Preparation and Pyrolysis of Stereoisomeric Bromobicyclo[n.1.0]alkanes (n = 6, 8, 10)

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Dibromocarbene Adducts, Stereoselective Debromination, Rearrangement, Allylic Bromides

The title compounds 1a–3c were prepared by stereoselective reduction of the respective dibromides. Pyrolysis gave allylic bromides (8, 9, 11) as primary and dienes (10, 12) as secondary products. Product ratios were independent of the stereochemistry of the starting materials. No differences of the rearrangement rates of the stereoisomers were observed in gas phase reactions of the derivatives of bicyclo[6.1.0]- and bicyclo[8.1.0]alkanes. With the larger bicyclo[10.1.0] derivatives, however, distinct differences in the thermal stability of cis-/trans-isomers 4c/5c or 2c/3c were found in condensed phase.

Halocyclopropanes open thermally to allyl halides, and the reaction has been interpreted to be concerted as early as 1967 [1]. Halobicyclo[n.1.0]alkanes with n = 3 and 4 in particular undergo thermal isomerizations yielding halocycloalkenes and products derived therefrom, the process being very facile if the halide is endo-positioned. At least in condensed phase the reaction is orbital symmetry controlled and follows the Woodward—Hoffmann—De Puy rules [2]. The literature, however, contains scattered observations only on the thermolysis of such halobicyclo[n.1.0]alkanes in which the larger ring is medium sized, and it is not clear whether and how the stereochernistry of the starting materials influences the course of isomerizations and eliminations [3]. The present investigation addresses this question.

Preparation of the Starting Materials

The desired compounds 1a to 3c were accessible by partial reductive debromination of the respective dibromides (4a–c or 5a–c). 4a–4c in turn were obtained from the pertinent alkenes by phase transfer catalytic (PTC) dibromocarbene addition. This method could not be applied to trans-cyclooctene because a mixture of 4a and 5a was formed [4]. Almost pure 5a was prepared by using KOt-Bu/HBr [5].

Starting material for 5b was cis,trans-1,5-cyclooctadiene. PTC-CBr2 addition yielded a 9:1 ratio of 6a/6b together with some 7, whereas the HCBBr2/KOt-Bu reaction known from the literature gave a ratio of ca. 3:1 [6].

5b was made by diimide reduction of 6a. When a commercial 1:2 mixture of cis- and trans-cyclo-dodecenes was converted with PTC dibromocarbene a 4c/5c mixture resulted. According to Waegell et al. [7], 4c is thermally much more labile than 5c. Conse-
quently, a distillation of the mixture isomerized most of 4c to the 2,3-dibromotridecenes 8, and virtually unchanged 5c could be isolated by crystallization. Thermolysis of the pure isomers 4c and 5c gave the results shown in Scheme 3.

Casanova and Waegell [7] had observed only Z-8 from 4c. Apparently, a partial Z/E isomerization is operative under the reaction conditions. The structures of the 8-isomers follow from the NMR spectra which exhibit allyl and methine hydrogen signal shifts conforming to trends known from smaller rings [8].

Partial debromination of 4a with tributyltinhydride led to a 26:74 mixture of 1a and 2a. Thus, the removal of the exo-bromine was not as prevalent as in some related cases studied previously [9]. Similar reductions of 4b and 4c, however, gave 8:92 and 11:89 mixtures, respectively, of 1b/2b and 1c/2c. The trans-fused bicyclic compounds 5a–c yielded 3a–c in the same way. To get exo-bromo-cis-bicyclo[6.1.0]nonane (1a) selectively as the major product, 4a was subjected to a halogen-metal exchange with butyl lithium at −93 °C and then quenched at this temperature with methanol [10, 11]. This method could not be extended advantageously to the preparation of 1b and 1c because in these cases mixtures of the 1/2 stereoisomers and the respective alkenes were formed. No method was found to prepare pure 1b or 1c.

**Pyrolysis Results**

Short path vacuum pyrolysis was performed in the commercially available apparatus developed by Seybold [12, 13]. The three bromobicyclo[6.1.0]nonanes (1a, 2a, 3a) gave identical products at 500–700 °C and 0.001 to 0.005 mbar, and there was no difference in the thermal sensitivity of the isomers. Rearrangement started around 500 °C, and at this temperature cis-3-bromocyclononene (9) was the only product found in small quantity together with much starting material. No trans-alkene could be detected. At higher temperatures, the pyrolysate contained cis,cis-1,3-cyclononadiene (10) besides 9 and starting material. The relative concentration of 10 changed with temperature until at 700 °C no educt and almost no 9 were present in the pyrolysate. These results indicate that 9 is the precursor of 10. Indeed, re-pyrolysis of mixtures of 9 and 10 gave almost pure 10.

As with the smaller ring examples, no differences in the thermal response of the bromobicyclo[8.1.0]undecanes 2b and 3b was found. Isomerization of these compounds occurred significantly easier than in the earlier mentioned case; at 500 °C a 50% conversion could be realized at a similar vacuum as before. Main products at 500 °C were the allylic bromides, the cis- and trans-3-bromocycloundecenes (E- and Z-11) in a 1:3 ratio. In addition, small amounts of cis,cis- and cis,trans-cycloundecadienes (Z,Z- and Z,E-12) could be observed. All mentioned products proved to be relatively unstable and exhibited fast tarring. At higher temperatures complex mixtures resulted which contained apparently further secondary products and which polymerized even more easily. Unfortunately, 1b was not available in a pure state and could not be compared.

Structures of E- and Z-11 were assigned again on the basis of their NMR spectra. In addition, one can be very certain that the major isomer has the trans configuration because the trans olefin is the more stable one in this ring system [14]. With the unsubsti-
tuted cyclononenes, however, the cis-compound is much more stable [14], which makes our contrasting results with 8 quite understandable.

In addition to the flash pyrolysis experiments just mentioned, compounds 2b and 3b were also thermolyzed in condensed phase at 200 °C. After ½ h, much HBr had been evolved and strong tarring had occurred. Nevertheless the reaction mixtures still contained substantial amounts of the starting materials besides E/Z-11 (the dienes had polymerized). There was some indication that the trans-compound 3b reacted a little faster than 2b.

The behavior of the two bromobicyclo[10.1.0]tridecans (2c and 3c) was investigated only in a cursory fashion because analogous results could be expected. Indeed, when 2c and 3c were also heated in substance to 200 °C, analogous conversions took place as judged from the NMR spectra of the mixtures. There was one remarkable difference in the reaction rates of the isomers in this series though: trans-bromide 3c was consumed totally after a few minutes whereas endo-cis compound 2c was still partially unchanged after 30 minutes.

### Discussion

The smaller ring halobicycloalkanes have been shown to exhibit differing reactivities of the exo- and endo-isomers. Japanese authors reported that exo-7-bromobicyclo[4.1.0]heptane was stable at 350 °C, whereas the other isomer was transformed into cycloheptadiene starting at 250 °C [15]. Nefedov et al. found similar stability differences in the 8-chlorobicyclo[5.1.0]octane series at 600 to 620 °C in the gas phase [16]. But when a mixture of endo- and exo-9-chlorobicyclo[6.1.0]nonane was pyrolyzed no such differences were observed apparently [16].

In the [4.1.0] and [5.1.0] bicyclic series, there can be only a cis ring junction. Starting with our bicyclo[6.1.0]nonanes cis and trans connections of the rings and consequently three monohalo isomers are possible. As the elimination of HBr occurs easier than the removal of HCl it was hoped that the isomers 1a/2a/3a would exhibit distinct differences. The results show clearly, however, that this is not so. Vacuum isomerization needs so high a temperature that no differences can be found. Rearrangement transition states are so rich in energy apparently that differences of the isomers are levelled off.

Our results with the monobromobicyclo[10.1.0]tridecans 2c and 3c and the dibromo derivatives 4c and 5c show that the thermal behavior of these larger ring derivatives is governed to some extent by the stereochemistry of the educt. It looks surprising at first sight that the trans isomer 5c is the more stable one of the dibromo series, whereas the cis isomer 2c is the more stable one of the two monobromo compounds. Assuming a concerted disrotatory movement of the two cyclopropane substituents trans to the leaving bromide (Woodward–Hoffmann–De Puy rule), this becomes easily understandable: Wandering of the exo-Br in 4c results in an outward movement of both cyclopropane substituents (which actually form the larger ring), and this is energet-
ically much better than the rearrangement of the endo-bromine resulting in an inward movement of the substituents. The analogous shifting of the bromine atom in trans-compound 5c must involve inward rotation of one cyclopropane substituent, and consequently the rearrangement of this compound must be less favored than the one of 4c. Similarly, endo-compound 2c with the necessity of two inward rotations of groups reacts less readily than 3c with just one such unfavorable interaction in the transition state. One can predict then that 1c as well as probably also 1b (unluckily, both are not available in pure form as yet) will be the most reactive compounds in their respective stereoisomeric series. Furthermore, 1c should be transformed into pure trans-3-bromocyclotridecene.

It turns out thus, that of our three series the smallest one exhibits no influence of the educt stereochimistry on the reaction and the largest one shows a small effect. Quite obviously, the behaviour of the bicyclo[8.1.0] compounds is intermediate to the two other series.

**Experimental**

Melting points were determined in an apparatus after Dr. Tottoli (Büchi) and are not corrected. Boiling points are given as air bath temperatures of a Kugelrohr distillation. 1H NMR spectra were measured in CDCl3 (TMS as internal standard) with the Bruker AM 300.

**General method for the PTC dibromocarbene reactions**

0.1 mol alkene, 1 mmol Aliquat 336 (commercial methyltrioctylammonium chloride) and 1 ml ethanol were mixed with 0.2 mol bromoform and 20 ml dichloromethane and stirred at 0 °C with 0.4 mol freshly prepared 50% NaOH.

Stirring was continued 1 h at 0 °C, over night at r.t., and then 3 h at 50 °C. After that the mixture was poured into much water, the aqueous layer was decanted, and the organic phase was washed with dilute HCl and water and finally dried with sodium sulfate. The solvents were removed in vacuo, and the products were purified by crystallization, distillation, or chromatography on silica gel with petroleum ether/little ether.

cis-9,9-Dibromobicyclo[6.1.0]nonane (4a), 85% yield, b.p. 77–81 °C/0.05 Torr, m.p. 19 °C, nD20 1.5521 (Lit. [17] b.p. 80–82 °C, nD20 1.5520). 300 MHz 1H NMR: δ 1.1–1.25 (2H), 1.3–1.7 (10H), 2.0–2.1 (2H).

trans-9,9-Dibromobicyclo[6.1.0]nonane (5a), prepared after lit. [5], m.p. 44.5 °C (Lit. [5] m.p. 43.5–44 °C). 300 MHz 1H NMR: δ 1.0–1.15 (4H), 1.15–1.25 (2H), 1.4–1.6 (2H), 1.9–2.1 (4H), 2.25–2.35 (2H).

cis-11,11-Dibromobicyclo[8.1.0]undecane (4b), m.p. 48 °C (Lit. [18] m.p. 48.5–49.5 °C). 300 MHz 1H NMR: δ 1.39 (s, broad, 8H), 1.55–1.8 (8H), 1.8–1.9 (m, 2H). 62% yield. The compound is partially isomerized on distillation (85–90 °C/0.01 Torr) to a mixture of much (Z)- and little (E)-2,3-dibromocyclodecenes which were characterized only by their 300 MHz 1H NMR data. Characteristic signals for (Z): δ 4.68 (dd, δ 5+10 Hz; allyl. H), 6.22 (dd, δ 6+10 Hz; vinyl. H); for (E): δ 5.20 (dd, δ 4+11 Hz; allyl. H), 6.05 (dd, δ 5+12 Hz; vinyl. H).

trans-11,11-Dibromobicyclo[8.1.0]undec- (Z)-4-ene (6a), m.p. 19.5–20.5 °C, nD20 1.5617, from reaction of cis TRANS-1,5-cyclooctadiene with 1 equivalent bromoform and distillative separation of the 6a6b 9:1 mixture (b.p. 110–160 °C/0.01 Torr; Lit. [6] b.p. 122–124 °C/1 Torr) from 7. 6a was crystallized from petroleum ether (b.p. 40–65 °C) at ~30 °C. 20% yield.

C11H18Br2 (308.1)
Calcld C 42.89 H 5.24
Found C 42.80 H 5.03

cis-13,13-Dibromobicyclo[10.1.0]tridecane (4c), m.p. 47–48 °C (from petroleum ether), 48% yield. The compound is mentioned in the literature up to now as an oil [19, 20] which was probably a mixture of 4c, Z-8 and E-8.

C13H22Br2 (338.1)
Calcld C 46.18 H 6.56
Found C 46.44 H 6.74

trans-13,13-Dibromobicyclo[10.1.0]tridecane (5c), m.p. 32 °C, from the commercial 2:1 trans cis cyclooctadecene, distillation of the 4c5c8 mixture at 150–160 °C/0.2 Torr, and crystallization from petroleum ether. 52% yield. As 4c, 5c is mentioned in the literature [20] only as an oil which was probably impure.

C13H22Br2 (338.1)
Calcld C 46.18 H 6.56
Found C 46.37 H 6.46

(Z)- and 2,3-Dibromocyclodecenes (Z-8 and E-8) were characterized only by their 300 MHz 1H NMR data. Characteristic signals for Z-8: δ 4.75 (dd, δ 4+12 Hz; allyl. H), 6.09 (dd, δ 5+10 Hz; vinyl. H); for E-8: δ 5.10 (dd, δ 5+10 Hz; allyl. H), 5.99 (dd, δ 5+11 Hz; vinyl. H).

trans-11,11-Dibromobicyclo[8.1.0]undecane (5b): A mixture of 0.1 mol 6a and 0.4 mol p-toluensul-
fonsyldrazide in 250 ml ethoxyethanol was stirred and refluxed at 114–121 °C for 4.5 h until the evolution of diimine subsided. The mixture was diluted by 150 ml of petroleum ether (b.p. 40–65 °C) and cooled to −30 °C, whereafter the decomposition product of the reagent, toluene-4-thiosulfonic acid-S-p-tolyl ester (m.p. 72–74 °C) crystallized. The solid was washed with petroleum ether, and the organic layer was stirred with a large volume of dilute NaOH, washed with water, dried over sodium sulfate, and concentrated in vacuo.

The product 5b was separated from the higher boiling by-product by repeated distillation at 90–100 °C/0.01 Torr and finally crystallized from petroleum ether at −30 °C. Yield 28%; m.p. 21–22 °C, nD 1.5494. 300 MHz 1H NMR: δ 0.9–1.05 (m, 2H), 1.1–1.2 (m, 2H), 1.2–1.65 (m, 10H), 1.75–1.9 (m, 2H), 2.2–2.35 (dd, 7.5 +14 Hz; 2H).

C15H18Br2 (310.1)
Calcd C 42.61 H 5.85, Found C 42.80 H 6.03.

General method for the partial reductive debrominations

0.1 mol of the gem-dibromide and a little azobisisobutyronitrile were stirred in 30 ml benzene. Exactly 0.1 mol (26.7 ml) of freshly prepared pure bis-(tributyltin) oxide which could be reused. The solution of iodine in benzene were added. A remaining violet color indicated that all hydride had been obtained discolored tars, a short path distillation was executed before further analysis by g.c. and NMR.

Endo-11-Bromobicyclo[10.1.0]tridecane (3b): b.p. 100–110 °C/0.1 Torr, nD 1.5182, 94% yield. Characteristic signal of the 300 MHz 1H NMR: δ 2.80 (dd, 3.9+7.6 Hz).

C17H19Br (231.2)
Calcd C 57.15 H 8.28, Found C 57.45 H 8.57.

13-Bromo-trans-bicyclo[10.1.0]tridecane (3e): b.p. 100–110 °C/0.1 Torr, nD 1.5170, m.p. 11.5–12.5 °C, 90% yield. Characteristic signal of the 300 MHz 1H NMR: δ 2.82 (dd, 3.6+7.5 Hz).

C17H19Br (231.2)
Calcd C 57.15 H 8.28, Found C 57.45 H 8.57.

Endo-11-Bromobicyclo[8.1.0]undecane (2b): The reaction of 4b as above gave a 92:8 mixture of 2b and 1b (b.p. 100–110 °C/0.5 Torr). Crystallization from petroleum ether yielded 29% 2b, m.p. 38 °C. Characteristic signal of the 300 MHz 1H NMR: δ 3.20 (t, 7.9 Hz) [exo-compound 1b exhibited: δ 2.21 (t, 3.8 Hz)].

C15H18Br2 (310.1)
Calcd C 57.15 H 8.28, Found C 57.11 H 8.51.

Endo-13-Bromobicyclo[10.1.0]tridecane (2c): Similarly a 89:11 mixture of 2c and 1c (b.p. 100–105 °C/0.09 Torr) was obtained. Crystallization from ether gave 44% yield, m.p. 46–47 °C. Characteristic signal of the 300 MHz 1H NMR: δ 3.19 (t, 7.7 Hz) [exo-compound 1c exhibited: δ 2.31 (t, 4.0 Hz)].

C15H18Br2 (310.1)
Calcd C 60.23 H 8.94, Found C 60.15 H 8.96.

9-Bromo-trans-bicyclo[6.1.0]nonane (3a): b.p. 80 °C/ca. 1 Torr [Lit. [21] b.p. 52–56 °C/0.25–0.4 Torr], 87% yield, nD 1.5155. Characteristic signal of the 300 MHz 1H NMR: δ 2.87 (dd, 4.2+7.3 Hz).

C9H12Br (203.2)
Calcd C 53.22 H 7.44, Found C 53.47 H 7.17.

11-Bromo-trans-bicyclo[8.1.0]undecane (3b): b.p. 75 °C/0.01 Torr, nD 1.5182, 94% yield. Characteristic signal of the 300 MHz 1H NMR: δ 2.80 (dd, 3.9+7.6 Hz).

C11H15Br (231.2)
Calcd C 57.15 H 8.28, Found C 57.45 H 8.57.

exo-(1a) and endo-(2a) 9-Bromo-cis-bicyclo[6.1.0]nonane (prepared according to lit. [10, cf. 11] or [22], respectively) had these characteristic signals in the 300 MHz 1H NMR spectra: 1a δ 2.33 (t, 3.5 Hz); 2a δ 3.24 (t, 7.5 Hz).

Execution of flash vacuum pyrolyses. The apparatus of Seybold [12, 13] with internal heating was used at 300–700 °C and 0.001 to 0.005 mbar. The hot zone had an internal diameter of 6 mm and a length of 100 mm. Compounds were distilled or sublimed through the hot zone at a rate of ca. 1 g/h, and the products were trapped a few cm behind the hot zone on a liquid nitrogen cold finger condenser. After thawing up, the products were dissolved in ether or dichloromethane. If the pyrolysate contained discolored tars, a short path distillation was executed before further analysis by g.c. and NMR.

(Z)-3-Bromocyclohexene (9), as primary product from 1a, 2a, and 3a. Characteristic signals of the 300 MHz 1H NMR: δ 5.65 (m, 2H), 5.05 (ddd, 12+9+5 Hz, 1H; allyl H).

(Z),Z-1,3-Cyclohexadiene (10), as secondary product from 1a, 2a, and 3a, b.p. 90–100 °C/
13 Torr. IR: 665, 735, 770, 1635, 3020 cm⁻¹ (cf. lit. [23]), characteristic signals of the 300 MHz ¹H NMR: δ 1.46 (m, 4H), 1.62 (m, 2H), 2.12 (m, 4H), 5.67 (m, 2H), 5.86 (m, 2H).

(Z)-3-Bromocycloundecene (Z-11), as minor primary product from the pyrolysis of 2b and 3b. The raw pyrolysate was distilled at 0.5 — 1 Torr up to 130 °C and analyzed by NMR spectroscopy. The product was unstable on standing at room temperature. Z-11 and E-11 were present in the ratio of 1:3. Characteristic signals in the 300 MHz ¹H NMR: δ 5.47 ("td", probably ddd, 11 + 11+4 Hz; 1-H atom), 5.60 (m; 2-H atom), 5.10 (“td”, probably ddd, 11 + 11+4 Hz; 3-H atom).

(E)-3-Bromocycloundecene (E-11), as major primary product from the pyrolysis of 2b and 3b. Characteristic signals in the 300 MHz ¹H NMR: δ 5.66 (m, 2H; 1-H and 2-H atoms), 4.46 (ddd, 12+11+4 Hz; 3-H atom).

(E,Z) and (Z,Z)-1,3-CycIoundecadienes (E,Z-12 and Z,Z-12), as secondary products from the pyrolysis of 2b and 3b. The mixture was isolated by preparative g.c. (2 m column with 5% silicon SE 30 on chromosorb W); the product was air sensitive. 300 MHz ¹H NMR: δ 1.3—1.5 (m, 10H each of both isomers), 2.1—2.2 (m, 4H each of both isomers), 5.4—5.7 (m, 2H each of both isomers, 1-H and 4-H atoms), 5.9—6.0 (m, 2H, 2-H and 3-H of Z,Z-12), 6.0—6.1 (m, 1H, belonging to E,Z-12), 6.1—6.2 (m, 1H, belonging to E,Z-12).

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