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Addition of dibromocarbene to tricyclo[4.3.0.$0^{3,7}$]nona-4,8-diene (brexadiene). Synthesis of *exo*-4,5,10,*exo*-11-tetrabromotricyclo[5.4.0.$0^{3,8}$]undeca-5,9-diene

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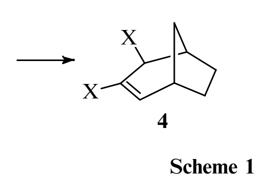
Addition of dibromocarbene to tricyclo[4.3.0.$0^{3,7}$]nona-4,8-diene (brexadiene) under phase-transfer catalysis conditions yields the only tricyclic tetrabromide, *exo*-4,5,10,*exo*-11-tetrabromotricyclo[5.4.0.$0^{3,8}$]undeca-5,10-diene.

Dihalocarbene addition to the double bond is a widely accepted synthetic procedure. It has been used as both a route to new bi- and tricyclic dihalocyclopropane-containing compounds[1,2] and as a ring-expansion method.[3–5]

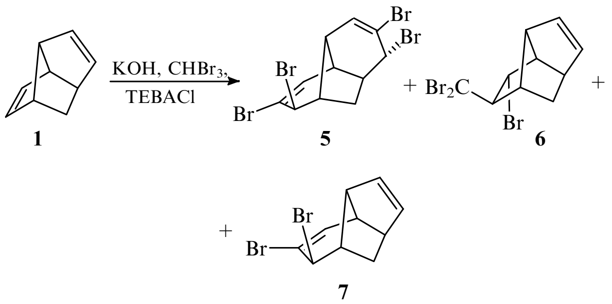
Earlier we reported on the synthesis of the novel tricyclic caged diene — tricyclo[4.3.0.$0^{3,7}$]nona-4,8-diene (brexadiene) **1**,[6] the bridged analogue of norbornene. Although some electrophilic reactions of the diene were reported earlier,[7,8] dihalocarbene addition to this hydrocarbon has not yet been investigated. In addition, these reactions are not known for the monounsaturated analogue of brexadiene, brexene, although the latter has been extensively studied.[7,9]

Addition of dichlorocarbene formed from potassium *tert*-butylate in chloroform at $-30\,^{\circ}$C to norbornene **2** leads to the formation of the dichlorocyclopropane-containing intermediate **3** (X = Cl) which rearranges to 2,3-dichlorobicyclo[3.2.1]oct-3-ene **4** upon heating.[10] No similar intermediate, **3** (X = Br) could be separated during addition of dibromocarbene.

Addition of dibromocarbene results in the formation of the only product in the tricycloundecadiene series, namely *exo*-4,5,10,*exo*-11-tetrabromotricyclo[5.4.0.$0^{3,8}$]undeca-5,9-diene **5** in 49% yield. The product of radical addition of bromoform **6** and the product **7** of equimolar addition of dibromocarbene to brexadiene were also observed in quantities less than 5%.

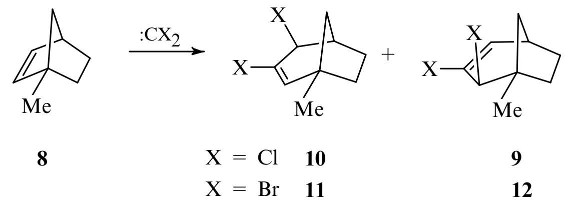


Scheme 1



Scheme 2 *Reagents and conditions*: $CHBr_3$ (2.96 ml, 8.56 g, 0.034 mol), CH_2Cl_2 (3.4 ml), EtOH (0.085 ml), 50% aqueous NaOH (13.7 ml, 0.16 mol), $PhCH_2NEt_3Cl$ (20 mg, 0.083 mmol), diene **1** (1 g, 8.5 mmol), 50 h.[†]

It should be noted that regioselective ring opening of the dihalocyclopropane intermediate was observed for carbene additions to substances with a strong electron donor at the double bond, such as dihydrofuran,[3] dihydropyran,[4] α-tetralone enol ether.[5] Addition of the carbenes to unsymmetric alkenes of the norbornene series, *e.g.* **8**, lead to a slight preference of **9** formation over **10** (53 : 43, X = Cl) and to prevailed formation of **11** over **12** (80 : 20, X = Br).[11]



In the case of the diene **1** the asymmetry of the double bond is caused by the bridge connecting the C-5 and C-7 atoms of norbornene[9] only. This remarkably high regioselectivity of ring opening in the dibromocyclopropane moiety is achieved in the absence of either strong electron donor groups or any hindering substituents. However, the influence of the inductive effect of the remote double bond on the course of the reaction might be supposed. Although the inductive effect is known to be drastically attenuated as the chain of σ-bonds is increased, transfer of electronic effects through longer chains of spatially arranged bonds is known.[12] Further study of the carbene reactions with brexadiene is now in progress.

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[†] *exo*-4,5,10,*exo*-11-Tetrabromotricyclo[5.4.0.0^{3,8}]undeca-5,9-diene **5**: mp > 220 °C (decomp.). NMR (AM-500 instrument) ^{13}C (127.5 MHz): $C_{1,3}$ 49.7, C_2 32.3, $C_{4,11}$ 58.4, $C_{5,10}$ 121.9, $C_{6,9}$ 136.9, $C_{7,8}$ 39.3; ^1H (500.1 MHz): $H_{1,3}$ 2.83, H_2 1.77, $H_{4,11}$ 4.57, $H_{6,9}$ 6.36, $H_{7,8}$ 2.97. Mass spectrum (Finnigan MAT 112S, ionization energy 12 eV): 460(1.7), 462(5.1), 464(4.7), 379(19), 381(62), 383(73), 385(15), 299(3.4), 301(8.5), 219(15), 220(42), 222(43), 223(19), 225(14), 227(7), 158(85), 159(100), 141(26), 83(20). Found: C 27.92 27.89; H 2.20, 2.24. Calc. for $C_{11}H_{10}Br_4$: C 28.61, H 2.18 %.

endo-5-Bromo-*exo*-4-dibromomethyltricyclo[4.3.0.0^{3,8}]non-8-ene **6**. ^{13}C: C_1 43.6, C_2 33.6, C_3 38.7, C_4 68.7, C_5 49.7, C_6 65.8, C_7 49.2, C_8 128.8, C_9 139.2; ^1H (shifts for *endo*/*anti* protons are given in parentheses): H_1 2.80, H_2 1.14(1.63), H_3 2.19, H_4 3.05, H_5 3.84, H_6 2.53, H_7 2.72, H_8 5.79, H_9 6.22.

exo-4,5-Dibromotricyclo[5.3.0.0^{3,8}]deca-5,9-diene **7**. ^{13}C: C_1 46.1, C_2 32.0, C_3 41.7, C_4 58.8, C_5 122.3, C_6 135.2, C_7 56.2, C_8 42.8, C_9 134.3, C_{10} 139.1; ^1H: H_1 2.71, H_2 1.29(1.36), H_3 2.20, H_4 4.12, H_6 6.05, H_7 2.23, H_8 3.02, H_9 5.79, H_{10} 6.21.