bicyclo[3.3.1]nonane-3,7-dione (**6**). Bicyclo[3.3.1]nonane-3,7-dione (**6**), m.p. 252–253°, was prepared from 7-methylene-bicyclo[3.3.1]nonan-3-one by the method of *Stetter & Tacke* [6a]. The 7-methylene-bicyclo[3.3.1]nonan-3-one was obtained from the hydrolysis of 1,3-dibromo- or 1,3-dichloro-adamantane using the method of *Gagneux & Meier* [6b]; 1,3-dibromo-adamantane was prepared from adamantane according to the procedure given by *Talaty, Cancienne & Dupuy* [6c] and 1,3-dichloro-adamantane was synthesized following the method of *Hamill et al.* [6d].

4β,8β,9β,10α-Tetrabromo-1,3-dihydroxy-2-oxa-adamantane (**8**). To a stirred solution of 0.60 g (3.95 mmol) bicyclo[3.3.1]nonane-3,7-dione (**6**) in 20 ml glacial acetic acid was added a solution of 2.56 g (16 mmol) Br_2 in 10 ml glacial acetic acid over about 30 min. After another hour of stirring, 200 ml water was added, the solution was concentrated under reduced pressure to 200 ml and allowed to stand for 12 h. Colorless needles of *4β,8β,9β,10α-tetrabrono-1,3-dihydroxy-2-oxa-adamantane* (**8**) precipitated slowly, were filtered and dried under high vacuum, yield 0.73 g (40%), m.p. 176–177°. *IR.* (KBr): 3410 s (broad), 2965 w, 1710 w (broad), 1623 w (broad). *MS.* (70 eV): 490 (0.2), 488 (0.7), 486 (1), 484 (0.7), 482 (0.2), 472 (0.2), 470 (0.7), 468 (1), 466 (0.7), 464 (0.2), 408 (8), 407 (5), 406 (25), 405 (5), 404 (24), 402 (8), 327 (6), 326 (10), 325 (12), 324 (17), 323 (6), 322 (8), 309 (7), 308 (12), 307 (11), 306 (19), 305 (5), 304 (8), 299 (5), 297 (10), 295 (6), 267 (5), 246 (8), 245 (42), 244 (16), 243 (42), 242 (8), 229 (15), 228 (19), 227 (63), 226 (19), 225 (50), 217 (23), 216 (5), 215 (27), 213 (5), 203 (7), 201 (8), 200 (13), 171 (22), 169 (20), 164 (23), 163 (29), 159 (27), 147 (40), 146 (32), 135 (48), 121 (20), 119 (74), 118 (43), 107 (58), 95 (37), 94 (22), 91 (100), 90 (52). *NMR.* (100 MHz, d_6-acetone): $\delta = 5.10/d$ ($J = 3.2$), 1 pr (H—C(10)); $4.95/d \times d \times d$ ($J = 1.2$ & 1.2 & 1.7), 1 pr (H—C(8)); $4.76/d \times d$ ($J = 2$ & 2), 1 pr (H—C(4)); $4.52/d \times d \times d$ ($J = 1.2$ & 1.2 & 1.7), 1 pr (H—C(9)); 2.66 to $2.96/m$, 3 pr (H—C(5), H—C(6), H—C(7)); $2.44/d \times m$ ($J = 14$), 1 pr (H—C(6)). Spin-decoupling experiments: Irradiation at $\delta = 2.78$ ppm (H—C(5), H—C(6), H—C(7)) simplified the spectrum between $\delta = 4.50$ and 5.20 ppm to give: $\delta = 5.10/s$ (H—C(10)); $4.95/d \times d$ ($J = 1.2$ & 1.2), (H—C(8)); $4.76/s$ (H—C(4)); $4.52/d \times d$ ($J = 1.2$ & 1.2), (H—C(9)). Irradiation at $\delta = 4.52$ ppm (H—C(9)) converted the signal at $\delta = 4.95$ ppm (H—C(8)) to $d \times d$ ($J = 1.2$ & 1.7). Double irradiation at $\delta = 4.52$ (H—C(9)) and 2.78 ppm (H—C(5), H—C(6), H—C(7)) further simplified the signal at $\delta = 4.95$ ppm (H—C(8)) to d ($J = 1.2$).

$C_9H_{10}Br_4O_3$ (485.793) Calc. C 22.25 H 2.08 Br 65.79% Found C 22,38 H 2.29 Br 65.60%

The possibility that the mother liquor may contain other isomers of **8** cannot be excluded.

4α,8α,9β,10β-Tetrabromo-1,3-dihydroxy-2-oxa-adamantane (**9**). To a stirred slurry of 11.15 g (29.6 mmol) phenyl-trimethyl-ammonium tribromide in 50 ml CH_2Cl_2 was added, all at once, 1.00 g (6.60 mmol) bicyclo[3.3.1]nonane-3,7-dione (**6**). Stirring was continued for 44 h., 20 ml water was added and the solution was decolorized by shaking with an aliquot of aq. $NaHSO_3$. The CH_2Cl_2 layer was separated, washed with water, dried and evaporated to yield a partially crystalline residue, which was triturated with cold $CHCl_3$. The insoluble material consisted of 1.59 g of colorless needles and the soluble material was 1.36 g of an orange oil.

The solid fraction was dissolved in hot benzene and added to a column of 100 g silica gel packed in benzene. Elution with benzene/$CHCl_3$ 1:1 yielded 0.19 g (10%) of a colorless crystalline product which was recrystallized from benzene/petroleum ether to give colorless needles of 2,6-dibromo-triasterane-3,7-dione (**10**), m.p. 211.5–212.5°, identical with a sample to be described in the next experiment. Further elution with $CHCl_3$ yielded 0.80 g of a partially crystalline product, which was recrystallized from benzene to afford 0.31 g (10%) of *4α,8α,9β,10β-tetrabromo-1,3-dihydroxy-2-oxa-adamantane* (**9**) as colorless plates, m.p. 179–180°. When the m.p. was determined in admixture with the isomer **8** (m.p. 176–177°), a depression was noted to m.p. 168–169°. *IR.* (KBr): 3522 m, 3420 s, 2996 w, 2980 w, 2940 w. *MS.* (70 eV): 490 (4), 488 (17), 486 (26), 484 (18), 482 (5), 472 (0.3), 470 (1), 468 (2), 466 (1), 464 (0.2), 409 (32), 408 (19), 407 (100), 406 (38), 405 (100), 404 (31), 403 (34), 402 (9), 389 (14), 387 (14), 351 (8), 349 (23), 347 (24), 345 (8), 327 (20), 325 (40), 323 (21), 315 (21), 313 (47), 311 (26), 307 (12), 297 (10), 279 (10), 269 (22), 267 (39), 265 (23), 253 (8), 251 (7), 245 (40), 244 (8), 243 (40), 227 (19), 225 (16), 218 (7), 217 (19), 216 (13), 215 (26), 214 (7), 213 (11), 207 (8), 205 (14), 203 (8), 201 (12), 200 (8), 199 (19), 198 (7), 197 (11), 193 (12), 191 (30), 189 (33), 188 (15), 187 (67), 186 (15), 185 (55), 121 (63), 119 (69), 107 (93), 91 (88). *NMR.* (100 MHz, d_6-acetone): $\delta = 5.08/d \times d$ ($J = 2.5$ and small), 2 pr (H—C(9), H—C(10)); $5.02/d$ ($J = 3.5$), 2 pr (H—C(4), H—C(8)); $2.80/d \times d \times t$ ($J = 3.5$ & 2.5 & 3), 2 pr (H—C(5), H—C(7)); $2.60/t \times d$ ($J = 3$ and small), 2 pr (2 × H—C(6)).

$C_9H_{10}Br_4O_3$ (485.792) Calc. C 22.25 H 2.08 Br 65.79% Found C 22.55 H 2.28 Br 64.69%

Chromatography on silica gel of the $CHCl_3$ soluble material yielded further amounts of the two products, namely 0.02 g (1%) 2,6-dibromo-triasterane-3,7-dione (**10**), m.p. *210–212°*, and 0.40 g (13%) of 4α,8α,9β,10β-tetrabromo-1,3-dihydroxy-2-oxa-adamantane (**9**) whose NMR.- and IR.-spectra were identical with those of a pure sample of **9**. The total yield of **9** was 0.71 g (23%).

It is not impossible that **10** was formed during chromatography and that the mother liquors contain other isomers of **9**.

Bromination of bicyclo[3.3.1]nonane-3,7-dione (**6**) *with 4.5 equivalents of phenyl-trimethyl-ammonium tribromide and subsequent dehydrobromination with triethylamine.* To a stirred slurry of 5.57 g (14.8 mmol) phenyl-trimethyl-ammonium tribromide in 25 ml CH_2Cl_2 was added, all at once, 0.50 g (3.30 mmol) bicyclo[3.3.1]nonane-3,7-dione (**6**). Stirring was continued for 1 h., then 25 ml water was added and the two phases were shaken and discolored with an aliquot of aq. $NaHSO_3$. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with more CH_2Cl_2. The combined CH_2Cl_2 solutions were washed with water, dried and evaporated to yield 1.41 g of a colorless oil. This was dissolved in 25 ml tetrahydrofuran and the solution was stirred while 3.30 g (33 mmol) $(C_2H_5)_3N$ in 10 ml tetrahydrofuran was added over a period of 5 min. After stirring for 1 h., the mixture was evaporated under reduced pressure, CH_2Cl_2 was added and the suspension was washed with water, dried and evaporated to afford 0.87 g of a pale orange, partially solid substance.

This material was dissolved in $CHCl_3$ and passed through a column of neutral aluminium oxide (10 g) yielding after evaporation 0.80 g (80%) of an almost colorless solid residue, m.p. 140–171°, which consists of a 1:1 mixture of *2,6-dibromo-triasterane-3,7-dione* (**10**) and *2,4-dibromo-triasterane-3,7-dione* (**11**). *NMR.* (100 MHz, $CDCl_3$): δ = 2.66 to 3.17/*m*; 2.60/*t* (J = 2.2) (2 × H—C(9) of isomer **10**); 2.40/*d* × *m* (J = 14) (H—C(9) *anti* to the two bromine atoms in isomer **11**). The last two signals appeared in an intensity ratio of about 2:1. This gives the above indicated proportion of the two isomers since the first signal is due to two protons and the second due to one. *MS.* (70 eV): Practically identical to that of the pure 2,6-dibromo-triasterane-3,7-dione (**10**), described below.

Fractional recrystallization from benzene/petroleum ether enabled the separation of 0.12 g (12%) *2,6-dibromo-triasteran-3,7-dione* (**10**), m.p. 211.5–212°. *IR.* ($CHCl_3$): 3010 w, 1705 s. *IR.* (KBr): 3070 w, 2930 w, 1705 s. *MS.* (70 eV): 308 (14), 306 (33), 304 (14), 227 (93), 225 (98), 199 (21), 197 (21), 171 (23), 169 (25), 146 (53), 118 (70), 90 (100). *NMR.* (100 MHz, $CDCl_3$): δ = 3.08 and 2.92/AB × *m* (J = 8.0), 4 pr ((H—C(1), H—C(4) and H—C(5), H—C(8)); 2.60/*t* (J = 2.4), 2 pr (2 × H—C(9)).

$C_9H_6Br_2O_2$ (305.953) Calc. C 35.33 H 1.98 Br 52.23% Found C 35.62 H 2.25 Br 51.85%

From the material in the mother liquors of the above fractional crystallization it was not possible to purify the second isomer **11**.

When the above bromination and dehydrobromination was carried out on 3.00 g of **6** a 7% yield of *2-bromo-triasterane-3,7-dione* (**12**) was isolated by chromatography in addition to the above mentioned two products. Recrystallization from benzene/petroleum ether furnished colorless needles of **12**, m.p. 171–172°. *IR.* ($CHCl_3$): 3010 w, 2930 w, 2870 w, 1695 s. *MS.* (70 eV): 228 (20), 226 (20), 200 (17), 198 (17), 147 (29), 119 (74), 91 (100). *NMR.* (100 MHz, $CDCl_3$): δ = 2.98–2.30/*m*, with maxima at 2.84, 2.70 and 2.50 ppm.

$C_9H_7BrO_2$ (227.057) Calc. C 47.61 H 3.11 Br 35.19% Found C 47.89 H 3.35 Br 35.12%

Triasteranedione (**7**). 1.00 g (3.29 mmol) 2,6-Dibromo-triasterane-3,7-dione (**10**) was mixed with 1.90 g (6.58 mmol) tri-*n*-butyl-tin hydride neat at room temperature and under nitrogen. The solid material dissolved as the mixture was warmed to 60°. This temperature was maintained for 24 h. then more tri-*n*-butyl-tin hydride (1.90 g) was added and the heating was continued for another 24 h. The entire reaction mixture was dissolved in benzene and the solution applied to a column of 30 g silica gel packed in benzene. The column was eluted with benzene and then with $CHCl_3$. The $CHCl_3$ eluant fraction yielded 0.52 g of a colorless crystalline product, m.p. 110–136°. Recrystallization from benzene/petroleum ether afforded 0.25 g (52%) of *triasteranedione* (**7**) as colorless needles, m.p. 153.5–154.5° (Lit. [3] m.p. 155°, [4] m.p. 153–155°). *IR.* ($CHCl_3$): 3000 w, 2925 w, 2870 w, 1685 s. *MS.* (70 eV): 148 (54), 120 (46), 92 (33), 91 (100). *NMR.* (100 MHz, $CDCl_3$): δ = 2.44/*s* (slightly broadened) which partially overlaps with 2.38/*s*, both sitting on top of 2.60–2.18/*m*.

The following results were obtained when the 100 MHz NMR.-measurement was made in the presence of $Eu(fod)_3$. Two signal groups with relative intensities of 1:1 became separated as follows: The low field signal (shifted to δ = 7.23 ppm) was a doublet of triplets (J = 8.2 & 2.0) and is assigned to H—C(2), H—C(4), H—C(6) and H—C(8). The high field signal group (shifted to 4.6–4.3 ppm) consisted of two overlapping structured multiplets, which on irradiation at $\delta = 7.23$ ppm simplified to two broadened singlets at $\delta = 4.57$ ppm (H—C(1), H—C(5)) and $\delta = 4.49$ ppm (2× H—C(9)).

$C_9H_8O_2$ (148.161) Calc. C 72.96 H 5.44% Found C 73.18 H 5.43%

This reductive debromination could also be performed on a mixture of **10**, **11** and **12** with the same result. When the reduction was attempted in benzene solution at 80° only starting material was recovered.

Triasteranedione (**7**) *from 2-bromo-triasterane-3,7-dione* (**12**). 0.06 g (0.26 mmol) 2-Bromo-triasterane-3,7-dione (**12**) was treated with two portions of 0.10 g (0.34 mmol) tri-*n*-butyl-tin hydride under the conditions described in the preceding experiment. The purification was achieved by preparative thin layer chromatography and the product recrystallized from benzene/petroleum ether to yield 0.02 g (51%) *triasteranedione* (**7**) as colorless needles, m.p. 153–154.5°.

Debromination of 2,6-dibromo-triasterane-3,7-dione (**10**) *with zinc in acetic acid.* To a stirred solution of 0.10 g 2,6-dibromo-triasterane-3,7-dione (**10**) in 10 ml acetic acid was added at room temperature 0.50 g zinc dust. Stirring was continued for 2 h., the zinc was removed and the solvent was evaporated under reduced pressure. Preparative thin layer chromatography on silica gel with ethyl acetate as eluant, enabled the separation of 0.03 g (60%) bicyclo[3.3.1]nonane-3,7-dione (**6**). Recrystallization from benzene/petroleum ether afforded colorless needles, m.p., alone and on admixture with authentic bicyclo[3.3.1]nonane-3,7-dione (**6**), 252–253°. Treatment of 41 mg **10** with 2.1 g zinc in 2 ml acetic acid and for 30 min. at 100° yielded 5 mg of a colorless product. *IR.* (KBr): 3350 s; no band in the C=O region. *MS.* (70 eV): 154.

Bromination of bicyclo[3.3.1]nonane-3,7-dione (**6**) *with 4 equivalents of bromine and subsequent debromination with copper.* To a stirred solution of 0.61 g (4 mmol) bicyclo[3.3.1]nonane-3,7-dione (**6**) in 20 ml acetic acid was added dropwise at room temperature under nitrogen a solution of 2.56 g (16 mmol) of bromine in 10 ml acetic acid for about 30 min. The solution decolorized rapidly until almost all the bromine was added. After the addition of half of the bromine, a solid started to deposit from the solution. The mixture was stirred for 1 h. after completion of the bromine addition; then the solid was filtered, yield 1.69 g, m.p. 160–186°.

An intimate mixture of a 0.41 g portion of this crude solid with 5.3 g activated [10] copper powder was heated in a sublimation apparatus first under nitrogen and then under reduced pressure at 160°. The *triasteranedione* (**7**) sublimed on to the cold finger and was recrystallized from tetrahydrofuran by the addition of pentane, yield 40 mg (29%), m.p. 153.5–154.5°. The NMR.- and MS.-spectra were the same as those of the sample of **7** described above.

When the residue of this sublimation was heated further for several hours at 10 Torr, *2-bromo-triasterane-3,7-dione* (**12**) was deposited on the cold finger; the yield after recrystallization from tetrahydrofuran/pentane was 6 mg (3%), m.p. 170–173°.

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139. Etude des mécanismes de réarrangement dans la fragmentation des benzoyloxy-cyclopentènes par impact électronique

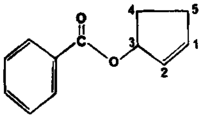
par **Gérard A. Singy** et **Armand Buchs**

Laboratoire de spectrométrie de masse, Département de chimie physique,
Université de Genève, 1211 Genève 4

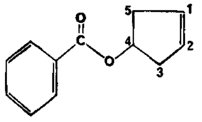
(27. II. 73)

Summary. The fragmentation modes of 3-benzoyloxy-cyclopentene and of 4-benzoyloxy-cyclopentene have been studied on deuterium-labelled analogues. A mathematical model is proposed for the study of the rearrangement reactions which occur during the expulsion of H_2O and of $CO_2H^{\cdot}$ from the molecular ion of 3-benzoyloxy-cyclopentene.

Le présent mémoire décrit une étude comparative de la fragmentation du benzoyloxy-3-cyclopentène (I) et de son isomère homoallylique II qui présentent des spectres de masse très différents. Une méthode de calcul basée sur une optimalisation quadratique des résultats a été utilisée pour déterminer les origines des atomes

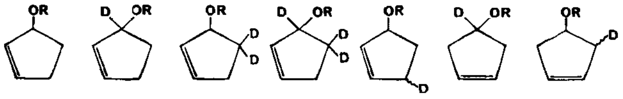


I



II

Tableau 1. *Composés marqués synthétisés*



R = R¹		III	IV	V	VI	XIV	XV
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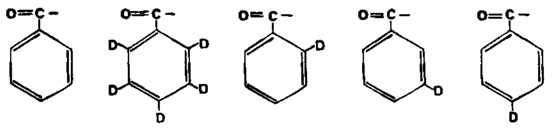
R = R³	XI						
R = R⁴	XII						
R = R⁵	XIII						



R¹ R² R³ R⁴ R⁵