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59. Substituted 9-Oxabicyclo[4.2.1]- and 9-Oxabicyclo[3.3.1]nonanes (Part II[1])

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(13. I. 71)

Summary. The preparation, isolation, structure determination, and some reactions of the two stereoisomers of 2-iodo-9-oxabicyclo[4.2.1]nonane (**9** and **10**) and of 2-iodo-9-oxabicyclo[3.3.1]-nonane (**11** and **12**), respectively, are described.

Iodine cleavage of the [4.2.1]-iodomercuri compound **3** yielded the iodides **9**, **10**, and **11**, and iododemercuration of the [3.3.1]-iodomercuri compound **6** afforded the iodo compounds **9**, **11**, and **12**, respectively. Direct treatment of 4-cycloocten-1-ol (**1**) with iodine in chloroform resulted in the exclusive formation of the two *endo*-iodides **9** and **11**.

Raney nickel treatment as well as lithium aluminium hydride reduction of each individual iodo compound **9**, **10**, **11**, and **12** gave the corresponding unsubstituted 9-oxabicyclononane (**4** or **8**, respectively) with the unaltered skeleton. No rearrangement products could be observed.

[1] For Part I see [1].

An oxonium ion is involved as an intermediate in the reaction of the *endo*-iodides **9** and **11** with silver acetate leading to an identical mixture of the two acetates **15** and **16** as well as in the isomerization of **9** to **11**.

Very recently *Paquette & Storm* [2] published results on 'Stereochemical Aspects of R_2O-3 Participation. Lithium Aluminium Hydride Reduction of 9-Oxabicyclononan-2-yl Iodides'[2]. Their paper prompts us to describe our own results[3] on the preparation, isolation, structure determination, and some reactions of the two stereoisomers of 2-iodo-9-oxabicyclo[4.2.1]nonane (**9** and **10**) and of 2-iodo-9-oxabicyclo[3.3.1]nonane (**11** and **12**), respectively. Several of our observations differ quite markedly from those reported by *Paquette & Storm* [2].

1. Syntheses of the Iodo Compounds 9, 10, 11, and 12 (Results and Discussion). – The four isomeric iodo compounds **9**, **10**, **11**, and **12** were all prepared using 4-cyclooctene-1-ol (**1**) as starting material. Two different pathways were applied for their syntheses: a) Oxymercuration of the alcohol **1** followed by treatment with potassium iodide and subsequent reaction of the iodomercuri compounds **3** or **6**, respectively with iodine. b) Direct treatment of the alcohol **1** with iodine. Depending on the reaction conditions [a) or b)] the isomeric iodides **9–12** are readily obtained in varying amounts (see Table 1). The iodo compounds **9–12** were separated with only very minor decomposition by column chromatography as described in the Experimental Section.

Oxymercuration of 4-cycloocten-1-ol (**1**) with mercuric acetate in the presence of sodium acetate, following the procedure of *Bordwell & Douglass* [3], yielded after several recrystallizations pure *endo*-2-acetoxymercuri-9-oxabicyclo[4.2.1]nonane (**2**). The corresponding [3.3.1]-acetoxymercuri compound **7** could be found in minor amounts in the mother liquor. Sodium borohydride reduction[4] of **2** gave pure 9-oxabicyclo[4.2.1]nonane (**4**) [5]. The acetoxymercuri compound **2** was easily converted into the corresponding iodomercuri compound **3** according to *Bordwell & Douglass* [3]. That no skeletal rearrangement occurred during this reaction was checked by retransforming **3** into **2** with silver acetate and subsequent reductive demercuration of **2** by sodium borohydride which again afforded pure 9-oxabicyclo-[4.2.1]nonane (**4**). Reaction of the iodomercuri compound **3** with iodine was carried out in carbon tetrachloride under argon at 0° with a 500 W visible light source (Table 1, experiment 2) as well as at room temperature and daylight (Table 1, experiment 3)[5]. In both cases three of the four possible isomeric 2-iodo-9-oxabicyclo-[4.2.1]nonanes and 2-iodo-9-oxabicyclo[3.3.1]nonanes were formed, namely the two [4.2.1]-isomers **9** and **10** as well as the *endo*-[3.3.1]-iodide **11**. The main product was always the *exo*-[4.2.1]-isomer **10** and no *exo*-[3.3.1]-iodide **12** could be detected.

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[2] We should like to thank Professor *L. A. Paquette* for making available a preprint of his paper [2] (September 11, 1970). The essential results of our report had already been obtained in our laboratory at that time.

[3] Part of the experiments described in the present paper were first carried out in our group by *C. Firmenich* (winter 1968/69) and *H. J. Borschberg* (summer 1969).

[4] For a recent paper on the mechanism of reduction of alkylmercuric halides by metal hydrides see [4].

[5] This experiment was carried out analogously to a procedure described by *Paquette & Storm* [2]. However, these authors did not separate the product mixture.

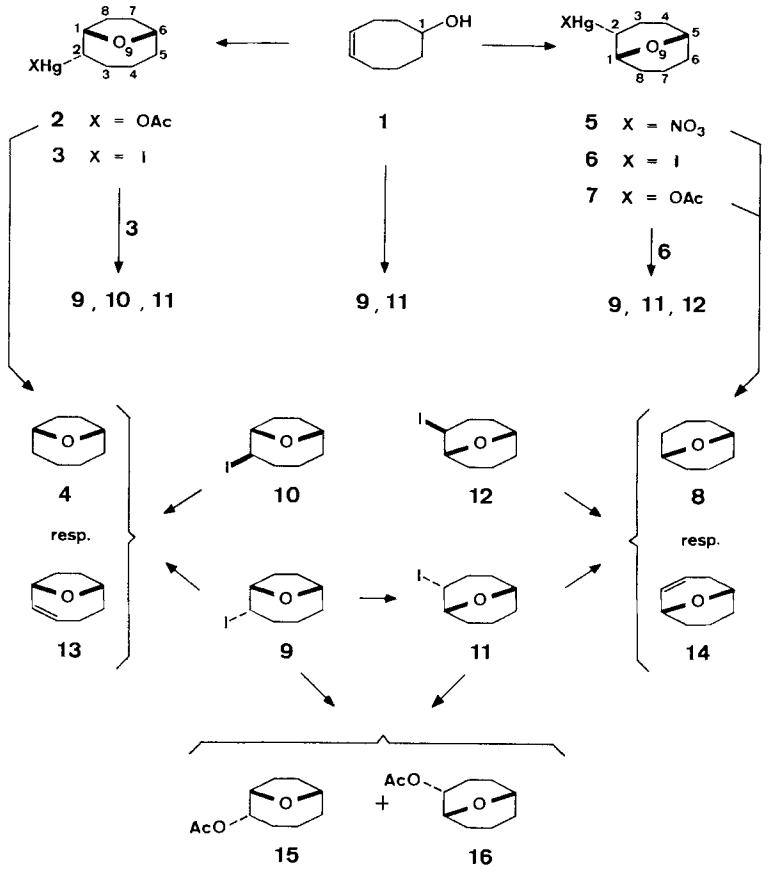


Table 1. *Preparation of the Iodo Compounds* **9**, **10**, **11**, *and* **12**

Experiment	Starting material	Reaction conditions					Product distribution in %[a]			
							9	**10**	**11**	**12**
1	949 mg of **1**	I_2, $CHCl_3$	room temp.	3 or 7 h	daylight	air	25	–	75	–
2	3.015 g of **3**	I_2, CCl_4	0°	6 h	500 watt lamp[b]	argon	30.5	64.5	5	–
3[c]	1.187 g of **3**	I_2, CCl_4	room temp.	8 h	daylight	N_2	33	49.5	17.5	–
4	724 mg of **6**	I_2, KI, H_2O	room temp.	7 h	darkness	air	24	–	20	56
5	755 mg of **6**	I_2, CCl_4	0°	$2^1/_2$ h	500 watt lamp[b]	argon	4	–	17	79
6[c]	4.5 g of **6**	I_2, CCl_4	room temp.	8 h	daylight	N_2	17	–	21	62

[a] Estimated values on the basis of column chromatographic separation and NMR. analysis of mixtures (see Experimental Section).
[b] Visible light source.
[c] See footnote [5]).

On the other hand oxymercuration of 4-cycloocten-1-ol (**1**) with mercuric nitrate in the presence of potassium nitrate following the procedure of *Bordwell & Douglass* [3] yielded after one recrystallization pure *endo*-2-nitratomercuri-9-oxabicyclo[3.3.1]-nonane (**5**). The corresponding [4.2.1]-isomer was not found in any appreciable

amount. Sodium borohydride reduction of **5** gave pure 9-oxabicyclo[3.3.1]nonane (**8**) [6]. The nitratomercuri compound **5** was easily converted into the corresponding iodomercuri compound **6** by treatment with potassium iodide in aqueous sodium hydroxide solution in analogy to a procedure by *Bordwell & Douglass* [3] for the preparation of the [4.2.1]-iodomercuri compound **3**. The iodomercuri compound **6** was then treated with silver acetate in chloroform as well as in hexamethylphosphoric-triamid (hexametapol, HMPT) affording *endo*-2-acetoxymercuri-9-oxabicyclo[3.3.1]-nonane (**7**). Subsequent reductive demercuration of **7** by sodium borohydride yielded again pure 9-oxabicyclo[3.3.1]nonane (**8**) demonstrating that the mercuri compounds **5**, **6**, and **7** were indeed pure [3.3.1]-isomers.

Iodine cleavage of the iodomercuri compound **6** was carried out under three conditions: a) In water in the presence of potassium iodide and air, in the dark at room temperature (Table 1, experiment 4), b) In carbon tetrachloride under argon at 0° and with a 500 W visible light source (Table 1, experiment 5), and c) In carbon tetrachloride under nitrogen at room temperature in daylight (Table 1, experiment 6)[5]). Each time again three of the four possible isomeric 2-iodo-9-oxabicyclo[4.2.1]- and 2-iodo-9-oxabicyclo[3.3.1]nonanes were formed, namely the *endo*-[4.2.1]-isomer **9** and the two [3.3.1]-isomers **11** and **12**. The *exo*-[3.3.1]-iodide **12** was always the main product and no *exo*-[4.2.1]-iodide **10** could be detected.

The above results show various remarkable features. Neither the iodine cleavage of the [4.2.1]-iodomercuri compound **3** nor the one of the [3.3.1]-iodomercuri compound **6** led to a statistical distribution of *endo*- and *exo*-iodides (**9** and **10** or **11** and **12**, respectively) even not under conditions which highly favor a free radical cleavage (carbon tetrachloride, inert atmosphere, 0°, light)[6])[7]). The corresponding *exo*-iodide with the same 9-oxabicyclononane skeleton (**10** or **12**, respectively) was always the predominant isomer formed. As the iodomercuri compounds **3** and **6** were pure *endo*-isomers the iodine cleavage proceeded therefore preferentially with inversion at C-2.

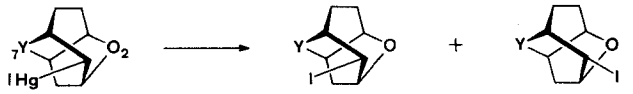
The stereochemistry of the oxymercuration products **2** and **5** was not determined by *Bordwell & Douglass* [3], but *endo* configurations of the substituents were assigned on the basis of the usual

[6]) For recent studies on iododemercurations see [7].

[7]) Likewise no statistical distribution for the six isomeric diiodo compounds (**c** and **d**) was observed in the iodine cleavage of 2,5-diiodomercuri-9-oxabicyclo[4.2.1]nonane (**a**) and 2,6-diiodomercuri-9-oxabicyclo[3.3.1]nonane (**b**) as well as in the iodine cleavage of the iodomercuri compounds of 2,7-dihetero-isotwistanes (**e**→**f** and **g**). See [1] [8] [9] and unpublished results by *C. Ganter, K. Wicker, N. Wigger* and *W. Zwahlen*.

a R = HgI **b** R = HgI

c R = I **d** R = I



e **f** **g**

Y = O, S

trans addition mechanism. Strong support for this stereochemical assignment is obtained by the known isomerization in neutral or slightly acidic media, *e.g.*, of the [4.2.1]-acetoxymercuri compound **2** into the [3.3.1]-isomer **7** (see [3]) and by IR. and NMR. data. The [3.3.1]-nitratomercuri compound **5**, the [3.3.1]-iodomercuri compound **6** and the [3.3.1]-acetoxymercuri compound **7** all exhibit in their IR. spectra, among others, absorption bands near 2980 and 1480 cm^{-1}. Such 'anomalous' C—H stretching and bending bands are characteristic for a bicyclo[3.3.1]nonane skeleton and for the presence of such compounds in a chair-chair conformation[8]). Taking in account that these compounds **5**, **6**, and **7** are in a chair-chair conformation their NMR. spectra (see Experimental Section) are in agreement only with *endo* orientations of the substituents at C-2. Furthermore, *endo*-2-substituted [3.3.1]-derivatives show a characteristic strong absorption band in the IR. spectra at about 980 cm^{-1} which is present in all of these compounds [**5** ($CHCl_3$): 977; **6** ($CHCl_3$): 976, (KBr): 970; and **7** (CCl_4): 978 cm^{-1}. For comparison see also **11** (liq.): 981 and *endo*-2-chloromercuri-9-oxabicyclo[3.3.1]nonane ($CHCl_3$): 980 cm^{-1} [3]].

Analogously, the *endo*-2-substituted [4.2.1]-derivatives exhibit three characteristic, strong absorption bands which are representative for the structural and configurational assignments [**2** (CCl_4): 1052, 932, 913; **3** (KBr): 1038, 922, 905; **9** (liq.): 1052, 938, 906].

A further important conclusion can be drawn from the above results: The iodomercuri compounds **3** and **6** were both isomerically pure (see also the results of the sodium borohydride reductions of **3** and **6**) and no isomerization of **3** and **6** occurred during the iodine cleavage step. This conclusion is based on the fact that starting from the [4.2.1]-iodomercuri compound **3** no *exo*-[3.3.1]-iodide **12**, and starting from the [3.3.1]-iodomercuri compound **6** no *exo*-[4.2.1]-iodide **10** was formed. As discussed before the main product from one individual iodomercuri compound is always the *exo*-iodide bearing the same 9-oxabicyclononane skeleton: **3** → **10** and **6** → **12**. Even partial isomerization of **3** or **6** during the iodine cleavage step could have been easily detected in the reaction mixture.

It remains to comment on two analogous observations that starting from the [4.2.1]-iodomercuri compound **3** not only the two [4.2.1]-iodides **9** and **10** were formed but also the *endo*-[3.3.1]-isomer **11**, and that starting from the [3.3.1]-iodomercuri compound **6** not only the two [3.3.1]-iodides **11** and **12** were formed but also the *endo*-[4.2.1]-isomer **9**. As seen above an isomerization of the iodomercuri compound **3** to **6** or *vice versa* can be excluded. Therefore the question arises if the *endo*-iodides **9** and **11** themselves isomerize under the reaction conditions applied. However, this seems very unlikely. As one can see from the very different amounts of **9** and **11** present in the reaction mixtures (see Table 1), **9** and **11** would at best be in a very slow equilibrium.

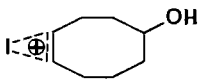
Furthermore, the results in Table 1 show a significant feature. Starting from one iodomercuri isomer (**3** or **6**) the amounts of the following products remained nearly constant under all experimental conditions: the *endo*-iodide with the unaltered skeleton (**3** → ca. 30.5–33% of **9**; **6** → ca. 17–21% of **11**) as well as the sum of the *exo*-iodide with the unaltered skeleton and the *endo*-iodide with the rearranged skeleton (**3** → ca. 66–69.5% of **10** and **11**; **6** → ca. 79–83% of **9** and **12**). The variable product portion consisted of the sum of the two *endo*-iodides **9** and **11** (**3** → ca. 35.5–50.5%; **6** → ca. 21–44%).

All these results imply that a more complex mechanism, or different mechanisms, than mere isomerization of **9** to **11** and *vice versa* are responsible for the product distributions in the iodine cleavages of the iodomercuri compounds **3** and **6**. The

[8]) See *Brown et al.* [10] and footnote [3]) in [11].

product distributions most likely depend on various factors such as, *e.g.*, solvent, temperature, light source, atmosphere etc.[9]).

A second approach for the synthesis of isomeric 2-iodo-9-oxabicyclononanes was direct treatment of 4-cycloocten-1-ol (**1**) with iodine in chloroform. In 86% yield a mixture of the two *endo*-isomers, the *endo*-[4.2.1]-iodide **9** and the *endo*-[3.3.1]-iodide **11**, was obtained in a ratio of approximately 1:3 (Table 1, experiment 1)[10]). This ratio was confirmed by treatment of the reaction mixture with *Raney* nickel which afforded a 1:3 mixture of unsubstituted 9-oxabicyclo[4.2.1]- (**4**) and 9-oxabicyclo[3.3.1]nonane (**8**). The exclusive formation of *endo*-iodides can best be explained by an intramolecular attack of the free hydroxyl group on a primarily established iodonium ion of type **h** yielding as a consequence of the stereochemical course of such a reaction the *trans* addition products **9** and **11**[11]).



h

2. Structure Determination and Reactions of the Iodo Compounds 9, 10, 11, and 12 (Results and Discussion). – The iodides **11** and **12** exhibit in their IR. spectra, among others, absorption bands near 2980 and 1480 cm^{-1}. As discussed above in connection with the nitratomercuri-, iodomercuri- and acetoxymercuri compounds **5**, **6**, and **7**, respectively, such 'anomalous' C–H stretching and bending bands are characteristic for a bicyclo[3.3.1]nonane skeleton present in a chair-chair conformation [see also footnote [8])]. Furthermore, **11** and **12** show three typical, strong bands [**11** (liq.): 1030, 900, 858 and **12**: 1031, 898, 852 cm^{-1}] which belong to compounds with a 2-substituted 9-oxabicyclo[3.3.1]nonane skeleton (see also the IR. spectra of **5**, **6**, and **7**). Corresponding bands in the IR. spectra of the iodides **9** and **10** are missing.

Conclusive proof for the ring skeletons was easily obtained by reducing each iodo compound individually with *Raney* nickel. The stereoisomers **9** and **10** yielded pure 9-oxabicyclo[4.2.1]nonane (**4**) whereas **11** and **12** afforded pure 9-oxabicyclo[3.3.1]-nonane (**8**).

The orientation of the iodine atoms, *i.e.*, the configuration at C-2 in the iodo compounds **9**, **10**, **11**, and **12** could be derived from spectroscopic measurements and chemical transformations[12]).

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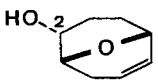
[9]) Further studies on the substitutions of halomercuri compounds are in progress.

[10]) The product distribution was identical after 3 h or 7 h reaction time.

[11]) The general applicability of this reaction (treatment of an unsaturated alcohol with iodine) was checked on several derivatives, *e.g.*, reaction of *endo*-2-hydroxy-9-oxabicyclo[3.3.1]-nonene-(6) (**i**) with iodine in chloroform led exclusively to the *trans* addition product, the tricyclic iodide **f** (see footnote [7])).



i

[12]) Determination of the configuration at C-2 in the iodides **9**, **10**, **11**, and **12** on the basis of 60 MHz and 100 MHz NMR. spectra is difficult and not absolutely conclusive. Therefore, the NMR. spectra of these compounds will not be discussed in details. However, the NMR. data (see Experimental Section) are in good agreement with the configurational assignments derived from other spectroscopic measurements and chemical transformations.

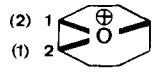
A first information was obtained from the UV. spectra of the four isomeric iodides (see Table 2). In our recent paper [1] on 2,5-diiodo-9-oxabicyclo[4.2.1]nonanes [see **c** in footnote [7])] and 2,6-diiodo-9-oxabicyclo[3.3.1]nonanes [see **d** in footnote [7])] we described the interesting feature that *exo*-oriented iodine atoms which are *cis* to the bridge oxygen O–9 show a remarkable interaction with the latter. This is manifested in absorption maxima at longer wavelengths, corresponding to less energetic $n \rightarrow \sigma^*$ transitions of the iodo compounds. The iodides **9**, **10**, **11**, and **12** described in the present paper again show such characteristically different absorption maxima which give good support for the configurational assignments at C-2: in **9** and **11** the iodine atom *endo*-equatorial, in **10** and **12** *exo*-axial.

Table 2. *Ultraviolet Spectra of the Iodo Compounds* **9**, **10**, **11**, *and* **12**

[4.2.1]-iodides	λ_{max}	(ε)	[3.3.1]-iodides	λ_{max}	(ε)
9	258	(615)	**11**	256	(595)
10	262	(595)	**12**	263.5	(635)

Further evidence was obtained by the qualitative investigation of the base treatment (in a 1N methanolic potassium hydroxide solution) of the four isomeric iodides **9**, **10**, **11**, and **12**. Smooth dehydrohalogenation is to be expected in compounds which fulfil the stereoelectronic requirement that the groups to be eliminated (H and I) be conformationally *trans*-antiplanar. Indeed, marked differences in reactivity were observed and the results clearly confirm the configurational assignments at C-2 made already on the basis of UV. spectra. From the two [4.2.1]-iodides **9** and **10**, the *endo*-isomer **9** shows much lower reactivity. After 2 h at reflux most of the *endo*-iodide **9** was unchanged whereas the *exo*-iodide **10** suffered almost complete reaction. Treatment of the two [3.3.1]-isomers **11** and **12** at room temperature was also informative: **11** reacted much more slowly than **12**.

A conclusive configurational assignment at C-2 was gained by reactions leading to products of a molecular rearrangement involving an oxonium ion (neighbouring group participation) of type **j** as an intermediate. Such an oxonium ion results from an intramolecular attack of an unshared oxygen electron pair either at C-2[13]) or at C-(2)[13]), respectively. Addition of an anion can proceed either at C-2[13]) (furnishing



j [13])

2-substituted [4.2.1]-derivatives) or at C-(2)[13]) (affording 2-substituted [3.3.1]-derivatives). The stereochemical course of the reaction implies that the outgoing iodine as well as the incoming group are *endo* oriented[14]).

Treatment of either the *endo*-[4.2.1]-iodide **9** or the *endo*-[3.3.1]-iodide **11** with silver acetate in acetic acid yielded the same mixture of the two acetates **15**[15]) and

[13]) The numbering without brackets corresponds to the [4.2.1]-isomers, the one in brackets to the [3.3.1]-isomers.

[14]) See also the corresponding discussion in [1].

[15]) See [12] and independent preparations from products described in [1], [8] and [9].

16[15]). Its ratio was determined by NMR. to be approximately 45:55. This result clearly implies a common intermediate, namely an oxonium ion of type **j**, and the *endo* orientation of the iodine atoms in **9** and **11**.

Furthermore, the *endo*-[4.2.1]-iodide **9** could easily be isomerized to the *endo*-[3.3.1]-iodide **11**. The best results were obtained with a I_2–KI–H_2O–C_2H_5OH solution. After 2 h of reflux the yield of isolated **11** was 71%. Analogous experiments with the *exo*-[4.2.1]-iodide **10** gave after 2 h reflux only the dehydrohalogenation product **13** [13] besides 47% of starting material **10**. A rearranged iodide could not be detected.

Paquette & Storm [2] reported that lithium aluminium hydride reduction of both the *endo*-[4.2.1]-iodide **9** and the *endo*-[3.3.1]-iodide **11** involve also an oxonium ion of type **j** then suffering rapid kinetically controlled reduction to yield exclusively 9-oxabicyclo[4.2.1]nonane (**4**), whereas the two *exo*-isomers **10** and **12** should undergo hydride reduction by direct S_N2 displacement of iodide ion yielding 9-oxabicyclo[4.2.1]nonane (**4**) from **10** and 9-oxabicyclo[3.3.1]nonane (**8**) from **12**. The authors [2] acknowledge that a most salient feature of this interpretation resides in the requirement that an approximate 1:1 distribution of the [3.3.1]-iodides **11** and **12** be realized in the iododemercuration step starting from the [3.3.1]-iodomercuri compound **6**. In accordance with this conclusion a ratio of the unsubstituted 9-oxabicyclononanes **4** and **8** of 1:1 is indeed claimed after the treatment of the iododemercuration mixture with lithium aluminium hydride.

However, our own results on the product distribution after the iodine cleavage of the iodomercuri compounds **3** and **6** and on the lithium aluminium hydride reduction of the iodides **9**, **10**, **11**, and **12** differ quite significantly from those published by *Paquette & Storm* [2]. Consequently, the proposed [2] involvement of an oxonium ion mechanism in the hydride reduction of the *endo*-iodides **9** and **11** must be discarded. As discussed above (see also Table 1) we examined different iododemercuration conditions and, starting from the [3.3.1]-iodomercuri compound **6**, found ratios of the two [3.3.1]-iodides **11** and **12** which differed markedly under all conditions from the 1:1 proportions claimed in the literature. The reliability of product distributions shown in Table 1 was checked, *e.g.*, by *Raney* nickel treatment[16]) of the crude iodide mixture of experiment 6[5]). In 80% yield a mixture of the unsubstituted 9-oxabicyclononanes **4** and **8** (ratio 17:83) was obtained, which corresponds exactly to the ratio of the [4.2.1]-iodide **9** and the sum of the [3.3.1]-iodides **11** and **12** (also 17:83, see Table 1). In addition this result implies that during the chromatographic separation of the iodides no rearrangement occurred and that the very minor decompositions had almost no effect on the product distribution.

Further interesting results were obtained when each iodo compound (**9**, **10**, **11**, and **12**) was reduced individually with lithium aluminium hydride. No skeletal rearrangements were observed. The stereoisomers **9** and **10** both yielded pure 9-oxabicyclo-[4.2.1]nonane (**4**) whereas the two [3.3.1]-iodides afforded pure 9-oxabicyclo[3.3.1]-nonane (**8**). The result of the lithium aluminium hydride treatment of the crude iodide mixture of experiment 6[5]) is in agreement with these experiments. In 52%

[16]) It has to be recalled that *Raney* nickel treatment of each iodide (**9**, **10**, **11**, and **12**) individually gave no rearrangement products; see above discussion.

yield[17]) a mixture of the unsubstituted 9-oxabicyclononanes **4** and **8** (ratio 12:88)[18]) was obtained. The small deviation from the ratio of 17:83 (see Table 1 and the result of *Raney* nickel treatment of the crude iodide mixture) of the [4.2.1]-iodide **9** and the sum of the [3.3.1]-iodides **11** and **12** is due to the different yields with which the individual iodides are reduced[19]).

From our results we conclude, therefore, that lithium aluminium hydride reductions of *endo*-[4.2.1]-iodide **9** and *endo*-[3.3.1]-iodide **11** do not proceed *via* an oxonium ion mechanism. The results of our studies on the mechanistic aspects of such lithium aluminium hydride reductions shall be the subject of a forthcoming paper.

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Experimental Section

General Remarks. – See the general remarks in the Experimental Section of [1].

The *Raney* nickel used had the activity C [14].

Lithium aluminium hydride reductions were carried out with colorless $LiAlH_4$ (crystalline powder, 95–98%, *Schuchardt*, München) in anh. ether distilled from $LiAlH_4$.

endo-2-Acetoxymercuri- and endo-2-Iodomercuri-9-oxabicyclo[4.2.1]nonane (2 and 3, respectively). – *endo-2-Acetoxymercuri-9-oxabicyclo[4.2.1]nonane* (**2**). – a) *From 4-cycloocten-1-ol* (**1**). Prepared following the procedure of *Bordwell & Douglass* [3]: m.p. 113–114° (after seven recrystallizations from $CHCl_3$-hexane). IR. (CCl_4): 1471, 1450, 1052, 932, 913. NMR. (C_5D_5N): 1.0–2.5/*bm* CH_2-3, -4, -5, -7, and -8; 2.90/*d* $J_{2exo,3endo}$ = 10.5 (further splitting by $J_{1,2exo}$ = $J_{2exo,3exo}$ = 5) CH-2^{exo}; 4.41/*m* ($W^1/_2$ approx. 18) CH-6; 4.84/*m* ($W^1/_2$ approx. 15) CH-1.

b) *From endo-2-Iodomercuri-9-oxabicyclo[4.2.1]nonane* (**3**). 151 mg (0.89 mmol) of silver acetate was added to a solution of 406 mg (0.89 mmol) of **3** in 5 ml of $CHCl_3$ and the reaction mixture was stirred at room temperature in the dark for 18 h. The yellow silver iodide formed was removed by filtration using Celite and the filtrate evaporated to dryness to yield 321 mg (93.5%) of **2**.

endo-2-Iodomercuri-9-oxabicyclo[4.2.1]nonane (**3**). Prepared from **2** following the procedure of *Bordwell & Douglass* [3]: m.p. 113–114°. IR. (KBr): 1465, 1446, 1038, 922, 905, 830, 780, 748, 665. NMR. (C_5D_5N): 1.0–2.5/*bm* CH_2-3, -4, -5, -7, and -8; 3.05/*d* $J_{2exo,3endo}$ = 11 (further splitting by $J_{1,2exo}$ = $J_{2exo,3exo}$ = 4.5) CH-2^{exo}; 4.41/*m* ($W^1/_2$ approx. 18) CH-6; 4.9/*m* ($W^1/_2$ approx. 14) CH-1.

Treatment of endo-2-Acetoxymercuri-9-oxabicyclo[4.2.1]nonane (**2**) *with Sodium borohydride.* – a) **2** *prepared from* **1**. A solution of 25.5 mg (0.67 mmol) of $NaBH_4$ in 0.4 ml of 2.5N aqueous NaOH was added to a solution of 344 mg (0.89 mmol) of **2** in 9 ml of 0.5N aqueous NaOH. After a few minutes the reaction mixture was filtered through Celite to remove the mercury and the filtrate was extracted with CH_2Cl_2. The solvent was carefully removed (*Vigreux* column, water bath 50°) and the residue distilled (80°/11 Torr) to give 93 mg (82%) of crystalline pure **4** [5] (identification by IR. and NMR.).

b) **2** *prepared from* **3**. A solution of 25 mg (0.66 mmol) of $NaBH_4$ in 0.4 ml of 2.5N aqueous NaOH was added to a solution of 321 mg (0.83 mmol) of crude **2** (prepared from **3**, see above) in 9 ml of 0.5N aqueous. After a few minutes the reaction mixture was filtered through Celite to remove the mercury and the filtrate extracted with CH_2Cl_2. The solvent was carefully removed (*Vigreux* column, water bath 50°) and the residue distilled (80°/11 Torr) to afford 89 mg (84%) of crystalline pure **4** [5] (identification by IR. and NMR.).

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[17]) This reduction was carried out analogously to a procedure by *Paquette & Storm* [2]. Their yield was 55%. However, if the reaction conditions were modified the yields could be increased (see Experimental Section).

[18]) *Paquette & Storm* [2] describe a ratio of 1:1.

[19]) In our own experiments the lowest yield was observed for the reduction of **9**, the highest one for the reduction of **12** (see Experimental Section).

Treatment of endo-2-Iodomercuri-9-oxabicyclo[4.2.1]nonane (**3**) *with Iodine.* – a) *In CCl_4 at 0° under argon with a 500 W visible light source* (Table 1, experiment 2). Argon was bubbled through a suspension of 3.015 g (6.675 mmol) of fine powdered iodomercuri compound **3** in 200 ml of CCl_4 for 2 h at 0°. 1.7 g (6.68 mmol) of iodine was added and the reaction mixture stirred under argon at 0° for 6 h in the presence of a 500 W visible light source. The precipitated mercuric iodide was removed by filtration. CH_2Cl_2 was added and the organic layer washed twice with a 10% aqueous KI solution and once with a 5% aqueous $Na_2S_2O_3$ solution. The water-phases were twice extracted with CH_2Cl_2 and the combined organic layers dried and evaporated to dryness to yield 1.644 g (98%) of a crude mixture of the iodides **9**, **10**, and **11** which was separated by chromatography in hexane-ether-(19:1) on 200 g of silicagel. A first chromatography gave in a total yield of 90% (relative to starting material **3**) 456 mg (27%) of pure **9**, 15 mg (1%) of a mixture of **9** and **11** (ratio approx. 1:1) and 1.048 g (62%) of a mixture of **10** and **11** (ratio 6.5:93.5, determined by NMR.). 960 mg of this mixture of **10** and **11** was rechromatographed once on 110 g of silicagel to afford 7 mg of almost pure **11**, 136 mg of a mixture of **10** and **11** (ratio approx. 3:1), 200 mg of a mixture of **10** and **11** (ratio approx. 9:1) and finally 608 mg of a mixture of **10** and **11** (ratio approx. 99:1)[20].

b) *In CCl_4 at room temperature under nitrogen and with daylight* (Table 1, experiment 3)[5]. To a mixture of 1.187 g (2.6 mmol) of the iodomercuri compound **3** in 80 ml of CCl_4 which was cooled to 0°, 660 mg (2.6 mmol) of iodine were added and the reaction flask flushed with N_2. The cooling was removed and the reaction mixture stirred for 8 h at room temperature in the presence of daylight. The precipitated mercuric iodide was removed by filtration and the filtrate after washing with a 5% aqueous $Na_2S_2O_3$ solution worked up in the usual manner to yield 677 mg of an oily crude mixture of the iodides **9**, **10**, and **11** which was separated by chromatography in hexane-ether-(19:1) on 70 g of silicagel. A first chromatography gave in a total yield of 94% (relative to starting material **3**) 189 mg (28.5%) of pure **9** and 432 mg (65.5%) of a mixture of **9**, **10**, and **11**. This latter mixture was rechromatographed once on 50 g of silicagel to afford further 11 mg (2%) of pure **9** and 399 mg (60.5%) of a mixture of **10** and **11** (ratio 74:26, determined by NMR.)[20].

endo-2-Nitratomercuri-, endo-2-Iodomercuri-, and endo-2-Acetoxymercuri-9-oxabicyclo[3.3.1]nonane (5, 6, and 7, respectively). – *endo-2-Nitratomercuri-9-oxabicyclo[3.3.1]nonane* (**5**). Prepared from **1** following the procedure of *Bordwell & Douglass* [3]: m.p. 97–98° (after one recrystallization from ethyl acetate). IR.: 2970, 1483, 1149, 1120, 1088, 1066, 1047, 1023, 977, 899, 866, 852.

Treatment of endo-2-Nitratomercuri-9-oxabicyclo[3.3.1]nonane (**5**) *with Sodium borohydride.* 600 mg (1.55 mmol) of **5** were dissolved in a few ml of 0.5 N aqueous NaOH and the mixture filtered through Celite to remove traces of mercury and mercuric oxide. After washing, **5** was finally dissolved in a total of 11 ml of 0.5 N aqueous NaOH. A solution of 45 mg (1.19 mmol) of $NaBH_4$ in 0.7 ml of 2.5 N aqueous NaOH was added. Immediately mercury was formed. The reaction mixture was filtered through Celite and the filtrate three time extracted with CH_2Cl_2. The solvent was carefully removed on a water bath (50°) through a *Vigreux* column and the residue distilled (75°/20 Torr) to yield 157 mg (80%) of crystalline pure **8** [6] (identification by IR. and NMR.).

endo-2-Iodomercuri-9-oxabicyclo[3.3.1]nonane (**6**). A solution of 1.72 g (10.36 mmol) of KI in 2 ml of H_2O was added dropwise to a solution of 401 mg (1.036 mmol) of **5** in 10 ml of 0.5 N aqueous NaOH. The reaction mixture was stirred at room temperature for 1/2 h and the precipitate filtered off and dissolved in $CHCl_3$. The filtrate was twice extracted with $CHCl_3$. The combined $CHCl_3$ solutions were dried and evaporated to dryness to afford 468 mg (99.5%) of crude **6**, m.p. 145–146° which was once recrystallized from $CHCl_3$-hexane to yield 426 mg (91%) of **6**, m.p. 145–147°. IR.: 2975, 1482, 1148, 1134, 1118, 1083, 1060, 1041, 1021, 976, 898, 863, 850; (KBr): 2970, 1478, 1144, 1130, 1126, 1112, 1081, 1054, 1037, 1016, 970, 893, 861, 843, 839. NMR. (C_5D_5N): 1.1–2.4/*bm* CH-3^{exo}, CH_2-4, -6, -7, and -8; 2.4–3.0/*m* CH-3^{endo}; 3.52/*d* $J_{2endo,3exo}$ = 13 (further splitting by $J_{1,2exo} = J_{2exo,3exo} = 5.5$) CH-2^{exo}; 3.94/*m* ($W^1/_2$ approx. 11) CH-5; 4.27/*m* ($W^1/_2$ approx. 12) CH-1.

[20] The original composition of the mixture of **9**, **10**, and **11** (see Table 1) was estimated on the basis of the chromatographically separated **9** and the ratio of the remaining mixture of **10** and **11** (ratio determined by NMR.).

endo-2-Acetoxymercuri-9-oxabicyclo[3.3.1]nonane (**7**). – a) *Prepared in $CHCl_3$.* 320 mg (1.92 mmol) of silver acetate was added to a solution of 840 mg (1.86 mmol) of the iodomercuri compound **6** in 15 ml of $CHCl_3$ and the reaction mixture stirred at room temperature in the dark for 22 h. The yellow silver iodide formed was removed by filtration using Celite and the filtrate evaporated to dryness under reduced pressure. The oily residue crystallised immediately to give 710 mg (99%) of the acetoxymercuri compound **7** which after one recrystallization from $CHCl_3$-hexane melted at 110.5–112°. IR. (CCl_4): 2970, 1486, 1625, 1595, 1149, 1119, 1087, 1067, 1048, 1028, 978, 900, 867, 857.

b) *Prepared in $[(CH_3)_2N]_3PO$* (HMPT). 232 mg (1.39 mmol) of silver acetate was added to a solution of 623 mg (1.38 mmol) of the iodomercuri compound **6** in 10 ml of HMPT. The reaction mixture was stirred at room temperature in the dark for 24 h. After filtration through Celite to remove the silver iodide the filtrate was evaporated to dryness under reduced pressure (90°/0.05 Torr). The oily residue was dissolved in $CHCl_3$ and filtrated again through Celite. After evaporation of the $CHCl_3$ one obtained 675 mg of **7** which still contained some HMPT.

Treatment of endo-2-Acetoxymercuri-9-oxabicyclo[3.3.1]nonane (**7**) *with Sodium borohydride.* – a) **7** *prepared in $CHCl_3$.* 539 mg (1.4 mmol) of the above acetoxymercuri compound **7** were dissolved in 10 ml of 0.5 N aqueous NaOH and treated at 0° with a solution of 45 mg (1.19 mmol) of $NaBH_4$ in 0.7 ml of 2.5 N aqueous NaOH. Mercury was removed by filtration through Celite and the filtrate extracted three times with CH_2Cl_2. The combined organic layers were dried and the CH_2Cl_2 carefully removed on a water bath (50°) through a *Vigreux* column. The residue was finally distilled (80°/11 Torr) to afford 156 mg (88%) of crystalline pure **8** [6] (identification by IR. and NMR.).

b) **7** *prepared in HMPT.* The above 675 mg of crude **7** which contained some HMPT were dissolved in 10 ml of 0.5 N aqueous NaOH and treated at 0° with a solution of 51 mg (1.35 mmol) of $NaBH_4$ in 0.75 ml of 2.5 N aqueous NaOH. After the work up (see above) and distillation (75°/20 Torr): 145 mg (83% relative to **6**) of crystalline pure **8** [6] (identification by IR. and NMR.) were obtained.

Treatment of endo-2-Iodomercuri-9-oxabicyclo[3.3.1]nonane (**6**) *with Iodine.* – a) *In water in the presence of potassium iodide and air, in the dark at room temperature* (Table 1, experiment 4). To a suspension of 724 mg (1.6 mmol) of fine powdered iodomercuri compound **6** in 20.7 ml of water a solution of 466 mg (1.84 mmol) of iodine in 20.7 ml of a 30% aqueous KI solution was added. After stirring for 7 h in the dark at room temperature the reaction mixture was extracted three times with CH_2Cl_2 and the combined organic layers washed with a 10% aqueous KI solution and subsequently with a 5% aqueous $Na_2S_2O_3$ solution, and worked up in the usual manner to yield 403 mg of an oily mixture of the iodides **9**, **11**, and **12** which was separated by chromatography in hexane-ether-(19:1) on silicagel (100-fold amount). A first chromatography gave in a total yield of 96% (relative to **6**) 94 mg (23.5%) of pure **9** and 292 mg (72.5%) of a mixture of **11** and **12**. This mixture of **11** and **12** yielded by rechromatography some pure **11**; the rest remained as a mixture of **11** and **12**. This separation procedure with the mixed fractions containing **11** and **12** was applied five times. Finally the total yield of isolated pure iodo compounds **9**, **11**, and **12**, relative to starting material **6**, was 85%[21]): 94 mg (23.5%) of **9**, 68 mg (17%) of **11**, and 180 mg (44.5%) of **12**. Further 5 mg (1%) were still a mixture (ca. 1:1) of **11** and **12**.

b) *In CCl_4 under argon at 0° with a 500 W visible light source* (Table 1, experiment 5). Argon was bubbled through 50 ml of CCl_4 for 2 h at room temperature. The solvent was subsequently cooled to 0°. Under further argon atmosphere 755 mg (1.67 mmol) of fine powdered iodomercuri compound **6** and 423 mg (1.67 mmol) of iodine were added. Under vigorous stirring the mixture was exposed for $2^1/_2$ h at 0° to the light of a 500 W visible light source. After addition of CH_2Cl_2 the organic layer was washed with a 10% aqueous KI solution and finally with a 5% aqueous $Na_2S_2O_3$ solution and worked up in the usual manner to yield a crude mixture of the iodides **9**, **11**, and **12** which was separated by chromatography in hexane-ether-(19:1) on silicagel (100-fold

[21]) By each chromatography of a mixture of **11** and **12** some pure **11** could be separated, the rest remained as a mixture of **11** and **12**. The total yield of isolated products after one chromatography was 96%, and 86% after further five rechromatographies of the each time remaining mixed fractions containing **11** and **12**, *i.e.*, the average loss for each rechromatography was about 2%. The original composition of the mixture of **9**, **11**, and **12** (see Table 1) was estimated taking in account the average loss of products by each chromatography.

amount). A first chromatography gave in a total yield of 90% (relative to starting material **6**) 16 mg (3.5%, after distillation at 80°/0.01 Torr) of pure **9** and 364.5 mg (86.5%) of a mixture of **11** and **12**. This mixture of **11** and **12** was rechromatographed yielding some pure **11** and the rest remained as a mixture of **11** and **12**. This separation procedure with the mixed fractions containing **11** and **12** was applied three times. Finally the total yield of isolated pure iodo compounds **9**, **11**, and **12**, relative to starting material **6**, was 82%[22]: 16 mg (3.5%) of **9**, 58 mg (14%) of **11**, and 265 mg (63%) of **12**. Further 6 mg (1.5%) were still a mixture (ca. 1:1) of **11** and **12**.

c) *In CCl_4 under N_2 at room temperature and daylight* (Table 1, experiment 6)[5]. – ca) *Iodination*[5]). To a mixture of 4.5 g (9.95 mmol) of the iodomercuri compound **6** in 300 ml of CCl_4 which was cooled to 0°, 2.508 g (9.9 mmol) of iodine were added and the reaction flask flushed with N_2. The cooling was removed and the mixture stirred for 8 h at room temperature under N_2 in daylight. The precipitated mercuric iodide was removed by filtration and the filtrate after washing with a 5% aqueous $Na_2S_2O_3$ solution worked up in the usual manner to yield 2.53 g of an oily mixture of the iodides **9**, **11**, and **12** (UV. of the mixture: 262). 1.34 g of this crude mixture was separated by chromatography in hexane-ether-(19:1) on silicagel (100-fold amount). A first chromatography gave in a total yield of 93.5%: 205 mg (15.5%, after distillation at 80°/0.01 Torr) of pure **9**, 3.5 mg (0.5%) of a mixture of **9** and **11** (mainly **9**) and finally 1.032 g (77.5%) of a mixture of **11** and **12**. This mixture was rechromatographed yielding some pure **11** and the rest remained as a mixture of **11** and **12**. This separation procedure with the mixed fractions containing **11** and **12** was applied four times. The total yield of isolated pure iodo compounds **9**, **11**, and **12**, relative to starting material **6**, was 88.5%[23]: 205 mg (15.5%) of **9**, 242.5 mg (18%) of **11** and 707 mg (53%) of **12**. Further 3.5 mg (0.3%) remained as a mixture of **9** and **11** (mainly **9**) and 21.5 mg (1.5%) as a mixture (ca. 1:1) of **11** and **12**.

cb) *Treatment of the iodination mixture [see above ca)] with* Raney *nickel.* 210 mg (0.84 mmol) of the above crude iodination mixture [see ca)] of **9**, **11**, and **12** were dissolved at 0° in 3 ml of 1N methanolic KOH. After addition of a slurry of approx. 1 g of *Raney* nickel in approx. 2 ml of CH_3OH, the reaction mixture was stirred for 1 h at room temperature and subsequently worked up at 0°. Filtration through Celite was followed by thorough washing of the residue with CH_2Cl_2. Saturated aqueous NaCl solution was added to the filtrate and the water-layer twice extracted with CH_2Cl_2. The CH_2Cl_2 was dried and carefully removed (*Vigreux* column, 50°). The residue was finally distilled (75°/20 Torr) to give 90 mg (80%) of a mixture containing 17% of **4** [5] and 83% of **8** [6] (ratio determined by NMR. in CCl_4).

cc) *Treatment of the iodination mixture [see above ca)] with lithium aluminium hydride*[24]). To a suspension of 55 mg (1.45 mmol) of $LiAlH_4$ was added at room temperature under stirring a solution of 340 mg (1.35 mmol) of the above [see ca)] crude iodination mixture (**9**, **11**, and **12**) in 1.35 ml of ether. After refluxing for 2 h the mixture was stirred at room temperature over night. 55 µl of H_2O followed by 55 µl of 25% aqueous NaOH, 165 µl of H_2O and some $MgSO_4$ were added to the reaction mixture. After filtration through Celite and washing the residue with ether the solvent was carefully removed (*Vigreux* column, 50°) and the residue distilled (80°/20 Torr) to afford 180 mg of an impure oil which contained some ether and water. It was therefore dissolved in CH_2Cl_2 and once washed with saturated aqueous NaCl solution. The CH_2Cl_2 was again removed through a *Vigreux* column at 50° and the residue distilled (75°/20 Torr) to yield 89 mg (52%) of a mixture: 12% of **4** [5] and 88% of **8** [6] (ratio determined by NMR. in CCl_4).

The Iodo Compounds 9, 10, 11, and 12. – *endo-2-Iodo-9-oxabicyclo[4.2.1]nonane* (**9**). Colorless liquid (distilled at 80°/0.01 Torr). IR. (liq.): 1471, 1226, 1052, 938, 906, 750, 662. UV.: 258 (615).

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22) See also footnote [21]). The original composition of the mixture of **9**, **11**, and **12** (see Table 1) was estimated on the basis of the following results: yield after one chromatography 90%, and 82% after further three rechromatographies of the each time remaining mixed fractions containing **11** and **12**, average loss by each chromatography ca. 3%.

23) See also footnote [21]). The original composition of the mixture of **9**, **11**, and **12** (see Table 1) was estimated on the basis of the following results: yield after one chromatography 93.5%, and 88.5% after further four rechromatographies of the each time remaining mixed fractions containing **11** and **12**, average loss by each chromatography ca. 1.5%.

NMR.: 1.0–2.7/*bm* CH_2-3, -4, -5, -7, and -8; 4.24/*d* $J_{2,3}$ = 11 (further splitting by $J_{1,2} = J_{2,3'}$ = 4.5) CH-2; 4.6/*bm* CH-1 and -6. MS.: M^+ = 252 ($C_8H_{13}IO$).

exo-2-Iodo-9-oxabicyclo[4.2.1]nonane (**10**). Colorless liquid (distilled at 80°/0.01 Torr). IR. (liq.): 1471, 1138, 1000, 981, 958, 920, 899, 882, 855, 835, 789, 751. UV.: 262 (595). NMR.: 1.0–2.5/*bm* CH_2-3, -4, -5, -7, and -8; 4.35/*m* (*W*1/2 approx. 15) CH-2 or -1; 4.56/*m* (*W*1/2 approx. 17) CH-6; 4.88/*m* (*W*1/2 approx. 14) CH-1 or -2. MS.: M^+ = 252 ($C_8H_{13}IO$).

endo-2-Iodo-9-oxabicyclo[3.3.1]nonane (**11**). Colorless liquid (distilled at 80°/0.01 Torr). IR. (liq.): 2970, 1484, 1208, 1152, 1090, 1068, 1030, 981, 900, 858, 772, 721, 651. UV.: 256 (595). NMR.: 1.4–3.0/*bm* CH_2-3, -4, -6, -7, and -8; 4.01/*m* (*W*1/2 approx. 12, two main peaks, line separation 5 Hz) CH-1 and -5; 4.66/*d* $J_{2,3}$ = 12 (further splitting by $J_{1,2} = J_{2,3'}$ = 5.5) CH-2. MS.: M^+ = 252 ($C_8H_{13}IO$).

exo-2-Iodo-9-oxabicyclo[3.3.1]nonane (**12**). Colorless liquid (distilled at 80°/0.01 Torr). IR. (liq.): ca. 2970 (shoulder), 1481, 1203, 1152, 1140, 1101, 1087, 1057, 1046, 1031, 972, 898, 852, 720, 677. UV.: 263.5 (635). NMR.: 1.2–2.7/*bm* CH_2-3, -4, -6, -7, and -8; 4.08/*m* (*W*1/2 = 22) CH-1 and -5; 4.60/*m* (*W*1/2 = 8) CH-2. MS.: M^+ = 252 ($C_8H_{13}IO$).

Treatment of 4-Cycloocten-1-ol (1) with Iodine (Table 1, experiment 1). – a) *Iodo compounds* **9** *and* **11**. – aa) *7 h.* 2.867 g (11.2 mmol) of iodine were added to a solution of 949 mg (7.5 mmol) of 4-cycloocten-1-ol (**1**) in 50 ml of $CHCl_3$. After 7 h of standing at room temperature the excess of iodine was reduced with a 10% aqueous $Na_2S_2O_3$ solution and the reaction mixture worked up in the usual manner to yield 1.64 g (86%) of a yellow liquid [mixture of **9** and **11**, see also below: ba) treatment of this mixture with *Raney* nickel]. Chromatography in hexane-ether-(19:1) on silicagel (100-fold amount) afforded 410 mg (21.5%) of the iodo compound **9** and 1.142 g (60%) of the iodide **11**.

ab) *3 h.* An analogous experiment was carried out but with a reaction time limited to 3 h at room temperature. The result was almost identical [see also below: bb) treatment of the iodide mixture with *Raney* nickel].

b) *Treatment of the mixture of* **9** *and* **11** [*see above* aa) *and* ab)] *with* Raney *nickel.* For the general procedure see below (treatment of the iodo compounds **9**–**12** with *Raney* nickel).

ba) *Mixture from above* aa). 252 mg (1.0 mmol) of the above mixture of the iodides **9** and **11** (7 h reaction time) in a solution of 108 mg KOH in 40 ml of CH_3OH, addition of a slurry of approx. 1 g of *Raney* nickel in 3 ml of CH_3OH, 90 min. at room temperature. Yield: 85 mg (67%) of a mixture of **4** [5] and **8** [6] (ratio determined by NMR. (CCl_4): 25% of **4** and 75% of **8**).

bb) *Mixture from above* ab). 252 mg (1.0 mmol) of the above mixture of the iodides **9** and **11** (3 h reaction time) in a solution of 108 mg of KOH in 40 ml of CH_3OH, addition of a slurry of approx. 1 g of *Raney* nickel in 3 ml of CH_3OH, 90 min. at room temperature. Yield: 79 mg (63%) of a mixture of **4** [5] and **8** [6] (ratio determined by NMR. (CCl_4): 26% of **4** and 74% of **8**).

Treatment of the Iodo Compounds 9–12 with *Raney* Nickel. – *General procedure.* The corresponding iodo compound was dissolved in a solution of KOH in CH_3OH. After addition of a slurry of *Raney* nickel in CH_3OH, the reaction mixture was stirred at room temperature and subsequently worked up at 0°. Filtration through Celite was followed by thorough washing of the residue with ether or CH_2Cl_2. The filtrate was washed twice with water and the water-layer again twice extracted with ether or CH_2Cl_2. The combined organic extracts were dried and the solvents carefully removed on a water bath (50°) through a *Vigreux* column. The residue was finally distilled (80°/11 Torr). The products were identified by TLC. (CH_2Cl_2 or benzene), IR. and NMR.

a) *Treatment of* **9**. 252 mg (1.0 mmol) of **9** in a solution of 108 mg of KOH in 40 ml of CH_3OH, addition of a slurry of approx. 1 g of *Raney* nickel in 3 ml of CH_3OH, 90 min. at room temperature. Yield: 75 mg (60%) of crystalline pure **4** [5].

b) *Treatment of* **10**. 200 mg (0.794 mmol) of **10** were dissolved in 3 ml of CH_3OH, addition of 2 ml of 1N methanolic KOH and a slurry of approx. 1 g of *Raney* nickel in 1 ml of CH_3OH, 2 h room temperature. Yield: 84 mg (84%) of crystalline pure **4** [5].

c) *Treatment of* **11**. 252 mg (1.0 mmol) of **11** in a solution of 108 mg of KOH in 40 ml of CH_3OH, addition of a slurry of approx. 1 g of *Raney* nickel in 3 ml of CH_3OH, 90 min. at room temperature. Yield: 95 mg (76%) of crystalline pure **8** [6].

[24]) This experiment was a reinvestigation of a procedure described by *Paquette & Storm* [2].

d) *Treatment of* **12**. 153 mg (0.607 mmol) of **12** in 4 ml of 1N methanolic KOH, addition of a slurry of approx. 1 g of *Raney* nickel in 2 ml of CH_3OH, 1 h at room temperature. Yield: 69.5 mg of a mixture of **8** [6] and **14** (approx. 9:1, determined by NMR.).

63 mg of the above mixture (**8** and **14**) was dissolved in 2 ml of CH_3OH. After addition of a slurry of approx. 500 mg of *Raney* nickel in 1 ml of CH_3OH, the reaction mixture was stirred for 2 h at room temperature and subsequently worked up as above to afford 55 mg (72% relative to 153 mg of starting material **12**) of crystalline pure **8** [6].

Treatment of the Iodo Compounds 9–12 with Lithium aluminium hydride. – After the work up the solvents were carefully removed by distillation through a *Vigreux* column (water bath approx. 60°) and the remaining residue distilled. The products (**4** and **8**, respectively) were identified by TLC., IR. and NMR.

a) *Treatment of* **9**. 149 mg (0.591 mmol) of the iodide **9** dissolved in 3.5 ml of ether was added to a suspension of 75 mg (1.97 mmol) of $LiAlH_4$ in 5 ml of ether. After refluxing for 23 h the mixture was cooled to 0° and treated with 90 µl of H_2O, 90 µl of 25% aqueous NaOH and finally with 270 µl of H_2O. After 7 h of stirring at room temperature the mixture was filtered through Celite and the residue subsequently washed with approx. 100 ml of ether-CH_2Cl_2. Yield: 49 mg (65%) of crystalline pure **4** [5].

b) *Treatment of* **10**. 210 mg (0.833 mmol) of the iodide **10** dissolved in 4 ml of ether was added to a suspension of 101 mg (2.66 mmol) of $LiAlH_4$ in 5 ml of ether. After refluxing for 8 h the mixture was stirred at room temperature for further 16 h and subsequently treated with 125 µl of H_2O, 125 µl of a 25% aqueous NaOH solution and finally with 375 µl of water. After 6 h of stirring at room temperature the mixture was filtered through Celite and the residue washed with approx. 100 ml of ether-CH_2Cl_2. Yield: 86 mg (81%) of crystalline pure **4** [5].

c) *Treatment of* **11**. 254 mg (1.0 mmol) of the iodide **11** dissolved in 3 ml of ether was added to a suspension of 80 mg (2.1 mmol) of $LiAlH_4$ in 5 ml of ether. After refluxing for 2 h the mixture was stirred at room temperature for 15 h and subsequently treated at 0° with 90 µl of H_2O, 90 µl of 25% aqueous NaOH, and finally with 270 µl of water. After 2 h of stirring at room temperature the mixture was filtered through Celite and the residue washed with approx. 100 ml of CH_2Cl_2. Yield: 98 mg (77%) of crystalline pure **8** [6].

d) *Treatment of* **12**. 278 mg (1.1 mmol) of the iodide **12** dissolved in 3 ml of ether was added to a suspension of 92 mg (2.4 mmol) of $LiAlH_4$ in 5 ml of ether. After refluxing for 2 h the mixture was stirred at room temperature for 15 h and subsequently treated at 0° with 104 µl of H_2O, 104 µl of 25% aqueous NaOH, and finally with 310 µl of H_2O. After 6 h of stirring at room temperature the mixture was filtered through Celite and the residue washed with approx. 50 ml of ether and 50 ml of CH_2Cl_2. Yield: 120 mg (86%) of crystalline pure **8** [6].

Treatment of the Iodo Compounds 9–12 with KOH-CH_3OH. – *General remarks.* The corresponding iodo compound was dissolved in 1N methanolic KOH and the mixture was stirred at room temperature or refluxed. The reaction was only followed qualitatively by TLC. (CH_2Cl_2).

a) *Treatment of* **9**. 5 mg of **9** in 10 ml of 1N methanolic KOH. After 2 h of reflux most of the starting material **9** was unchanged.

b) *Treatment of* **10**. 5 mg of **10** in 10 ml of 1N methanolic KOH. After 2 h of reflux the starting material **10** had almost completely disappeared.

c) *Treatment of* **11**. 27.5 mg of **11** in 1 ml of 1N methanolic KOH was stirred at room temperature. After 22 h the starting material **11** was mainly unchanged.

d) *Treatment of* **12**. 38.5 mg of **12** in 1.4 ml of 1N methanolic KOH was stirred at room temperature. Already after 2 h product formation could be observed and after 75 h the ratio of starting material **12** to product **14** was approx. 1:1.

Treatment of the Iodo Compounds 9 and 11 with Silver Acetate. – A mixture of 60 mg (0.24 mmol) of the corresponding iodo compound (**9** or **11**, respectively) and 170 mg (1.02 mmol) of silver acetate in 5 ml of acetic acid was stirred at 80° for 25 min. The reaction mixture was poured on saturated aqueous NaOAc and extracted with CH_2Cl_2. After removal of the solvent in both cases 41 mg (94%) of a mixture of the two acetates **15**[15]) and **16**[15]) were obtained in a ratio of 46:54 (starting from **9**) and 45:55 (starting from **11**). The ratios were determined by NMR., see Table 3.

Table 3. *NMR.-analysis of the Mixtures of the two Acetates* **15** *and* **16**

Signals δ	Integral [a]	ratio [b]	Assignment	
			15[15]	**16**[15]
1.0–2.8/*bm*	10	10	CH_2-3, -4, -5, -7, and -8	CH_2-3, -4, -6, -7, and -8
2.03/*s*	3	3	2-$OCOCH_3$	2-$OCOCH_3$
3.8–4.0/*bm*	1.08	1.10		CH-1 and -5
4.15–4.60/*bm*	0.92	0.90	CH-1 and -6	
4.6–5.2/*bm*	1	1	CH-2	CH-2

[a]) Starting material: **9**. [b]) Starting material: **11**.

Isomerization Experiments with the Iodo Compounds 9 and 10. – The experimental details and the results are listed in Table 4. The products were identified by IR.

Table 4. *Isomerization Experiments with the Iodo Compounds* **9** *and* **10**

Starting material	Reaction conditions	Time h	Temperature	Product distribution
20 mg **9**	20 mg I_2, 20 ml $CHCl_3$	2	reflux	18.5 mg (92.5%) **9**
20 mg **9**	20 ml I_2–KI–H_2O–C_2H_5OH solution[a])	15	room temp.	12.5 mg (62.5%) **9**
83.5 mg **9**	100 ml I_2–KI–H_2O–C_2H_5OH solution[a])	15	reflux	35.5 mg (42%) **11**[b])
20 mg **9**	10 ml I_2–KI–H_2O–C_2H_5OH solution[a])	2	reflux	14.2 mg (71%) **11**
30 mg **10**	15 ml I_2–KI–H_2O–C_2H_5OH solution[a])	2	reflux	14.1 mg (47%) **10**[b])

[a]) 35 g I_2, 100 g KI, 500 ml H_2O, 250 ml C_2H_5OH.
[b]) Lower yields are mainly due to formation of volatile **13** or **14**, respectively.

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