ν_1 (Messkanal ^{1}H) und ν_2 (Doppelresonanzkanal ^{13}C) werden durch Spannungs/Frequenz-Wandler mit einer Frequenzkonstanz von 0,1 Hz über den ganzen Frequenzbereich von ±11400 Hz in beiden Kanälen oder 0,01 Hz über einen Regelbereich von ±1140 Hz erzeugt. Die beiden «Frequenzsweeps» ermöglichen in Doppelresonanzexperimenten grundsätzlich das Arbeiten in folgenden zwei «Sweepmodes»:

ν_1 variabel, ν_2 konstant: üblicher «Frequenzsweep»
ν_1 konstant, ν_2 variabel: *INDOR*

Infolge der Protonenstabilisation werden sämtliche Doppelresonanzfrequenzen direkt auf Tetramethylsilan bezogen, was die Verwendung einer internen ^{13}C-Referenz erübrigt. Die in Stellung $\nu_2 - \nu_0$ am Frequenzmesser abgelesene Referenzniederfrequenz bezieht sich auf einen virtuellen Standard, der jedoch gegenüber der Frequenz des Stabilisationssignals konstant ist.

Acetonitril (*Fisher Scientific Company*) gelangte ohne weitere Reinigung oder Entgasung in Proberöhrchen von 5 mm Aussendurchmesser zur Messung. Die Verbindung enthielt ca. 5% Tetramethylsilan, das als Protonenreferenz und zur Kernstabilisation diente. Die erreichbare Messgenauigkeit liegt in der Grössenordnung von ±0,2 Hz, entsprechend 0,002 ppm.

Die vorliegende Arbeit wurde vom *Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung* unterstützt.

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191. Oxymercuration. Substituted 9-Oxabicyclo[4.2.1]- and 9-Oxabicyclo[3.3.1]nonanes

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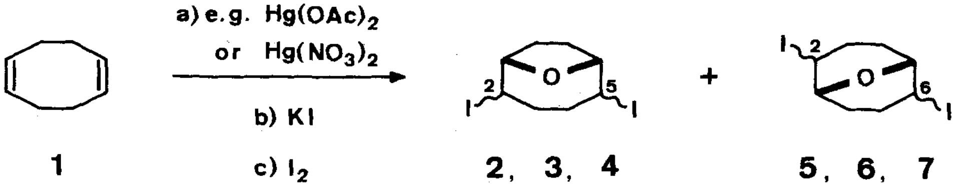
(27. VII. 70)

Summary. Oxymercuration of *cis, cis*-1,5-cyclooctadiene (**1**), followed by treatment with potassium iodide and subsequent reaction with iodine, leads to six isomeric diiodides which represent the three possible stereoisomers **2**, **3**, and **4** of 2,5-diiodo-9-oxabicyclo[4.2.1]nonane as well as **5**, **6**, and **7** of 2,6-diiodo-9-oxabicyclo[3.3.1]nonane. The isolation, structure determination and some reactions of these diiodo compounds **2**–**7** are described.

In connection with studies on heterocyclic compounds we recently synthesized 2-oxa-6-thia-adamantane [1]. As starting material we used 9-oxabicyclo[3.3.1]nona-2,6-diene (**13**), the synthesis of which was described by *Stetter et al.* [2]. Following the published procedure (treatment of *cis, cis*-1,5-cyclooctadiene (**1**) with mercuric acetate followed by adding potassium iodide and subsequent reaction with iodine [2]), we isolated a mixture of isomeric diiodo-9-oxabicyclononanes, while *Stetter et al.* [2] reported the formation of a single product. Depending on the reaction conditions applied, one can easily obtain different amounts of six isomeric diiodo compounds[1]),

Chart 1



which represent the three possible stereoisomers **2**, **3**, and **4** of 2,5-diiodo-9-oxabicyclo[4.2.1]nonane, and **5**[2]), **6**, and **7**[3]) of 2,6-diiodo-9-oxabicyclo[3.3.1]nonane.

In the present paper we describe the isolation, structure determination and some reactions of these diiodo compounds **2**–**7**[4]).

The six isomeric diiodo compounds **2**, **3**, **4**, **5**, **6**, and **7** were obtained as pure compounds by column chromatography and fractional crystallization as described in the Experimental Section.

Compounds **5**, **6**, and **7** exhibit in their IR. spectra, among others, absorption bands near 2990 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

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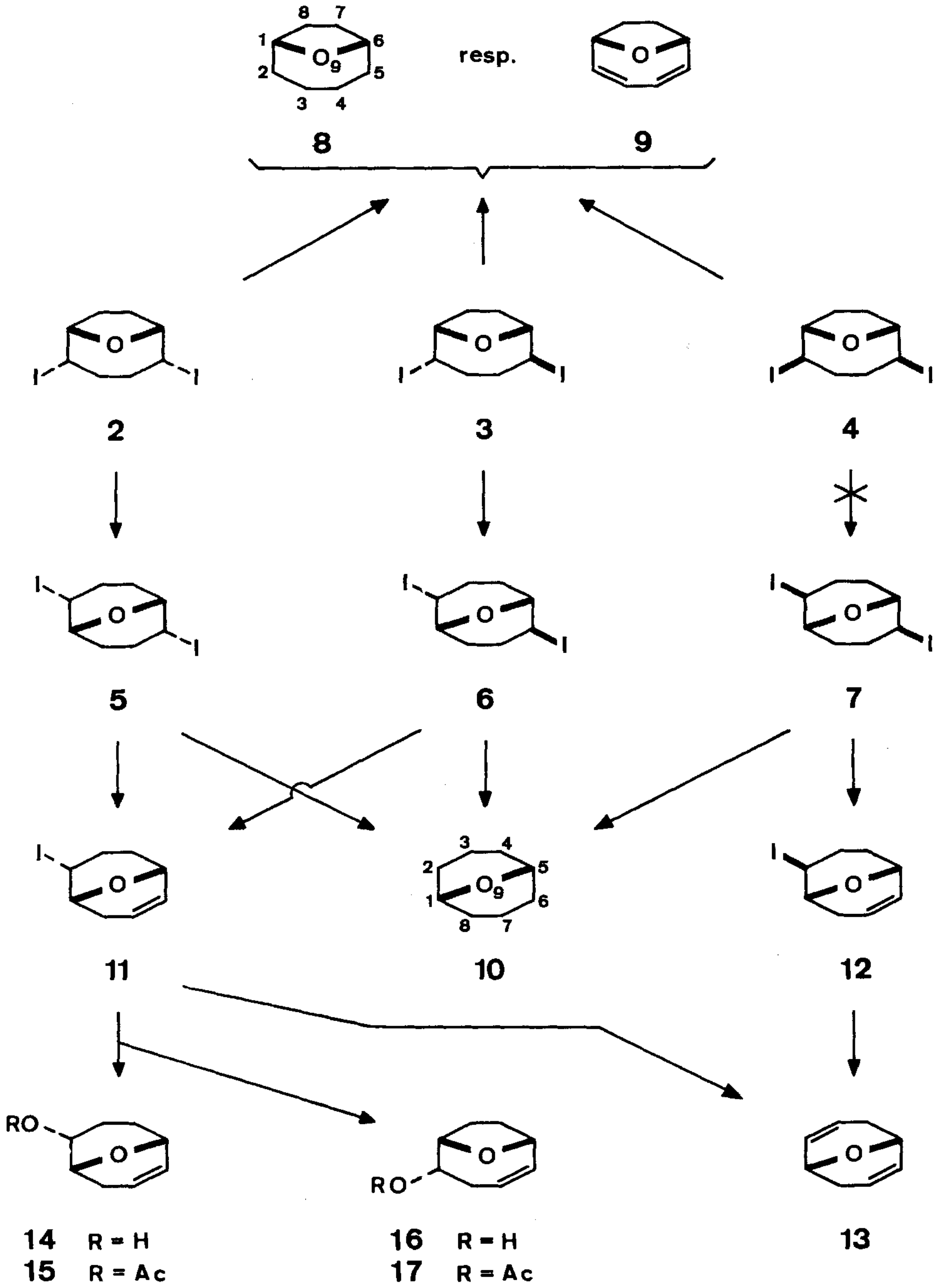
[1] In the experimental section a typical procedure is described by which the ratio of isolated 2,5-diiodo-9-oxabicyclo[4.2.1]nonanes **2**, **3**, and **4** to 2,6-diiodo-9-oxabicyclo[3.3.1]nonanes **5**, **6**, and **7** is about 2:1.

[2] *Cope et al.* [3] added iodine to a mixture of *cis,cis*-1,5-cyclooctadiene (**1**) and mercuric oxide in chloroform, which led to the formation of mercuric iodide and a crystalline solid. Vapour phase chromatography analysis showed the presence of two compounds in the ratio 3:2. The above crystalline mixture was treated with potassium *t*-butoxide in ether to give a liquid and a crystalline solid which was identified as a 2,6-diiodo-9-oxabicyclo[3.3.1]nonane of m.p. 120–121°. The authors give no configurational assignment. We reinvestigated their procedure and obtained the following result: The crystalline solid (before treatment with potassium *t*-butoxide) is a mixture (ratio 3:2) of *endo,endo*-2,5-diiodo-9-oxabicyclo[4.2.1]nonane (**2**) and *endo,endo*-2,6-diiodo-9-oxabicyclo[3.3.1]nonane (**5**). The product of m.p. 120–121° isolated by *Cope et al.* [3] corresponds to our isomer **5**. It is interesting to note that only the two isomeric *endo,endo*-diiodo compounds **2** and **5** are formed, both having the iodine atoms *trans* to the oxygen bridge O-9. This result can best be interpreted by assuming I_2O (produced *in situ* from mercuric oxide and iodine in chloroform analogously to the well known formation of Cl_2O or Br_2O from mercuric oxide and chlorine or bromine, respectively) to be the species reacting with *cis,cis*-1,5-cyclooctadiene (**1**).

[3] In their synthesis of 9-oxabicyclo[3.3.1]nona-2,6-diene (**13**) (see above), *Stetter et al.* [2] describe the isolation of a single 2,6-diiodo-9-oxabicyclo[3.3.1]nonane of m.p. 159–160° in 64% yield. The authors give no configurational assignment. We reinvestigated their procedure and obtained not a single diiodo compound but a mixture of three isomeric diiodides [72% relative to *cis,cis*-1,5-cyclooctadiene (**1**)]. Separation by column chromatography yielded 10% of **5**, 22% of **6**, and 32% of **7**. The product of m.p. 159–160° described by *Stetter et al.* corresponds to our isomer **7**. It can easily be isolated from the reaction mixture by fractional crystallization.

[4] The results of our studies on the oxymercuration reaction itself and the subsequent substitution of the halomercury compounds are the subject of a forthcoming paper.

Chart 2


8
7
1
6
O9
2
5
3
4
resp.
O
8
9
2
3
4
5
6
7
3
4
2
5
O9
1
6
8
7
11
10
12
RO
RO
14 R = H
15 R = Ac
16 R = H
17 R = Ac
13

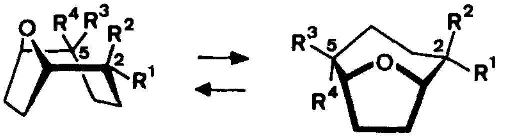
compounds in a chair-chair conformation[5]). Corresponding bands in the IR. spectra of **2**, **3**, and **4** are missing.

Conclusive proof for the ring skeletons were easily determined by reducing each diiodo compound individually with *Raney* nickel. From the three stereoisomers **2**, **3**, and **4** the known 9-oxabicyclo[4.2.1]nonane (**8**) [6] was obtained, whereas **5**, **6**, and **7** yielded the known 9-oxabicyclo[3.3.1]nonane (**10**) [7].

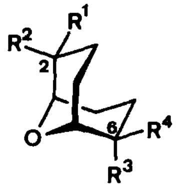
The orientation of the iodine atoms, *i.e.* the configuration at C-2 and C-5 in the diiodo compounds **2**, **3**, and **4** (see **a** and **b** in Chart 3), the configuration at C-2 and C-6 in **5**, **6**, and **7** (see **c** in Chart 3), and the configuration at C-2 in the monoiodides **11** and **12** (see **d** in Chart 3) could be derived from spectroscopic measurements and chemical transformations.

A first information was obtained from the NMR. spectra of the three 2,6-diiodo-9-oxabicyclo[3.3.1]nonanes **5**, **6**, and **7**. Between δ 4.0 and 5.0 the spectra of **5** and **7** both show two multiplets (two protons each). The signal at higher field (δ 4.05 and 4.22, resp.) is assigned to the protons at C-1 and C-5, the one at lower field (δ 4.62 and 4.53, resp.) to the protons at C-2 and C-6. Contrary to these spectra the one of **6** gives rise to four multiplets in the same region, which are assigned to the protons at C-1 (δ 4.05), C-5 (δ 4.26), C-6 (δ 4.55), and C-2 (δ 4.60). The simpler spectra of **5** and **7** are indicative of higher molecular symmetry and, therefore, support the assignment of the *endo,exo*-orientation of the iodine atoms at C-2 and C-6 in **6**. The correctness of this argument has been put on a firmer basis by comparing the line widths of the HC-2 and HC-6 signals in **5**, **6**, and **7**. In compounds with an *endo*-equatorial iodine (at C-2 and C-6 in **5** and at C-2 in **6**) the proton at the same carbon is axial. As a consequence it should

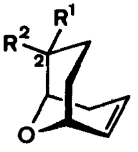
Chart 3. *Three-dimensional representations of* **2**, **3**, **4**, **5**, **6**, **7**, **11**, *and* **12**



a **b**



c



d

	R¹	R²	R³	R⁴
2	I	H	H	I
3	I	H	I	H
4	H	I	I	H
5	I	H	H	I
6	I	H	I	H
7	H	I	I	H
11	I	H		
12	H	I		

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[5]) See *Brown et al.* [4] and footnote 3 in [5].

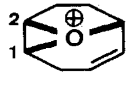
couple more strongly with the protons of the adjacent methylene group than the proton in a compound with an *exo*-axial iodine (at C-6 in **6** and at C-2 and C-6 in **7**), where the proton at the same carbon is equatorial. The spectra of **5**, **6**, and **7** are in full agreement with this prediction[6].

Support for the stereochemical assignments of the iodine atoms was obtained by the investigation of the base treatment (in a 10% methanolic potassium hydroxide solution) of the three 2,6-diiodo-9-oxabicyclo[3.3.1]nonanes **5**, **6**, and **7** as well as of the two 2-iodo-9-oxabicyclo[3.3.1]nonenes **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 and C-6, respectively, made already on the basis of NMR. analysis (see the three-dimensional representations **c** and **d** in Chart 3): in **5** both iodine atoms and in **11** the single one *endo*-equatorial, in **6** one of them *endo*-equatorial and the other *exo*-axial, in **7** both and in **12** the single one *exo*-axial. The *endo,endo*-diiodo compound **5** showed by far the lowest reactivity. After 2 h at reflux one obtained 63.5%[7] of unreacted starting material **5** and 18%[7] of the *endo*-monoiodo compound **11**. Even after $7^{1}/_{2}$ h of reflux, still 44%[7] of **5** was recovered. However, similar treatment of the *endo,exo*-diiodide **6** for only 10 min gave almost quantitatively[7] **11**. In both cases diene **13** [2] was detected only in traces at the best. Contrary to the above results, already treatment of the *exo,exo*-diiodide **7** for only 10 min of reflux showed quantitative conversion to yield 66.5%[7] of *exo*-monoiodo compound **12** and 17.5%[7] of diene **13**; 2 h of reflux afforded exclusively diene **13** (84.5%[7]).

The same trend of reactivity was observed with the monoiodo compounds **11** and **12**. After 2 h of reflux the *endo*-monoiodide **11** was recovered (95%[7]) unchanged whereas the *exo*-monoiodide **12** was almost quantitatively[7] converted into diene **13**.

That an axial iodine prefers elimination of HI over substitution was also demonstrated by treatment of the *exo*- and *endo*-monoiodo compounds **12** and **11**, respectively, with a boiling 10% aqueous NaOH solution. The *exo*-monoiodide **12** was almost quantitatively converted to the diene **13**. The *endo*-monoiodide **11**, however, underwent mainly substitution, yielding a mixture of the two alcohols **14** and **16**. The exact ratio of the two products formed was determined by NMR. analysis of their acetates **15** and **17**[8], which were also obtained directly from the *endo*-monoiodide **11** upon treatment with silver acetate in acetic acid. **14** and **15** still possess the bicyclo[3.3.1]-

Chart 4



e

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[6] Qualitatively the same information was obtained from the NMR. spectra of *endo,endo*- and *exo,exo*-2,6-dihydroxy- and -2,6-diacetoxy-9-oxabicyclo[3.3.1]nonanes [1] [8].

[7] The indicated percentages are yields of products after isolation and purification as e.g. chromatography, recrystallization or distillation.

[8] Compounds **14–17** were identical with authentic samples obtained by a different synthetic approach, see [8] and unpublished results by *C. Ganter* & *K. Wicker*.

nonane skeleton, whereas **16** and **17** are bicyclo[4.2.1]nonane derivatives. The latter obviously are products of a molecular rearrangement which most likely involves an oxonium ion (neighbouring-group participation) of type **e** as an intermediate.

Such an oxonium ion results from an intramolecular attack of an unshared oxygen electron pair at C-2. Addition of a hydroxyl or an acetate anion can proceed either at C-1 (furnishing the alcohol **16** or the acetate **17**, resp.) or at C-2 (affording the alcohol **14** or the acetate **15**, resp.). The stereochemical course of the reaction implies that the outgoing iodine as well as the incoming hydroxyl or acetate group are *endo* oriented[9]).

The molecular rearrangement via an oxonium ion was subsequently used to assign the configurations at C-2 and C-5 in the 2,5-diiodo-9-oxabicyclo[4.2.1]nonanes **2**, **3**, and **4**. Among several reaction conditions examined (see Experimental Section), the best results were obtained with a I_2–KI–H_2O–C_2H_5OH solution. After 15 h of reflux, the *endo,endo*-[4.2.1]-diiodide **2** yielded 96%[7]) of *endo,endo*-[3.3.1]-diiodide **5**. The *endo,exo*-[4.2.1]-compound **3** gave 68%[7]) of *endo,exo*-[3.3.1]-diiodide **6**, whereas the *exo,exo*-[4.2.1]-diiodo compound **4** did not rearrange at all. These results allow a conclusive configurational assignment at C-2 and C-5 in the three stereoisomeric 2,5-diiodo-9-oxabicyclo[4.2.1]nonanes **2**, **3**, and **4**.

The NMR. spectra of **2**, **3**, and **4** could not be interpreted in such details as those of the corresponding [3.3.1]-diiodides **5**, **6**, and **7**. Nevertheless, the spectra of the *endo,endo* and the *exo,exo* compounds (**2** and **4**, respectively) were again more simply structured than the spectrum of **3**, *i.e.* they show only two multiplets (two protons each) between δ 4.0 and 5.1. The multiplet at higher field (δ 4.43 and 4.29, resp.) is assigned to the protons at C-1 and C-6, the one at lower field (δ 4.62 and 4.92, resp.) to the protons at C-2 and C-5. The greater complexity of the spectrum of the *endo,exo*-diiodide **3** indicates a less symmetrically substituted compound. It exhibits a broad multiplet at δ 4.0–4.4 (HC-1 and HC-6) and two more multiplets assigned to the protons at C-2 (δ 4.69) and C-5 (δ 5.07). The line widths of the HC-2 and HC-5 signal do not allow an unambiguous interpretation. This may be due to the greater mobility of the seven-membered ring in **2**, **3**, and **4** [compared with the six-membered rings in fixed chair-chair conformations in **5**, **6**, and **7** (see above)], which by consequence may allow several favourable conformations.

This latter interpretation finds support in results of the treatment of **2**, **3**, and **4** with methanolic potassium hydroxide solution. In no case a monoiodo-compound could be isolated. Diene **9** [3] was the only observed and isolable reaction product.

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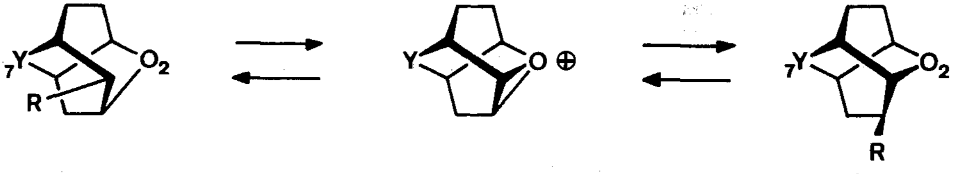
[9]) Analogous rearrangements via an oxonium ion of type **g** were observed with 2,7-dihetero-isotwistanes (**f**) and 2,7-dihetero-twistanes (**h**); see [8] and unpublished results by *C. Ganter, K. Wicker & N. Wigger.*

Chart 5



f **g** **h**

Y = O or S R = J, OAc, resp.

Probably the monoiodides can adopt conformations which are even more favourable for elimination of HI than those of the diiodides.

An interesting feature was observed in the UV. spectra of the discussed iodo-compounds. The data are listed in Table 1.

Table 1. *Ultraviolet spectra of* **2**, **3**, **4**, **5**, **6**, **7**, **11**, *and* **12**

[4.2.1]-diiodides	$\lambda_{max}(\varepsilon)$	[3.3.1]-diiodides	$\lambda_{max}(\varepsilon)$	[3.3.1]-monoiodides	$\lambda_{max}(\varepsilon)$
2	258.5 (1300)	**5**	256 (1180)	**11**	256 (600)
3	258.5 (1340)	**6**	258.5 (1260)		
4	263 (1295)	**7**	263.5 (1205)	**12**	263 (600)

Exo-oriented iodine atoms which are *cis* to the bridge oxygen O-9 show a remarkable interaction with the latter. This is evidenced in absorption maxima at longer wavelenghts, corresponding to less energetic $n \rightarrow \sigma^*$ transitions of the iodo compounds. The trend of the shifts of the absorption bands toward longer wavelengths with increasing number of *exo*-iodine atoms is a further support for the configurational assignment at C-2 and C-5 in **2**, **3**, and **4**, at C-2 and C-6 in **5**, **6**, and **7**, as well at C-2 in **11** and **12**. The only exception in this general picture is introduced by the two diiodides **2** and **3** which possess a bicyclo[4.2.1]nonane skeleton. They both exhibit the same λ_{max} at 258.5 nm regardless of an *exo*-iodine in **3**. An explanation may be derived from the possibility that the seven-membered ring in the 9-oxabicyclo[4.2.1]nonane system with two *endo* substituents prefers conformation **a** (see Chart 3) with both iodine atoms equatorial. The isomer with one *endo* and one *exo* iodine may prefer conformation **b** (see Chart 3), having again both substituents in equatorial positions.

The ETH group gratefully acknowledges the financial support of this research by *J. R. Geigy AG*, Basle.

Experimental Section

General Remarks. – *After the working up*, the organic layer was dried over $MgSO_4$ and the solvent either removed in vacuo in a rotary evaporator or carefully distilled through a *Vigreux* column.

Preparative column chromatography was performed (unless otherwise stated) on silicagel *Merck* (0.05–0.2 mm). Mostly multibore columns [9] were applied.

For *thin layer chromatography* (tlc.), *Merck* TLC-plates Silica Gel F_{254} precoated were used. The spots were located by the use of UV. light, iodine vapors or spraying the plates with conc. H_2SO_4 and subsequent heating.

Vapor phase chromatography (vpc.) was performed on an Aerograph Model A-90-P gas-chromatograph (thermal conductivity detector).

Melting points (m.p.) were measured in open capillaries in an oil bath and are uncorrected.

Ultraviolet (UV.) *spectra* were measured in C_2H_5OH solutions (unless otherwise stated); λ_{max} are given in nm, ε values added in parentheses.

Infrared (IR.) *spectra* were recorded in $CHCl_3$ solutions (unless specified otherwise); ν_{max} are given in cm^{-1}.

Nuclear magnetic resonance (NMR.) *spectra* were obtained in $CDCl_3$ at 100 MHz (unless otherwise noted). Chemical shifts are expressed in δ values (ppm) downfield from tetramethylsilane as internal standard. Multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad unresolved signal. Coupling constants (J) are measured in hertz (Hz). $W^1/_2$ means line width at half hight. Proton integration of each signal is in agreement with the given assignments.

Mass spectra (MS.) were recorded on a *Hitachi Perkin-Elmer* (RMU-6A or RMU-6D) mass spectrometer.

2,5-Diiodo-9-oxabicyclo[4.2.1]nonanes 2, 3, and 4, and 2,6-Diiodo-9-oxabicyclo[3.3.1]nonanes 5, 6, and 7. – To a solution of 6.36 g (20 mmol) of mercuric acetate in 50 ml of H_2O and 20 ml of 1N NaOH (Titrisol *Merck*) a solution of 1.08 g (10 mmol) of *cis,cis*-1,5-cyclooctadiene (**1**) in 25 ml of Tetrahydrofuran was added. The yellow color immediately formed disappeared after 130 min of vigorous stirring at room temperature. Treatment of the reaction mixture with a solution of 3.32 g of KI in 100 ml of H_2O yielded a white precipitate which was filtered off and washed twice with H_2O, twice with acetone and finally with ether to give 6.623 g of a mixture of crude *di-iodomercuri compounds*.

To a stirred slurry of the above 6.623 g of a mixture of crude di-iodomercuri compounds in 50 ml of H_2O, 100 ml of a I_2–KI–H_2O–C_2H_5OH solution (35 g of I_2, 100 g of KI, 500 ml of H_2O and 250 ml of C_2H_5OH) were added. After 20 h of stirring 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 2.954 g of an oily mixture of diiodides **2**–**7**.

A first chromatography in ether-hexane-(1:1) on 400 g of silicagel afforded 1.39 g of a mixture of the diiodo compounds **2**, **3**, **5**, and **6**, 683 mg of **7** and 652 mg of **4**. The above first fraction (1.39 g of the mixture of **2**, **3**, **5**, and **6**) was re-chromatographed in ether-hexane-(1:8) on 200 g of silicagel. Elution gave 775 mg of isomer **3**, 130 mg of a mixture of **2** and **5** as well as 256 mg of **6**. The mixture of **2** and **5** (130 mg) was separated into pure compounds by treatment with boiling hexane. Isomer **5** was insoluble and could be filtered off (51 mg). From the hexane solution 79 mg of **2** were recovered.

The total yield of isolated pure diiodo compounds **2**–**7**[10]), relative to *cis,cis*-1,5-cyclooctadiene (**1**), was therefore 66%: 2% of **2**, 20.5% of **3**, 17% of **4**, 1.5% of **5**, 7% of **6**, and 18% of **7**.

endo, endo-*2,5-Diiodo-9-oxabicyclo[4.2.1]nonane* (**2**). Recrystallized from hexane and sublimed (60°/0.01 Torr): m.p. 81–82°. IR.: 1472, 1036, 916, 897. UV.: 258.5 (1300). NMR.: 1.8–2.6/*bm* H_2C-3, -4, -7 and -8; 4.43/*m* ($W^1/_2$ approx. 13 Hz) HC-1 and -6; 4.62/*m* ($W^1/_2$ approx. 16 Hz) HC-2 and -5. MS.: *m/e* 378 (M^+).

$C_8H_{12}I_2O$ Calcd C 25.42 H 3.20% Found C 25.12 H 3.19%

endo, exo-*2,5-Diiodo-9-oxabicyclo[4.2.1]nonane* (**3**). Recrystallized from CH_2Cl_2 and sublimed (80°/0.1 Torr): m.p. 107–108°. IR.: 1472, 1063, 1052, 981, 929, 909. UV.: 258.5 (1340). NMR.: 1.5 to 2.5/*bm* H_2C-3, -4, -7 and -8; 4.0–4.4/*m* HC-1 and -6; 4.69/*m* ($W^1/_2$ approx. 10 Hz) HC-2; 5.07/*m* ($W^1/_2$ approx. 13 Hz) HC-5. MS.: *m/e* 378 (M^+).

$C_8H_{12}I_2O$ Calcd C 25.42 H 3.20% Found C 25.63 H 3.28%

exo, exo-*2,5-Diiodo-9-oxabicyclo[4.2.1]nonane* (**4**). Recrystallized from CH_2Cl_2 and sublimed (100°/0.1 Torr): m.p. 149–151° (decomp.). IR.: 1471, 1058, 1027, 998, 958, 911. UV.: 263 (1295). NMR.: 1.4–2.7/*m* H_2C-3, -4, -7 and -8; 4.29/*m* ($W^1/_2$ approx. 14 Hz) HC-1 and -6; 4.92/*m* ($W^1/_2$ approx. 13 Hz) HC-2 and -5. MS.: *m/e* 378 (M^+).

$C_8H_{12}I_2O$ Calcd C 25.42 H 3.20% Found C 25.28 H 3.22%

endo, endo-*2,6-Diiodo-9-oxabicyclo[3.3.1]nonane* (**5**). Recrystallized from hexane and sublimed (95°/0.1 Torr): m.p. 120–121°. IR.: 2990, 1482, 1107, 1069, 1022, 963, 897, 854. UV.: 256 (1180). NMR.: 1.8–3.0/*bm* H_2C-3, -4, -7 and -8; 4.05/*m* (three main peaks, line separation 5 Hz) HC-1 and -5; 4.62/*m* (five main peaks, line separation 6 Hz) HC-2 and -6. MS.: *m/e* 378 (M^+).

$C_8H_{12}I_2O$ Calcd C 25.42 H 3.20% Found C 25.16 H 3.27%

endo, exo-*2,6-Diiodo-9-oxabicyclo[3.3.1]nonane* (**6**). Recrystallized from CH_2Cl_2 and sublimed (85°/0.02 Torr): m.p. 106–107°. IR.: 2998, 1480, 1080, 1046, 1022, 976, 898, 852. UV.: 258.5 (1260). NMR.: 1.4–2.9/*bm* H_2C-3, -4, -7 and -8; 4.05/*m* (three main peaks, line separation 5 Hz) HC-1; 4.26/*m* (two main peaks, line separation 6 Hz) HC-5; 4.55/*m* ($W^1/_2$ approx. 9 Hz) HC-6; 4.60/*m* (five main peaks, line separation 6 Hz) HC-2. MS.: *m/e* 378 (M^+).

$C_8H_{12}I_2O$ Calcd C 25.42 H 3.20% Found C 25.51 H 3.05%

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[10]) The diiodides **2**–**7** show characteristically different retention times in vpc. using, e.g., a 10′ × $^1/_4$″ column of 2% SE-30 on 60–80 mesh chromosorb W.

exo, exo-*2,6-Diiodo-9-oxabicyclo[3.3.1]nonane* (**7**). Recrystallized from CH_2Cl_2 and sublimed (105°/0.04 Torr): m.p. 162–163°. IR.: 2998, 1471, 1107, 1033, 899, 859. UV.: 263.5 (1205). NMR.: 1.3–1.8/*m* (2 protons) and 1.8–2.7/*m* (6 protons) H_2C-3, -4, -7 and -8; 4.22/*m* (two main peaks, line separation 6 Hz) HC-1 and -5; 4.53/*m* ($W^{1}/_{2}$ approx. 9 Hz) HC-2 and -6. MS.: *m/e* 378 (M^+).

$C_8H_{12}I_2O$ Calcd C 25.42 H 3.20% Found C 25.06 H 3.16%

Treatment of the Diiodo Compounds 2–7 with *Raney* Nickel. – 378 mg (1 mmol) of the corresponding diiodo compound were dissolved in a solution of 108 mg of KOH in 40 ml of CH_3OH. After addition of a slurry of approx. 1 g of *Raney* nickel in 3 ml of CH_3OH, the reaction mixture was stirred for 20 min at 50° and subsequently worked up at 0°. Filtration through Celite was followed by thorough washing of the residue with ether. To the filtrate 400 ml of a saturated NaCl solution were added. The water-layer was twice extracted with ether and the combined ether extracts washed twice with saturated NaCl solution and dried. The ether was carefully removed on a water-bath (50°) through a *Vigreux* column. The residue was finally distilled (80°/0.1 Torr). The results are listed in Table 2. Identification by tlc. (CH_2Cl_2 or benzene), IR. and NMR.

Table 2. *Treatment of Compounds* **2–7** *with* Raney *Nickel*

starting material (diiodide)	product	
	8 [6]	**10** [7]
378 mg of **2**	103 mg (81%)	
378 mg of **3**	109 mg (86.5%)	
378 mg of **4**	99 mg (79%)	
378 mg of **5**		101 mg (80%)
378 mg of **6**		96 mg (76%)
378 mg of **7**		98 mg (78%)

Treatment of the 2,5-Diiodo-9-oxabicyclo[4.2.1]nonanes 2, 3, and 4 with KOH–CH_3OH. – *General remarks.* The following procedure was applied: The corresponding diiodo compound was dissolved in a 10% solution of KOH in CH_3OH and the reaction mixture was stirred at room temperature or refluxed. After a certain time it was cooled by adding ice and water and subsequently twice to three times extracted with CH_2Cl_2. The combined organic layers were washed twice with saturated NaCl solution and dried. The solvent was carefully removed by distillation through a *Vigreux* column. The reaction was followed by tlc. and the products identified by tlc., IR. and NMR.

a) *Treatment of* **2**. – aa) *22 h at room temperature.* 700 mg (1.85 mmol) of **2** in 15 ml of KOH solution; yield 681 mg (97%) of starting material **2**.

ab) *1 h reflux.* 378 mg (1 mmol) of **2** in 20 ml of KOH solution. 225 mg of isolated material were chromatographed in CH_2Cl_2 on 26 g of silicagel. The first fraction gave 155 mg (41%) of starting material **2**. Further elution and distillation (80°/11 Torr) of the product yielded 52 mg (43%) of *9-oxabicyclo[4.2.1]nona-2.4-diene* (**9**) [3]. – A second run with 378 mg (1 mmol) of **2** afforded 156 mg (42%) of unchanged **2** and 42 mg (34.5%) of diene **9** [3].

b) *Treatment of* **3**. – ba) *64 h at room temperature.* 539 mg (1.4 mmol) of **3** in 20 ml of KOH solution; yield 519 mg (96%) of starting material **3**.

bb) *1 h reflux.* 378 mg (1 mmol) of **3** in 20 ml KOH solution. The isolated material was chromatographed in CH_2Cl_2 on 26 g of silicagel. The first fraction gave 215 mg (57%) of starting material **3**. Further elution and distillation (80°/11 Torr) of the product yielded 32.5 mg (30%) of *diene* **9** [3]. – A second run (539 mg of **3**) afforded 340 mg (63%) of **3** and 50 mg (29%) of diene **9** [3].

c) *Treatment of* **4**. – ca) *15 h at room temperature.* 20 mg (0.05 mmol) of **4** in 15 ml of KOH solution; yield 18 mg (90%) of starting material **4**.

cb) *2 h reflux.* 378 mg (1 mmol) of **4** in 20 ml of KOH solution. The isolated material was distilled (80°/11 Torr) to yield 105 mg (83%) of *diene* **9** [3].

Treatment of the 2,6-Diiodo-9-oxabicyclo[3.3.1]nonanes 5, 6, and 7 with KOH–CH_3OH. – *General remarks.* The following procedure was applied unless specified otherwise:

378 mg (1 mmol) of the corresponding diiodo compound were dissolved in 15 ml of a 10% solution of KOH in CH_3OH and the reaction mixture was refluxed. After a certain time it was worked up as above. The reaction was followed by tlc. (benzene).

a) *Treatment of* **5**. – aa) *2 h*. The 338 mg of isolated material were chromatographed in CH_2Cl_2 on 33 g of silicagel. Sublimation (95°/0.05 Torr) of the product (248 mg) from the first fraction gave 240 mg (63.5%) of unchanged starting material **5**. Further elution afforded 57 mg of a product which after distillation (80°/0.1 Torr) yielded 47 mg (18%) of viscous endo-*2-iodo-9-oxabicyclo-[3.3.1]non-6-ene* (**11**). IR.: 1656, 1456, 1069, 1056, 1042, 1019, 968, 942, 889, 878, 861. UV.: 256 (600). NMR.: 1.0–3.0/*m* H_2C-3, -4 and -8; 4.22/*m* (three main peaks, line separation approx. 5 Hz) HC-1; 4.35–4.70/*m* HC-2 and -5; 5.72/*d* $J_{6,7} = 10$ (further splitting by $J_{5,6} = 4$ and $J_{6,8} = J_{6,8'} = 2$) HC-6; 6.00/*d* $J_{6,7} = 10$ (further splitting by $J_{7,8} = J_{7,8'} = 3.5$) HC-7. MS.: *m/e* 250 (M^+), 123 ($M^+ - 127$).

$C_8H_{11}IO$ Calcd C 38.42 H 4.43% Found C 38.07 H 4.56%

ab) *7½ h*. The 321 mg of isolated material were chromatographed in benzene on 30 g of silicagel. Sublimation (95°/0.1 Torr) of the product (175 mg) from the first fraction gave 170 mg (44%) of unchanged starting material **5**. Further elution afforded 141 mg of a product which after distillation (80°/0.1 Torr) yielded 106 mg (42.5%) of *endo*-monoiodide **11** (see above).

ac) *63 h*. The 133 mg of isolated material were chromatographed in CH_2Cl_2 on 14 g of silicagel. The first fraction consisted of 2 mg (0.5%) of crude unreacted starting material **5**. Further elution afforded 112 mg of a product which after distillation (80°/0.1 Torr) gave 100 mg (40%) of *endo*-monoiodide **11** (see above).

b) *Treatment of* **6**. 30 min of reflux. Distillation (80°/0.1 Torr) of the isolated material (254 mg) yielded 241 mg (96.5%) of endo-*monoiodide* **11** (see above).

c) *Treatment of* **7**. – ca) *10 min*. 500 mg (1.32 mmol) of **7** in 20 ml of a 10% methanolic KOH solution. The 304 mg of isolated material were chromatographed in CH_2Cl_2 on 30 g of silicagel. Distillation (75°/0.06 Torr) of the product (236 mg) of the first fraction gave 220 mg (66.5%) of exo-*2-iodo-9-oxabicyclo[3.3.1]non-6-ene* (**12**). m.p. 50.5–51.5° (after sublimation at 45°/0.01 Torr). IR.: 1657, 1432, 1090, 1060, 1052, 1039, 1022, 1008, 943, 923, 890, 880, 845. UV.: 263 (600). NMR.: 1.0–3.0/*m* H_2C-3, -4 and -8; 4.10–4.45/*m* HC-1 and -5; 4.55/*m* ($W^1/_2$ approx. 7 Hz) HC-2; 5.60–6.05/*m* HC-6 and -7. MS.: *m/e* 250 (M^+), 123 ($M^+ - 127$).

$C_8H_{11}IO$ Calcd C 38.42 H 4.43% Found C 38.30 H 4.41%

Further elution afforded 51 mg of a product which after distillation (80°/11 Torr) yielded 28 mg (17.5%) of *9-oxabicyclo[3.3.1]nona-2,6-diene* (**13**) [2].

cb) *2 h*. Distillation (80–85°/11 Torr) of the isolated homogeneous material (124 mg) yielded 103 mg (84.5%) of diene **13** [2].

Treatment of the Monoiodo Compounds 11 and 12 with KOH–CH_3OH. – *General remarks*. 250 mg (1 mmol) of the corresponding monoiodo compound were dissolved in 10 ml of a 10% methanolic KOH solution. The reaction mixture was refluxed for 2 h, cooled by adding ice and water and three times extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were washed twice with saturated NaCl solution and dried. The solvent was carefully removed through a *Vigreux* column. The reaction was followed by tlc. (benzene) and the products identified by IR., NMR. and tlc.

a) *Treatment of* **11**. Distillation (80°/0.1 Torr) of the isolated material yielded 238 mg (95%) of unreacted starting material **11**. Diene **13** [2] could only be detected in traces by tlc.

b) *Treatment of* **12**. Distillation (80°/11 Torr) of the isolated homogeneous material (106 mg) yielded 90 mg (74%) of *diene* **13** [2].

Treatment of the Monoiodo Compounds 11 and 12 with aqueous NaOH solution. – a) *Treatment of* **12**: 250 mg (1 mmol) of the *exo*-iodide **12** in 15 ml of a 10% aqueous NaOH solution was refluxed for 2 h. The reaction mixture was twice extracted with ether and the organic phase washed with saturated NaCl solution. The crude product (106 mg) yielded after distillation (80°/11 Torr) 90 mg (74%) of *diene* **13** [2].

b) *Treatment of* **11**: An emulsion of 250 mg (1 mmol) of the *endo*-iodide **11** in 15 ml of a 10% aqueous NaOH solution was heated to reflux for 20 h. The two phases were separated and the aqueous one continuously extracted for 24 h with ether. To the organic phase again 15 ml of a

10% aqueous NaOH solution were added and the reaction mixture heated to reflux for further 20 h. The aqueous phase obtained was continuously extracted for 24 h with ether. The ether extracts were combined and the solvent removed by distillation to yield 157 mg of crude product. Chromatography in CH_2Cl_2 on 15 g of silicagel gave 47 mg (18%) of distilled (135°/13 Torr) starting material **11** and 6 mg (5%) of distilled (85°/13 Torr) *diene* **13** [2].

Further elution with ether and distillation (125°/12 Torr) of the product gave 71 mg (51.5%) of a *mixture of the alcohols* **14** *and* **16**. The ratio of **14**:**16** was determined after acetylation (see below).

c) *Acetylation of the mixture of alcohols* **14** *and* **16**. 68 mg of the above mixture of the alcohols **14** and **16** were acetylated with 0.5 ml of acetic anhydride in 0.5 ml of pyridine at 80° for 2 h. 1 ml of methanol was added with cooling. Afterwards the reaction mixture was evaporated to dryness by azeotropic distillation with benzene, adding six times 10 ml of benzene. 82 mg of crude product were obtained, which after distillation (135–140°/20 Torr) yielded 77 mg (88%) of a mixture of the two *acetates* **15**[8]) *and* **17**[8]) in the ratio of 88:12 (as determined by NMR. analysis, see Table 3).

Table 3. *NMR. Analysis of the Mixture of the two Acetates* **15** *and* **17**

signals δ	integral ratio	assignment	
		15	**17**
1.45–2.85/*bm*	6	H_2C-3, -4 and -8	H_2C-3, -7 and -8
2.02/*s*	3	2-$OCOCH_3$	2-$OCOCH_3$
4.04–4.33/*bm*	1.76	HC-1 and -5	
4.39–4.67/*bm*	0.24		HC-1 and -6
4.81–5.16/*bm*	1	HC-2	HC-2
5.32–6.08/*bm*	2	HC-6 and -7	HC-4 and -5

Treatment of *endo*-2-Iodo-9-oxabicyclo[3.3.1]non-6-ene (11) with Silver acetate. – A mixture of 60 mg (0.24 mmol) of the *endo*-iodide **11** and 170 mg of silver acetate in 5 ml of acetic acid was stirred at 80° for 25 min. After addition of 10 ml of CH_2Cl_2–H_2O the reaction mixture was neutralized by adding first anh. sodium carbonate and subsequently saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous one twice extracted with CH_2Cl_2. After

Table 4. *Isomerization Experiments with the Diiodo Compounds* **2**, **3**, *and* **4**

starting material	reaction conditions	time h	temperature	product distribution
90 mg **2**	200 mg I_2, 50 ml $CHCl_3$	7	room temp.	87 mg (97%) **2**
28 mg **2**	63 mg I_2, 15 ml $CHCl_3$	15	reflux	26 mg (93%) **2**+**5** (ratio 3:1)[a]
57 mg **2**	160 mg KI, 30 ml H_2O	7	room temp.	52 mg (91%) **2**
85 mg **2**	300 mg KI, 50 ml H_2O	15	reflux	65 mg (76%) **2**+**5** (ratio approx. 1:1)[a]
159 mg **2**	20 ml I_2–KI–H_2O–C_2H_5OH solution[b]	7	room temp.	148 mg (91.5%) **2**
40 mg **2**	10 ml I_2–KI–H_2O–C_2H_5OH solution[b]	15	reflux	38 mg (96%) **5**
115 mg **3**	20 ml I_2–KI–H_2O–C_2H_5OH solution[b]	7	room temp.	105 mg (91%) **3**
51 mg **3**	10 ml I_2–KI–H_2O–C_2H_5OH solution[b]	15	reflux	35 mg (68%) **6**[c]
40 mg **4**	20 ml I_2–KI–H_2O–C_2H_5OH solution[b]	7	room temp.	36 mg (90%) **4**
40 mg **4**	10 ml I_2–KI–H_2O–C_2H_5OH solution[b]	15	reflux	22 mg (52%) **4**[c]

[a] Ratio determined by NMR. analysis.
[b] 35 g I_2, 100 g KI, 500 ml H_2O, 250 ml C_2H_5OH.
[c] Lower yields mainly due to formation of volatile diene **9** [3].

removal of the solvent 41 mg (94%) of a *mixture of the two acetates* **15**[8]) *and* **17**[8]) were obtained. The ratio of **15** to **17** (as determined by NMR. see above) was 4:1.

Isomerization Experiments with the Diiodo Compounds 2, 3, and 4. – The experimental details and the results are listed in Table 4.

The elemental analyses were carried out in the Microanalytical Laboratory of the ETH Zürich (Mr. *W. Manser*). Nuclear magnetic resonance spectra were measured in our Instrumental Division (Prof. *W. Simon*). For the mass spectra we are indebted to PD Dr. *J. Seibl.*

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192. ESR. Spectra of the Radical Anion of Dimethyl-phenyl-phosphine

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Herrn Prof. Dr. *Eugen Müller* zum 65. Geburtstag gewidmet

(27. VII. 70)

Summary. ESR. spectra of the radical anion ($I^{\ominus}$) produced from dimethyl-phenyl-phosphine (I) both by electrolysis and reaction with alkali metals have been studied upon variation of temperature. The coupling constant assigned to the ^{31}P nucleus depends strongly on temperature, whereas the coupling constants attributed to protons do not exhibit such a dependence. The π-spin populations at the benzene ring of $I^{\ominus}$ give evidence – in accordance with other experimental data [1] [2] – that the dimethylphosphino substituent is electron-attracting. This effect is thought to be due mainly to $P \leftarrow C_{\pi}$ delocalization, which is analogous to the Si–C_{π} interaction in trimethylsilyl-substituted π-systems [3].

The ESR. spectrum previously [4] ascribed to $I^{\ominus}$ is shown to arise from a secondary radical. The formation and structure of this radical are briefly discussed.

A dimethylphosphino group attached to a benzene ring behaves as an electron-attracting substituent, in sharp contrast to the structurally related dimethylamino group. This behaviour has been evidenced by various physico-chemical properties of dimethyl-phenyl-phosphine (I) as compared with those of N,N-dimethylaniline (II). For example, the dipole moments (μ) of the two compounds point in opposite directions [1], and their ionisation potentials (IP) differ by as much as 1.35 eV [2].

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