The 1-Norbornene Skeleton by Carbene Rearrangement

Sascha Dorok, Burkhard Ziemer, and Günter Szeimies*[a]

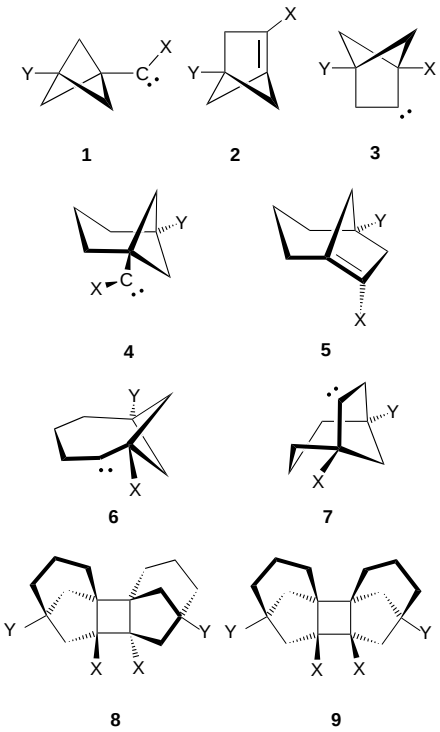
Abstract: 4-Bromo-1-(dibromomethyl)bicyclo[2.1.1]hexane (**18**) was synthesized by formation of the dienolate of dimethyl cyclopentanedicarboxylate **15b**, which is then transformed into **16**. Reaction of **16** with diiodomethane gives the diester **14b**, and selective saponification leads to the half-ester **14c**. Degradation of **14c** to methyl 4-bromobicyclo[2.1.1]hexane-1-carboxylate (**17a**), reduction of the ester to the corresponding carbinol **17b**, oxidation of **17b** to the aldehyde **17c**, and conversion of the aldehyde with triphenyl phosphite/bromine gives compound **18**. Reaction of **18** with $NaN(SiMe_3)$ in diethyl ether in the presence of diphenylisobenzofuran afforded a 3.3:1 mixture of the Diels–Alder adducts **22** and **23**, indicating the presence of 2,4-dibromobicyclo[2.1.1]hept-1-ene as a reactive intermediate generated by rearrangement of carbene **19**.

Keywords: bisenolates · bridgehead alkenes · cycloaddition · reactive intermediates · ring expansion

Introduction

A successful route for the generation of bridgehead alkenes is the rearrangement of carbenes in which the carbenic carbon is bound to a bridgehead of a bicyclic or polycyclic carbon framework.[1] We have recently shown that bicyclo[1.1.1]pentyl carbenes of type **1** rearrange to 1-bicyclo[2.1.1]hexenes **2**.[2–4] These strongly twisted olefins could be trapped only rather inefficiently, because the alkenes **2** isomerized over low energy barriers to carbenes of type **3**. When one of the bridges in **1** was enlarged by two methylene groups, the analogous rearrangement of carbene **4** to alkene **5** took place, but the destabilization of the olefinic bond was not sufficiently high to cause the consecutive rearrangement to carbenes **6** or **7**. Instead, **5** dimerized to afford a mixture of the stereoisomers **8** and **9**.[5] The application of computational methods indicated that the rearrangement of carbenes **1** and **4** to the corresponding bridgehead alkenes should be fast, but that only bridgehead alkene **2** could be further converted into carbene **3** by a subsequent rearrangement.[2, 5]

The barrier of isomerization of 1-bicyclo[2.1.1]hexylcarbene **10** to 1-norborne **11** was computed to be as low as 2.3 kcal mol^{-1}, whereas the barrier leading to 1-bicyclo[2.1.1]-heptene **12** was somewhat higher (7.3 kcal mol^{-1}).[5] The barrier of **11** to give 2-norbornylidene **13** was calculated as 22.3 kcal mol^{-1}.[5] This leads to the prediction that at low temperature 1-norbornene **11** will not further rearrange.



To investigate these predictions experimentally, the tribromide **18** has been synthesized. We report here on the results that were obtained when **18** was treated with one equivalent of methyllithium in the presence of a suitable trap. It should be remembered that 1-norbornene **11** has been generated as a reactive intermediate by Keese and Krebs and trapped by furan as a mixture of stereoisomeric Diels–Alder adducts.[6, 7]

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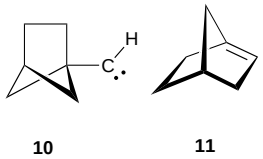

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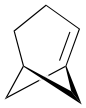

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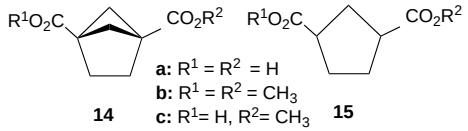
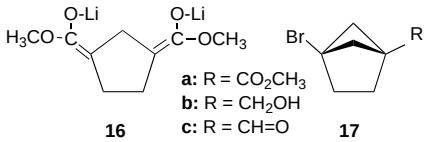
Results

Access to 1,4-bicyclo[2.1.1]hexane dicarboxylic acid (**14a)** has been reported by Wiberg[8] and by Warner.[9] We followed the procedure of Warner, starting from cyclopentane-1,3-dicarboxylic acid (**15a**); however, it seemed appropriate to develop a one-pot synthesis of the diester **14b**. This was achieved by adopting the methodology of Della and Tsanaktsidis, who converted the diester dienolate **16** in a one-pot procedure with 1,2-dichloroethane into dimethyl bicyclo[2.2.1]heptane-1,4-dicarboxylate.[10] A solution of the diester **15b** in diethyl



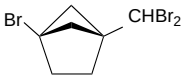
a: $R^1 = R^2 = H$
b: $R^1 = R^2 = CH_3$
c: $R^1 = H$, $R^2 = CH_3$

14 15



a: $R = CO_2CH_3$
b: $R = CH_2OH$
c: R = CH=O

16 17



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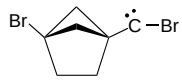
ether with four equivalents of hexamethylphosphorus triamide (HMPA) was treated with 2.7 equivalents of lithium diisopropylamide (LDA) at $-78\,^{\circ}C$; this led to the formation of the bisenolate **16**. Reaction of **16** with diiodomethane at room temperature afforded a 58% yield of **14b**.

After partial saponification of the diester **14b** to the half-ester **14c**, this compound was converted by the procedure of Barton, Crich, and Motherwell[11] into methyl 4-bromo-1-bicyclo[2.1.1]hexylcarboxylate (**17a**) in 70% yield. $LiAlH_4$ reduction of **17a** to the corresponding carbinol **17b** and Dess–Martin periodane oxidation[12] afforded the aldehyde **17c**. Reaction of **17c** with a reagent prepared from triphenylphoshite and bromine[13] gave a 65% yield of 4-bromo-1-dibromomethylbicyclo[2.1.1]hexane (**18**).

(4-Bromo-1-bicyclo[2.1.1]hexyl)bromocarbene (**19**) was generated from **18** by metalation with sodium bis(trimethylsilyl)amide via carbenoid **20** in diethyl ether in the presence of diphenylisobenzofuran in the temperature range of -15 to $20\,^{\circ}C$. The high propensity of **19** to rearrange by enlargement of the four-membered ring of **19** to give 2,4-dibromobicyclo[2.2.1]hept-1-ene **21** was seen from the fact that compounds **22** and **23**, the two adducts formed from **21** and diphenylisobenzofuran, formed in 44% yield as a 3.3:1 mixture.



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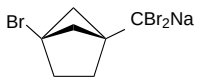

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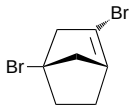

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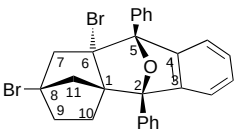
Proof of the structures of **22** and **23** has been obtained by NMR spectroscopy as well as single-crystal X-ray analysis (Figure 1).



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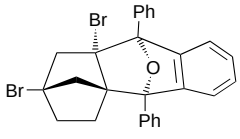

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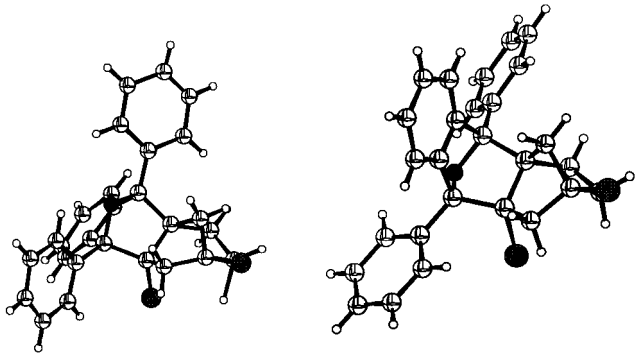

Figure 1. ORTEP Plots of **22** (left) and **23** (right).

Concerning the structures of the adducts, a significant point is the location of the bromine at C6 of the norbornane subunit of **22** and **23**; it is found in the *endo* position in both cases. This is consistent with the results of our calculation on 1-norbornene **24**; these showed that only the *endo* configuration **24-*endo*** of this pyramidalized bridgehead alkene was a local minimum on the corresponding energy hypersurface.[5]

24-endo

In conclusion we note that (4-bromo-1-bicyclo[2.1.1]hexyl)-bromocarbene **19** rearranges by migration of the one-carbon bridge to give 2,4-dibromo-1-norbornene (**21**). Compound **21** is trapped by diphenylisobenzofuran to form adducts **22** and **23**. The structure of these adducts show that it is the *endo*-pyramidalized bridgehead alkene **21** that has been trapped. A further rearrangement of **21** to the 1,4-dibromobicyclo[2.1.1]hept-2-ylidene, a derivative of carbene **13**, was not observed.

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Table 1. Crystal data and structural refinement of **22** and **23**.

	22	**23**
formula	$C_{27}H_{22}Br_2O$	$C_{27}H_{22}Br_2O$
T [K]	180(2)	180(2)
λ [Å]	0.71073	0.71073
crystal system/space group	orthorhombic/$P2_12_12_1$	monoclinic/$P2_1/c$
a [Å]	8.3446(13)	14.140(8)
b [Å]	14.963(3)	10.525(3)
c [Å]	17.611(3)	15.646(6)
V [Å^3]	2198.9(7)	2145.0(17)
Z	4	4
ρ [Mg m^{-3}]	1.578	1.617
μ [mm^{-1}]	3.703	3.796
F(000)	1048	1048
crystal size [mm]	$0.39 \times 0.20 \times 0.08$	$0.48 \times 0.40 \times 0.20$
θ range [°]	2.31 – 25.5	1.56 – 25.24
index range	$-10 \le h \le 9$	$-16 \le h \le 16$
	$-18 \le k \le 18$	$0 \le k \le 12$
	$-21 \le l \le 21$	$-18 \le l \le 18$
reflections collected/unique	14656/4073	4246/3886
	[R(int) = 0.0977]	[R(int) = 0.0256]
completeness to $\theta = 25.50$ [%]	99.3	99.9
max/min transmission	0.7560/0.3261	0.5173/0.2630
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	4073/7/270	3886/0/272
goodness-of-fit on F^2	1.115	1.138
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0875$, $wR2 = 0.1993$	$R1 = 0.0441$, $wR2 = 0.1049$
R indices (all data)	$R1 = 0.1078$, $wR2 = 0.2078$	$R1 = 0.0719$, $wR2 = 0.1271$
extinction coefficient	0.036(3)	0.0019(4)
largest diff. peak/hole [e Å^{-3}]	0.570/ – 0.728	0.766/0.599

Experimental Section

General: Melting points were determined on a Büchi 530 and are uncorrected. ^{1}H (at 300 MHz) and ^{13}C NMR spectra (at 75 MHz) were measured in $CDCl_3$ on a Bruker DPX300 with TMS as an internal standard. IR spectra were recorded on a Perkin – Elmer 881 spectrometer. MS spectra were taken on a MSI Concept 1H. Elemental analysis were carried out by the Analytisches Labor des Instituts für Chemie der Humboldt-Universität zu Berlin. Data collection for X-ray analysis was carried out on the Stoe diffractometers pds (**22**) and stadi4 (**23**). Both data sets were corrected for absorption by psi-scan measurements (**23**) and after the isotropic refinement by DIFABS (Walker et al.[14]) modeling (**22**). The structures were solved by direct methods and refined by the least-squares basing on F_o^2 data. The methods are implemented in the SHELX97 program package (Sheldrick, 1990 and 1997[15]).[16] Dimethyl 1,3-cyclopentanedicarboxylate (**15b**) was prepared as described in the literature.[10]

Dimethyl bicyclo[2.1.1]hexane-1,4-dicarboxylate (14b): Lithium diisopropylamide was prepared by addition of *n*-butyllithium (17.04 mL, 27.3 mmol, 1.6 M in hexane) to a solution of diisopropylamine (3.54 mL, 27.2 mmol) in diethyl ether (60 mL) at 0 °C followed by further stirring at – 20 °C to – 30 °C for 15 min. Dry hexamethylphosphoric triamide (HMPT, 7.90 mL, 45.1 mmol) was then added to this solution. The mixture was cooled to – 78 °C, and a solution of **15b** (2.00 g, 10.7 mmol) in diethyl ether (10 mL) was added dropwise over a period of 5 min. The mixture was warmed to 0 °C and maintained at that temperature for 15 min. Diiodmethane (980 mL, 12.2 mmol) in dry diethyl ether (20 mL) was added to the bisenolate over a period of 15 min. The mixture was stirred for 2 h at room temperature and then treated with an aqueous solution of saturated ammonium chloride (100 mL) and diethyl ether (100 mL). The aqueous layer was extracted twice with diethyl ether (100 mL). Distillative workup of the remaining oil of the diethyl ether extract under reduced pressure afforded the diester **14b** as a colorless waxy solid (1.24 g, 58 %). B.p. 58 – 60 °C (1.0×10^{-3} mbar); analytical sample (from hexane): m.p. 27 – 28 °C; IR (film): $\tilde{\nu} = 1723$ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.72 – 1.70$ (m, 2H; 5-, 6-H$_{endo}$), 1.97 – 2.01 (m, 4H; 2-H$_2$, 3-H$_2$), 2.12 – 2.16 (m, 2H; 5-, 6-H$_{exo}$), 3.69 (s, 6H; OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.72$ (C-2, C-3), 44.51 (C-5, C-6), 48.98 (C-1, C-4), 51.65 (OCH_3), 172.96 (C=O); MS (70 eV, EI): *m/z* (%): 198 (0.40) [M^+], 167 (18), 166 (36), 138 (24), 137 (18), 107 (89), 79 (100), 78 (16), 77 (36), 59 (43); elemental analysis calcd (%) for $C_{10}H_{14}O_4$ (198.22): C 60.60, H 7.12; found: C 60.31, H 6.86.

4-Carbomethoxy-1-bicyclo[2.1.1]hexane carboxylic acid (14c): A solution of potassium hydroxide (404 mg, 7.20 mmol) in methanol (10.0 mL) was added slowly over a period of 1.5 h to a refluxing solution of dicarboxylic ester **14b** (2.00 g, 10.1 mmol) in methanol (60 mL). The mixture kept refluxing for 1 h. The solvent was removed in vacuo, and the remaining oil was dissolved in water (40 mL). The solution was washed with dichloromethane (2×25 mL), and from the organic layer of **14b** (180 mg, 0.91 mmol) was recovered. The aqueous solution was saturated with sodium chloride and acidified with dilute HCl to pH 1. The mixture was extracted with dichloromethane (4×25 mL). From the combined organic layers the crude monoester **14c** (1.44 g) was isolated as a yellow solid. After recrystallization from a mixture of chloroform/heptane (1:1), **14c** was obtained as colorless crystals (1.36 g, 73 %). M.p. 69 °C; IR (KBr): $\tilde{\nu} = 1728$ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.69 – 1.80$ (m, 2H; 5-, 6-H$_{endo}$), 2.00 – 2.07 (m, 4H; 2-H$_2$, 3-H$_2$), 2.15 – 2.25 (m, 2H; 5-, 6-H$_{exo}$), 3.70 (s, 3H; OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.61$, 29.73 (C-2, C-3), 44.48 (C-5, C-6), 48.76, 49.06 (C-1, C-4), 51.73 (OCH_3), 172.82 (CO_2Me), 178.29 (COOH); MS (70 eV, EI): *m/z* (%): 184 (0.42) [M^+], 152 (22), 139 (7), 124 (16), 123 (15), 107 (69), 97 (10), 81 (21), 80 (17), 79 (100), 77(35); elemental analysis calcd (%) for $C_9H_{12}O_4$ (184.19): C 58.69, H 6.57; found: C 58.34, H 6.30.

Methyl (4-bromo-1-bicyclo[2.1.1]hexyl carboxylate (17a): Monoester **14c** (1.04 g, 5.65 mmol) in dichloromethane (14 mL) was added dropwise to a solution of dicyclohexyl carbodiimide (1.30 g, 6.30 mmol) and *N*-hydroxypyridine-2-thione (767 mg, 6.03 mmol) in dichloromethane (25 mL), cooled in an ice bath. The mixture was stirred for 12 h at room temperature, and the bright yellow suspension filtered through a bed of silica gel. Bromotrichloromethane (1.20 g, 6.05 mmol) was added, and the mixture was irradiated with a 250 W tungsten lamp for 2 h under reflux. The solvent was removed, the residue dissolved in diethyl ether, and the diethyl ether layer was extracted four times with dilute HCl. After evaporation of the diethyl ether in vacuo, the remaining oil was purified by flash column chromatography (silica, petroleum ether/ethyl acetate 25:1) to give **17a** (874 mg, 71 %, $R_f = 0.39$) as a colorless oil. IR (film): $\tilde{\nu} = 1737$ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.92 – 1.95$ (m, 2H; 5-, 6-H$_{endo}$), 1.98 – 2.05 (m, 2H; 2-H$_2$), 2.09 – 216 (m, 2H; 3-H$_2$), 2.24 – 2.29 (m, 2H; 5-,6-H$_{exo}$), 3.70 (s, 3H; OCH_3); ^{13}C NMR (75 MHz; $CDCl_3$): $\delta = 30.69$ (C-2), 36.74 (C-3), 48.41 (C-1), 50.42 (C-5, C-6), 51.06 (C-4), 51.89 (OCH_3), 171.53 (C=O); elemental analysis calcd (%) for $C_8H_{11}BrO_2$ (219.08): C 43.86, H 5.06, Br 36.47; found: C 43.55, 5.08, Br 36.69.

(4-Bromo-1-bicyclo[2.1.1]hexyl)methanol (17b): A solution of **17a** (1.60 g, 7.30 mmol) in diethyl ether (10 mL) was added to a suspension of lithium aluminum hydride (612 mg, 16.1 mmol) in diethyl ether (50 mL) at 0 °C. The mixture was then heated under reflux for 2 h and then treated with a saturated aqueous sodium sulfate solution (5 mL). The mixture was stirred for 10 min and filtered, and the residue washed with diethyl ether ($3 \times$ 15 mL). After removal of the solvent, flash column chromatography of the oily residue (silica, dichloromethane) afforded the alcohol **17b** (1.24 g, 89 %) as a colorless solid. IR (KBr): $\tilde{\nu} = 2957$, 2955, 2925, 2876, 1435, 1406, 1170, 1155, 1045, 1044, 1026, 821, 700, 673, 667, 664, 663 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.65 – 1.73$ (m, 4H; 2-H$_2$, 5-, 6-H$_{endo}$), 1.89 – 1.94 (m,

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2H; 5-, 6-H$_{exo}$), 2.07–2.14 (m, 2H; 3-H$_2$), 3.72 (s, 2H; CH_2OH); ^{13}C NMR (75 MHz; $CDCl_3$): $\delta = 30.10$ (C-2), 37.33 (C-3), 48.76 (C-5, C-6), 49.35 (C-1), 52.57 (C-4), 64.11 (CH_2OH); HRMS (70 eV, EI): *m/z* calcd for $C_7H_{11}O$ [$M^+ - Br$]: 111.08099; found: 111.08095; elemental analysis calcd (%) for $C_7H_{11}BrO$ (191.07): C 44.00, H 5.80, Br 41.82; found: C 43.80, H 5.77, Br 41.56.

4-Bromo-1-bicyclo[2.1.1]hexylcarbaldehyde (17c): Alcohol **17b** (278 mg, 1.45 mmol) in dichloromethane (10 mL) was added dropwise to a solution of Dess–Martin periodinane (683 mg, 1.61 mmol) in dichloromethane (30 mL) in an ice-bath. The mixture was stirred for 30 min at 0 °C and for 4 h at 20 °C. Subsequently the mixture was first washed (4 × 10 mL) with an aqueous solution of potassium hydrogencarbonate (saturated) and sodium thiosulfate (1.6 M) and then with water (2 × 10 mL). The organic layer was dried with magnesium sulfate, and the solvent was removed under reduced pressure. The crude aldehyde **17c** (238 mg, 87%) was used without further purification. IR (KBr): $\tilde{\nu} = 1710$ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 1.66–1.85 (m, 4H; 2-H$_2$, 5-, 6-H$_{endo}$), 1.92–2.03 (m, 2H; 3-H$_2$) 2.05–2.13 (m, 2H; 5-, 6-H$_{exo}$), 9.74 (s, 1H; CH=O); HRMS (70 eV, EI): *m/z* calcd for [$M^+ - Br$]: 109.06534; found: 109.06534.

4-Bromo-1-(dibromomethyl)bicyclo[2.1.1]hexane (18): A solution of bromine (491 mg, 3.07 mmol) in dichloromethane (3.0 mL) was added dropwise to a stirred mixture of triphenylphosphite (951 mg, 3.07 mmol) in dichloromethane (6 mL) at 0 °C. The mixture was cooled to −10 °C, a solution of the aldehyde **17c** (276 mg, 1.46 mmol) in dichloromethane was added slowly by syringe, and the mixture stirred for 30 min at 0 °C. Then basic aluminium oxide (ca. 50 mg) was added, and the suspension stirred for further 15 min. After filtration through a bed of basic aluminum oxide and washing with diethyl ether, flash column chromatography (silica gel, petroleum) of the residual oil, which was obtained after evaporation of the solvent, afforded the desired tribromide **18** ($R_f = 0.38$, 316 mg, 65%). IR (KBr): $\tilde{\nu} =$ 2996, 2981, 2961, 2879, 1450, 1434, 1307, 1280, 1246, 1221, 1208, 1190, 1177, 1158, 1144, 1098, 1032, 972, 955, 941, 921, 818, 715, 674, 630 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.87 - 1.90$ (m, 2H; 5-, 6-H$_{endo}$), 1.94–2.00 (m, 2H; 3-H$_2$), 2.00–2.05 (m, 2H; 5-, 6-H$_{exo}$), 2.15–2.21 (m, 2H; 2-H$_2$), 5.91 (s, 1H; 1′-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 30.35$ (C-3), 38.05 (C-2), 47.37 (C-1′), 49.29 (C-4), 50.79 (C-5, C-6), 54.60 (C-1); elemental analysis calcd (%) for $C_7H_9Br_3$ (332.86): C 25.26, H 2.73, Br 72.02; found: C 25.38, H 2.77, Br 72.26.

Generation and trapping of 2,4-dibromobicyclo[2.2.1]hept-1-ene (21): Tribromide **18** (250 mg, 0.751 mmol) in ether (3 mL) was added to a solution of sodium (bistrimethylsilyl)amide (840 mL, 0.92 mmol, 1.09 M solution in THF) and diphenylbenzo[c]furan (308 mg, 1.14 mmol) in diethyl ether (4 mL) at −15 °C. The mixture was stirred for 20 h at 20 °C and then treated with maleic anhydride (110 mg, 1.12 mmol) and triethylamine (230 mg, *2.27* mmol) in THF (4 mL). After stirring for 30 min, the mixture was added to an aqueous solution of sodium hydroxide (10 mL, 2 N). The phases were separated, and the organic layer extracted twice with water (10 mL). The combined aqueous layers were extracted with diethyl ether (15 mL), and the combined organic layers were dried with magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum/ethyl acetate 25:1) and afforded the Diels–Alder adduct of **21** with diphenylisobenzofuran as a diastereomeric mixture (172 mg, 44%, 22:23 = 3.3:1).

(1-*R*,2-*R*,5-*S*,6-*S*,8-*R*)- and (1-*S*,2-*S*,5-*R*,6-*R*,8-*S*)-6,8-Dibromo-2,5-diphenyl-benzo[c]-12-oxatetracyclo[6.2.1.1^{2,5}.0^{1,6}]dodec-3-ene (22): M.p. 184 °C; IR (KBr): $\tilde{\nu} =$ 3364, 3349, 2950, 2923, 1445, 1299, 1002, 979, 805, 765, 753, 734, 701, 685 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.78$ (dd, $^3J_{HH} = 4.1$ Hz, 1H; 11-H$_{anti}$), 1.95–2.06 (m, 1H; 10-H$_{exo}$), 2.20–2.30 (m, 3H; 10-H$_{endo}$, 9-H$_{endo}$, 11-H$_{syn}$), 2.45–2.58 (m, 1H; 9-H$_{exo}$), 2.66 (d, $^1J_{HH} = 13.6$ Hz, 1H; 7-H$_{exo}$), 2.87 (dd, $^1J_{HH} = 13.6$ Hz, $^3J_{HH} = 4.1$ Hz, 1H; 7-H$_{endo}$), 7.10–7.30 (m, 4H; aromatic H), 7.35–7.57 (m, 6H; aromatic H.), 7.65 (d, 2H; aromatic H), 7.96 (d, 2H; aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.14$ (C-10), 39.08 (C-9), 52.51 (C-11), 55.78, 65.36, 82.73 (C-1, C-8, C-6), 59.65 (C-7), ,88.80, 92.40 (C-1, C-5), 120.74, 121.69, 124.81, 126.32, 126.50, 126.88, 127.83, 128.31, 128.57 (aromatic C-H), 134.67, 136.59, 141.85, 151.34 (aromatic C); HR-MS (70 eV, EI): *m/z* calcd for $C_{27}H_{22}{}^{79}Br_2O$: 520.00374; found: 520.00337; elemental analysis calcd (%) for $C_{27}H_{22}Br_2O$ (522.28): C 62.09, H 4.25; found: C 62.04, H 4.29.

(1-*R*,2-*S*,5-*R*,6-*S*,8-*R*)- and (1-*S*,2-*R*,5-*S*,6-*R*,8-*S*)-6,8-Dibromo-2,5-diphenyl-benzo[c]-12-oxatetracyclo[6.2.1.1^{2,5}.0^{1,6}]dodec-3-ene (23): M.p. 203 °C; IR (KBr): $\tilde{\nu} =$ 3032, 2997, 2942, 1456, 1447, 1306, 1274, 1111, 1049, 1007, 979, 843, 803, 766, 748, 698, 681, 657, 632 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.52–0.60 (m, 1H; 11-H$_{syn}$), 1.83–1.95 (m, 1H; 10-H$_{exo}$), 2.06 (dd, $^3J_{HH} =$ 3.8 Hz, 1H; 11-H$_{anti}$), 2.15–2.30 (m, 2H; 10-H$_{endo}$, 9-H$_{endo}$), 2.58–2.69 (m, 1H; 9-H$_{exo}$), 2.75 (dd, $^1J_{HH} = 13.2$ Hz, 1H; 7-H$_{exo}$), 3.06 (dd, $^1J_{HH} = 13.2$ Hz, $^3J_{HH} = 3.8$ Hz, 1H; 7-H$_{endo}$),7.12–7.25 (m, 4H; aromatic H), 7.38–7.66 (m, 10H; aromatic H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 34.89$ (C-10), 39.21(C-9), 54.39 (C-11), 57.01 (C-7), 56.14, 68.72, 85.70, 88.14, 94.12 (C-2, C-1, C-8, C-6, C-5), 117.73, 123.50, 125.10, 127.18, 127.72, 127.79, 127.98, 128.33, 128.61 (aromatic C-H), 139.48, 143.11, 149.82, 150.74 (aromatic C); HR-MS (70 eV, EI): *m/z* calcd for $C_{27}H_{22}{}^{79}Br_2O$: 520.00374; found: 520.00307; elemental analysis calcd (%) for $C_{27}H_{22}Br_2O$ (522.28): C 62.09, H 4.25; found: C 61.68, H 4.26.

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[16] CCDC-189712 (**22**) and CCDC-189713 (**23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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