

201. Preparation of 1,2*exo*- and 1,2*endo*-Diiodo-bicyclo[2.2.1]heptane

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Summary

1,2*exo*-Diiodo-norbornane (**4**) was prepared from norcamphor hydrazone by oxidative iodination and subsequent rearrangement of the 2,2-diiodo-bicyclo[2.2.1]heptane (**2**). The stable α -iodohydrazone **11** was obtained from 1-iodo-bicyclo[2.2.1]heptan-2-one (**10**), which itself was prepared from 1-iodo-norbornene (**5**). Subsequent treatment of **11** with iodine lead to 1,2,2-triiodo-norbornane (**12**) and 1,2-diiodo-norborn-2-ene (**13**). 1,2*endo*-Diiodo-norbornane (**14**) was obtained by stereoselective reduction of **12** with tributyltinhydride or by reaction of **13** with diimide.

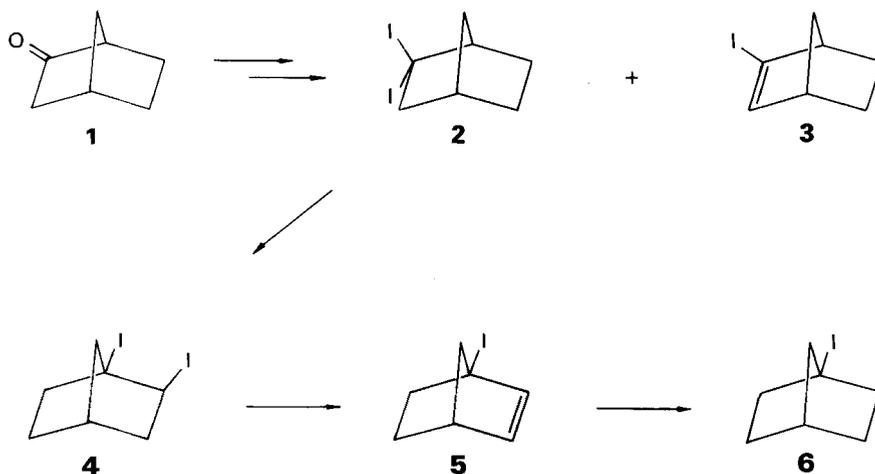
One of the well-established methods for the preparation of bridgehead olefins is the reductive bisdehalogenation of appropriate dihalides [1]. This procedure was particularly successful for the generation of $\Delta^{1,2}$ -norbornene [2]. In the course of further transformations and mechanistic investigations of these reductive bisdehalogenations, the two configurational isomers of 1,2-diiodo-norbornane were needed. We now describe the preparation of 1,2*exo*-diiodo-norbornane (**4**) and 1,2*endo*-diiodo-norbornane (**14**) in detail.

Results and discussion. – As reported previously 1,2*exo*-diiodo-norbornane (**4**) had been obtained from the hydrazone of norbornan-2-one (**1**) [2]. The key step in this preparation is the oxidation of the hydrazone of **1** with iodine in the presence of a base (*Barton-Sternhell* reaction) [3] which leads to a mixture of 2,2-diiodo-norbornane (**2**) and 2-iodo-norborn-2-ene (**3**). In variance with the published procedure, a mixture of hydrazone and triethylamine was added to a solution of iodine in benzene. However, these inverse reaction conditions had no significant effect on yield and ratio of **2** and **3**.

Lewis-acid catalyzed rearrangement of **2** gave **4** in 42% yield (over two steps). The structure of this compound was established by transformation into the known 1-iodo-norbornane (**6**) via 1-iodo-norbornene (**5**) [4] (*cf. Scheme 1*). A detailed

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Scheme 1



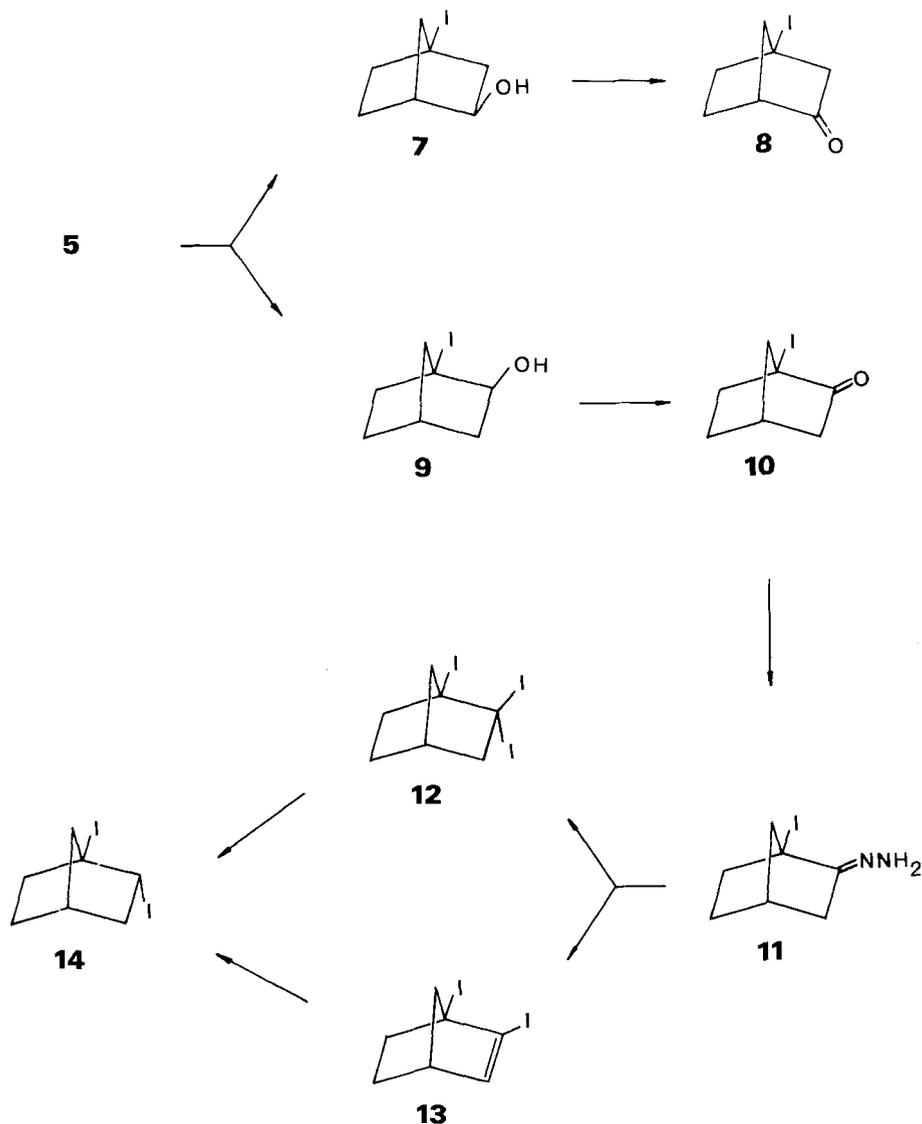
$^1\text{H-NMR}$. analysis by the INDOR method provided convincing evidence for the *exo*-configuration in **4** [5].

With 1-iodo-norborn-2-ene (**5**) in hand, it appeared possible to prepare 1,2-*endo*-diodo-norbornane (**14**) by procedure which had been so successful for the preparation of 2-*endo*-iodo-norbornane from norbornene [6]. However, when **5** was treated with borane, followed by CH_3ONa and ICl , **6** and products formally derived from $\Delta^{1,2}$ -norbornene were observed; when ICl was replaced by furan, 3% of the furan adducts which are indicative of free $\Delta^{1,2}$ -norbornene [2] were obtained. It was therefore decided to follow the route outlined in *Scheme 2*.

Hydroboration of **5** gave a mixture of the iodoalcohols **7** and **9** in a 34:66 ratio [7]. Subsequent oxidation of the separated alcohols with pyridinium chlorochromate led to the stable, colorless iodoketones **8** and **10**. The structure of these compounds is based on spectroscopic data; their $^{13}\text{C-NMR}$ and mass spectra were particularly informative. The chemical shift of the individual ^{13}C -signals of the isomers **8** and **10** were compared with calculated values. These latter data were obtained by addition of the corresponding values in 1-iodo-bicyclo[2.2.1]heptane (**6**) [8] and bicyclo[2.2.1]heptan-2-one (**1**) [8] and subtracting from it the corresponding values of bicyclo[2.2.1]heptane (**15**) [9]. This method has been tested in the closely related case of 1-chloro-bicyclo[2.2.1]heptan-2-one *vs.* 1-chloro-bicyclo[2.2.1]heptan-3-one [10]; the structure of these regioisomers had been determined by a different route [11].

Comparison of the experimental with the calculated values for the individual chemical shifts in the iodoketones **8** and **10** shows good agreement, except for the substituted bridgehead C-atom and the ^{13}C of the carbonyl group (*Table 2*). These rather large differences between the experimental and calculated values in the ^{13}C -shifts of C(1) and C(2) in **10**, resp. C(1) and C(3) in **8** are however acceptable, because similar discrepancies have been observed in the pair of 1-chloro-bicyc-

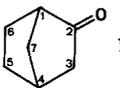
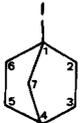
Scheme 2



lo[2.2.1]heptan-2-one and 1-chloro-bicyclo[2.2.1]heptan-3-one [10]. The mass spectra of **8** and **10** show different fragmentation patterns in the region $m/z > 100$.

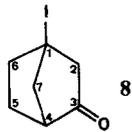
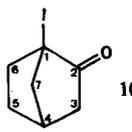
Whereas **10** shows $m/z = 192$ ($M^+ - 44$) as base peak, the intensity of this signal in **8** is only 0.4% of the base peak which in this compound is $m/z = 81$. Also, the intensity of M^+ in **10** is larger than $m/z = 109$ ($M^+ - I$), whereas it is much smaller in **8**. These observations are corroborated by the mass spectra of the corresponding chloroketones [10].

Table 1. ^{13}C -NMR-shifts of reference compounds^{a)}

C-Atom			
1	49.3	37.7	36.4
2	216.8	43.0	29.8
3	44.7	32.1	29.8
4	34.8	34.6	36.4
5	26.7	32.1	29.8
6	23.7	43.0	29.8
7	37.1	50.8	38.4

a) δ -Values in ppm, relative to TMS.

Table 2. Experimental and calculated δ -values for the ^{13}C -NMR. shifts in **8** and **10**

C-Atom				
	Exper.	Calc. ^{a)}	Exper.	Calc.
1	27.1	36.1	44.9	50.6
2	56.4	57.9	208.8	230.0
3	211.7	219.1	42.3	47.0
4	49.07	47.5	35.4	33.0
5	26.1	26.0	29.9	29.0
6	40.8	39.9	37.4	36.9
7	49.2	49.5	49.2	49.5

a) For calculation, the numbering in **1** of Table 1 is based on exchange **1** \leftrightarrow **4** accordingly with the other centers.

Reaction of **10** with hydrazine in refluxing CHCl_3 yielded the α -iodohydrazone **11** in excellent yield. This stable, crystalline compound, which to our knowledge is the first example of a stable α -iodohydrazone to be reported, could be heated up to its melting point at 85°C without decomposition [12] and thus further supports the importance of *Bredt's rule* [1]. *Sternhell-Barton* reaction of **11** gave a mixture of 1,2,2-triiodo-dobicyclo[2.2.1]heptane (**12**) and 1,2-diiodo-bicyclo[2.2.1]hept-2-ene (**13**) in a 63:37 ratio. Reduction of **12** with tributyltinhydride in ether yielded a mixture of **14** and **4** in a 72:28 ratio, from which pure **14** could be obtained by HPLC. Alternatively, pure **14** could be prepared from the rather unstable 1,2-diiodo-norborn-2-ene (**13**) by reduction with diimide.

The two diastereoisomers **4** and **14** show only small differences in their physical properties. Particularly noteworthy are their ^1H -NMR. spectra: the chemical shift and coupling pattern of the proton in 2*endo*- and 2*exo*-position are too similar to allow immediate distinction between **4** and **14**. However, they show clear differences in their ^{13}C -NMR. spectra. Similarly their mass spectra, run under identical condi-

tions, show only small differences in intensity. The chemistry of these rather stable 1,2-diiodoalkanes will be described elsewhere [13].

Experimental Part

Reactions have not been optimized. If not stated otherwise, reactions were worked up by pouring the reaction mixture on ice water and extracting three times with ether. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo* (*i. v.*) on a rotatory evaporator at temperatures $<40^\circ$. Silica gel used for preparative separations was *Merck Silicagel 60*; silica gel plates *Merck 60F-254* were used for thin layer chromatography. Melting points were taken in a *Tottoli* melting-point apparatus in an open capillary tube and are uncorrected. UV. spectra were measured in hexane spectograde on *Perkin-Elmer 402* and *554* instruments. If not stated otherwise, IR. spectra (bands in cm^{-1}) were measured in $CHCl_3$ on *Perkin-Elmer 125*, *257* and *457* instruments. NMR. spectra were obtained in $CDCl_3$ using *Varian EM 360*, *Bruker WP 80* and *Varian A-60*, *HA-100* and *XL 100 FT*. Chemical shifts are recorded in ppm downfield from TMS as an internal standard (*s*=singlet, *d*=doublet, *qa*=quartet, *m*=multiplet, *stack*=heavily overlapping signals), coupling constants are reported in Hz. Mass spectra were recorded on *Varian Mat CH5-DF* and *CH-7*, signals are recorded as *m/z* in % of the base peak. Elemental analyses were performed by *W. and M. Manser*, Mikroanalytisches Laboratorium, ETH, Zürich.

Preparation of 2,2-diiodo-norbornane (2). A solution of 1.0 g (8.05 mmol) of norcamphor hydrazone [14] and 5 ml triethylamine in 5 ml benzene was slowly added at 0° to a solution of 5 g (19.7 mmol) iodine in 50 ml benzene. After stirring for 1 h, the precipitate was filtered off through *Celite* and the filtrate washed with 100 ml 2 M HCl, 100 ml 1 M Na_2SO_3 and sat. NaCl-solution. The volatile component was removed *i. v.* ($20^\circ/0.002$ Torr) to give after Kugelrohr distillation ($85^\circ/11$ Torr) 0.355 g (20%) of **3**. Analytically pure **3** was obtained by GC. (*Carbowax 20 M*, 120°). Rf (pentane) 0.5 $n_D^{25.5}$ 1.5670. – IR (neat): 1448, 1300, 675, 530. – 1H -NMR.: 1.9–2.2 (stack, 3H); 2.4–2.7 (stack, 3H); 2.80 (*m*, 1H); 2.96 (*m*, 1H); 6.36 (*d*, *J*=3, 1H). – MS. (200°): 220 (M^+), 192, 93, 91.

C_7H_9I (220.0) Calc. C 38.20 H 4.12 I 57.67% Found C 38.29 H 4.19 I 57.53%

The residual oil was quickly chromatographed under subdued light over silica gel with pentane to give 1.310 g (47%) of **2** as yellowish, viscous oil. Off-white crystalline **2** was obtained by two crystallizations from pentane at -70° , mp. 28° , Rf (pentane) 0.35. Compound **2** is unstable in light. – UV./VIS.: 303 (1060), 330 (680, *S*), 340 (590, *S*). – IR. (neat): 1450, 1445, 1438, 1305, 1060, 635, 560. 1H -NMR.: 1.0–1.8 (stack, 4H); 1.9–2.1 (stack, 2H); 2.3 (*m*, 1H); 2.93 (*m*, *J*=15.5 and 3.0, 1H); 3.05 (*m*, 1H); 3.49 (*m*, *J*=15.5, 5.0 and 2.0, 1H). – MS 348 (M^+), 221, 192, 93, 91.

Preparation of 1,2-exo-diiodo-norbornane (4). A solution of 0.143 g (0.41 mmol) **2** in 5 ml CS_2 was stirred, after addition of 5 drops of 2M AlI_3 [15] in CS_2 , at 0° until all the starting material had disappeared (25 min). After dilution with 20 ml ether, the reaction mixture was treated with 10 ml 1M Na_2SO_3/H_2O 1:1. Chromatography of the crude oil over silica gel with pentane gave 0.123 g (86%) of a colorless oil, which crystallized upon addition of seeding crystals. An analytically pure sample of **4** was obtained by recrystallizing the precipitate 3 times from pentane at -24° , m.p. 33.5° , Rf (pentane) 0.2. – UV./VIS.: 265 (940). – IR. (KBr): 1193, 980, 965, 765. – 1H -NMR.: 1.0–2.8 (stack, 9H); 4.30 (*d* × *d* × *d*, *J*=8.0, 4.0 and 2.1, 1H) (for detailed analysis see [5]). – ^{13}C -NMR.: 31.85 (*t*), 36.62 (*d*), 40.56 (*t*), 41.05 (*d*), 44.94 (*t*), 45.32 (*s*), 47.62 (*t*). – MS.: 348 (M^+), 221, 93, 91.

$C_7H_{10}I_2$ (348.0) Calc. C 24.22 H 2.90 I 73.13% Found C 24.26 H 2.92 I 73.40%

Preparative-scale synthesis of 4: A solution of 60 g (0.483 mmol) norcamphor hydrazone [14] and 200 ml triethylamine in 800 ml benzene was added slowly at 0° to a solution of 254 g (1 mol) iodine in 2 l benzene. After analogous workup 138.6 g of a red oil was obtained, which consisted of a 71:29 mixture of **2** and **3**. This crude product, essentially free of benzene, was used for preparation of **4** without further purification: 42.3 g of this mixture was dissolved in 100 ml CS_2 and treated with proportionate quantities of AlI_3 . In several experiments, an induction period has been observed, which made further addition of the catalyst (up to 10%) necessary. The crude product in pentane was treated with charcoal and silica gel and yielded after crystallization 27.1 g (74.7%) of crystalline **4**.

Preparation of 1-iodo-norbornene (5). A solution of 0.419 g (1.2 mmol) **4** and 0.611 g *t*-BuONa in DMSO was stirred at 45° under argon for 90 min. The crude oil, which remained after workup, gave upon repeated Kugelrohr-distillation 0.177 g (67%) of colourless **5**, $n_D^{23.5}$ = 1.5628, Rf (pentane) 0.45. – IR.

(neat): 1330, 983, 790, 765, 710. – $^1\text{H-NMR}$: 1.0–2.3 (stack, 6H); 2.6 (*m*, 1H); 5.88 (*qa*, $J=5.5$ and 3.0, 1H); 6.18 (*d*, $J=5.5$, 1H). – MS: 220 (M^+), 192, 91; metastable peaks: 168.0, 89.0.

$\text{C}_7\text{H}_9\text{I}$ (220.0) Calc. C 38.20 H 4.12 I 57.67% Found C 37.98 H 4.12 I 57.25%

Preparation of 1-iodo-norbornane (6). After hydrogenation of 0.101 g (0.46 mmol) **5** in 3 ml CH_3OH with Pd/C (10%), the solvent was evaporated at 0° i. v. (12 Torr) and the crude oil purified by GC. (*Carbowax 20M*, 130°). The IR. spectrum of pure **6** and that of a sample prepared by a known route [5] were identical.

Preparation of the iodoalcohols 7 and 9. Hydroboration [16] of 12 g (54.5 mmol) **5** with 33 ml 1.03 M $\text{BH}_3 \cdot \text{THF}$ gave a reddish oil, which was chromatographed over silica gel with CH_2Cl_2 giving 3.60 g (27.7%) of **7** and 6.97 g (53.8%) of **9**.

Data of 7. M.p. $93\text{--}94^\circ$; Rf (CH_2Cl_2) 0.16. – IR.: 3610, 1450, 1303, 1040, 970. – $^1\text{H-NMR}$: 0.88–2.55 (stack, 9H); 2.63 (*s*, 1H); 3.75 (*m*, *ca. d*, 1H). – MS.: 238 (M^+), 111, 93, 91.

$\text{C}_7\text{H}_{11}\text{IO}$ (238.1) Calc. C 35.32 H 4.66 I 53.31% Found C 35.78 H 4.54 I 53.27%

Data of 9. M.p. 25° , Rf (CH_2Cl_2) 0.36. – IR.: 3555, 1450, 1329, 1080, 1041, 1010, 985. – $^1\text{H-NMR}$: 0.9–2.53 (stack, 10H); 3.62 (*m*, 1H). – MS.: 238 (M^+), 111, 93, 91.

$\text{C}_7\text{H}_{11}\text{IO}$ (238.1) Calc. C 35.32 H 4.66 I 53.31% Found C 35.46 H 4.78 I 53.22%

Preparation of 1-iodo-norbornan-2-one (10). Oxidation of 4.0 g (16.8 mmol) **9** with 5.4 g (25.05 mmol) pyridinium chlorochromate in CH_2Cl_2 [17] gave after filtration through silica gel and evaporation of the solvent an oil, which crystallized from 30 ml ether/pentane 1:2 at -25° . Further crystals were obtained from the mother liquor giving a total yield of 3.09 g (77.9%) of **10**. A pure sample was obtained by GC. (*Carbowax 20M*, 190°), m.p. 59° , Rf (CH_2Cl_2) 0.57. – IR.: 1750, 1285, 1065. – $^1\text{H-NMR}$: 1.27–2.35 (stack, 8 H); 2.5–2.8 (*ca. s*, 1H). – $^{13}\text{C-NMR}$: see Table 2. – MS.: 236 (M^+), 192, 109, 81, 79.

$\text{C}_7\text{H}_9\text{IO}$ (236.1) Calc. C 35.62 H 3.84 I 53.76% Found C 35.53 H 3.75 I 53.52%

Preparation of 1-iodo-norbornan-3-one 8. In an analogous way as for the preparation of **10** 1.0 g (4.2 mmol) **7** was oxidized with 2.0 g (9.28 mmol) pyridinium chlorochromate [17]. Crystallization from pentane at -25° yielded 0.714 g (72%) of **8** as yellow crystals. A pure sample was obtained by GC., m.p. $60\text{--}61^\circ$, Rf (CH_2Cl_2) 0.44. – IR.: 1745, 1280, 1065. – $^1\text{H-NMR}$: 1.33–2.67 (stack). – $^{13}\text{C-NMR}$: see Table 2. MS.: 236 (M^+), 109, 81, 79.

$\text{C}_7\text{H}_9\text{IO}$ (236.1) Calc. C 35.62 H 3.84 I 53.76% Found C 34.96 H 3.73 I 53.56%

Preparation of 1-iodo-norbornan-2-one hydrazone (11). In a flask equipped with a Soxhlet extractor containing molecular sieves (4 Å) and a reflux condenser, a mixture of 2.28 g (9.66 mmol) **10** in 60 ml CHCl_3 and 41 g hydrazine hydrate was refluxed for 15 h. The CHCl_3 -phase was separated and combined with the ether extract of the hydrazine phase. Workup gave 2.20 g (91%) of white, crystalline **11**. A pure sample was obtained by crystallization from ether/hexane 3:1, m.p. $85\text{--}86^\circ$, Rf (ether) 0.22. Compound **11** is unstable on standing in CDCl_3 . – IR. (KBr): 3350, 1610, 955, 770, 760, 720. – $^1\text{H-NMR}$: 1.1–2.38 (stack, 8H); 2.55 (*m*, 1H); 4.97 (*ca. s*, 2H). – $^{13}\text{C-NMR}$: 30.6 (*t*), 32.7 (*t*), 35.0 (*d*), 39.5 (*s*), 40.8 (*t*), 50.5 (*t*), 157.3 (*s*). MS.: 250 (M^+), 221, 193, 123, 94.

$\text{C}_7\text{H}_{11}\text{IN}_2$ (250.1) Calc. C 33.62 H 4.43 I 50.74 N 11.20% Found C 33.62 H 4.39 I 50.80 N 11.15%

Preparation of 1,2,2-triiodo-norbornane (12). Analogous to the preparation of **2**, a solution of 2.2 g (8.8 mmol) **11** and 3 ml triethylamine in 20 ml benzene was added slowly below $+6^\circ$ to 5 g (19.7 mmol) iodine in 50 ml benzene. The crude, yellow product was crystallized from CH_2Cl_2 /ether/pentane 1:1:4 at -25° and gave 1.05 g of **12** as yellow needles. Chromatography of the mother liquor over silica gel with pentane gave 0.482 g (15.8%) 1,2-diiodo-norborn-2-ene **13** and additional 0.073 g of **12** (total yield of crystalline **12**: 1.123 g (26.9%)). A pure sample of pale yellow **12** was obtained by recrystallisation, m.p. 127° , Rf (pentane) 0.28. – $^1\text{H-NMR}$: 1.0–3.03 (stack, $\approx 7\text{H}$); 3.17 ($d \times d$, $J=15.0$ and 2.0, 1H); 4.0 ($d \times d \times d$, $J=15.0$, 4.0 and 3.5, 1H). – $^{13}\text{C-NMR}$: 19.10, 32.39, 37.57, 42.09, 44.00, 56.41, 61.17. – IR.: (KBr) 989, 766, 641. MS.: 474 (M^+), 347, 220, 93, 91.

Preparation of 1,2-endo-diiodo-norbornane (14). – a) Tributyltinhydride (0.33 g, 113 mmol) was injected into a solution of 0.51 g (1.07 mmol) **12** in 5 ml ether at 0° . After 4 h, the reaction mixture was diluted with 20 ml ether and shaken with a NH_4Cl -solution. After workup, the colorless oil was chromatographed over 40 g silica gel in a cooled column. Pentane eluted, after some by-products, 0.141 g (37.9%) **14** as an oil and 0.056 g (14.2%) of **4** (Rf (pentane) 0.32). An analytically pure, crystalline sample of **14**

was obtained by HPLC. (silica gel 7 μ m, mobile phase hexane with 0.05% acetonitrile); t_R (**14**): 10.8 min, t_R (**4**): 12.2 min. M.p. 42–43°, Rf (pentane) 0.32. – IR. (KBr) 1205, 1170, 970, 768. – $^1\text{H-NMR}$: 1.1–2.7 (stack, 9H); 4.38 ($d \times d \times d$, $J = 11.3, 5.0$ and $2.4, 1\text{H}$). – $^{13}\text{C-NMR}$: 31.92 (t), 35.59 (d), 41.79 (t), 42.98 (s), 43.29 (d), 44.48 (t), 47.62 (t). – MS.: 348 (M^+), 221, 94, 93, 91.

$\text{C}_7\text{H}_{10}\text{I}_2$ (348.0) Calc. C 24.16 H 2.90 I 72.94 Found C 24.02 H 2.73 I 72.46

b) A solution of 0.79 g (13.1 mmol) of glacial acetic acid in 10 ml dioxane was added during 15 h to a mixture of 0.44 g (1.27 mmol) **13** and 1.25 g (6.44 mmol) potassium azadicarboxylate in 20 ml dioxane. After additional 22 h the reaction mixture was poured into ice water and extracted with pentane. The crude material was chromatographed on silica gel with pentane to give 0.392 g **14** of m.p. 42–43° (yield 89.2%).

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