Addition of dichlorocarbene to tricyclo[4.3.0.0^{3,7}]nona-4,8-diene

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Addition of dichlorocarbene to tricyclo[4.3.0.0^{3,7}]nona-4,8-diene (brexadiene) under conditions of phase transfer catalysis occurs from the *exo* side. Cyclopropyl—allyl rearrangement of intermediate chlorocyclopropanes yields tricyclo[5.4.0.0^{3,8}]undecadienes.

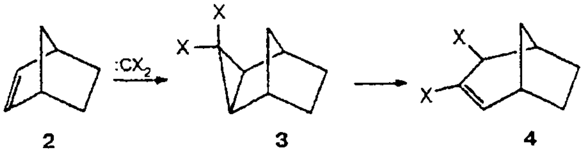
Key words: addition, dichlorocarbene, tricyclo[5.4.0.0^{3,8}]undecadiene.

Reactions of dihalocarbenes with unsaturated substrates have long been known. These reactions have been used in the synthesis of new bi- and polycyclic compounds with a dihalocyclopropane fragment as well as for the purpose of enlarging the rings.[1,2]

The aim of this work is to study the reaction of dichlorocarbene with tricyclo[4.3.0.0^{3,7}]nona-4,8-diene (brexadiene) (**1**) synthesized from tetrahydroindene according to the procedure developed previously.[3]

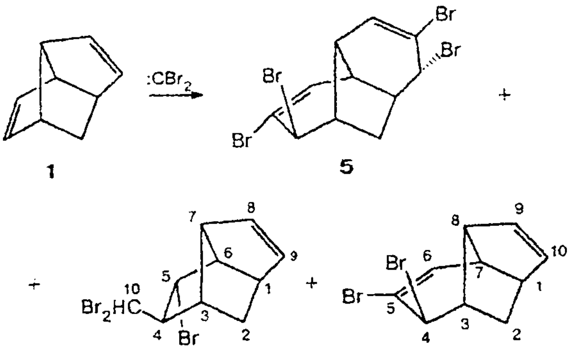
It is known[4] that the addition of dichlorocarbene, which is generated by the reaction of Bu^{t}OK with chloroform at −30 °C, to norbornene (**2**) yields the dichlorocyclopropane-containing adduct (**3**) (X = Cl) as an intermediate. When heated, adduct **3** undergoes rearrangement with ring opening to give dichlorobicylco[3.2.1]octene (**4**) (Scheme 1). We failed to detect adduct **3** (X = Cl or Br) in the course of the addition of dibromocarbene under analogous conditions or in the addition of dihalocarbenes under conditions of phase transfer catalysis.

Scheme 1



Previously,[5] we have demonstrated that the addition of dibromocarbene to diene **1** under the conditions of phase transfer catalysis also proceeds with rearrangement of the corresponding dibromocyclopropane bisadduct to form only the tetrabromide, *exo*-4,5,10-*exo*-11-tetrabromotricyclo[5.4.0.0^{3,8}]undeca-5,9-diene, (**5**) in a yield of 49% (Scheme 2).

Scheme 2



Analysis of the reaction mixture and the mixture obtained after isolation of compound **5** by ^{13}C NMR spectroscopy revealed two more compounds, namely, the product of the radical addition of bromoform, dibromobrexene (**6**), and the product of the addition of dibromocarbene at one double bond, dibromohomobrexadiene (**7**). The total amount of **6** and **7** was ~5%. However, we did not found tetrabromides isomeric to compound **5**.

The structures of the resulting compounds were determined by NMR spectroscopy using 2D ^{1}H—^{1}H- and ^{1}H—^{13}C-COSY techniques and the values of the spin-spin coupling constants in the ^{1}H NMR spectra and taking into account the characteristic features of the ^{13}C NMR spectra of substituted brexanes and brexenes.[3,6] In compound **6**, the *exo* and *endo* configurations of the substituents at positions 4 and 5 are confirmed by the values of the spin-spin coupling constants ($J_{4,10}$ = 11.4, $J_{4,5}$ = 2.4, and $J_{5,6}$ = 4.9 Hz). In dibromide **7**, the H(4)

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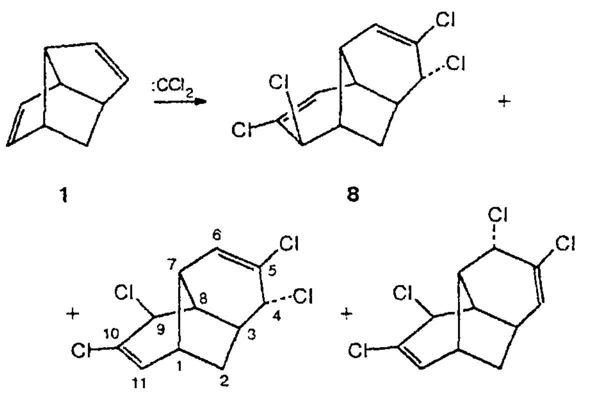
Table 1. Data of ^{13}C and ^{1}H NMR spectroscopy of the products of the addition of dichlorocarbene to brexadiene **1** (δ)

Compound	Type of nuclues	Atom										
		1	2	3	4	5	6	7	8	9	10	11
exo-4,5,10-*exo*-11-Tetrachlorotricyclo[5.4.0.0^{3,8}]undeca-5,9-diene (**8**)	^{13}C	48.29	30.32	48.29	64.45	131.00	132.63	37.69	37.69	132.63	131.00	64.45
	^{1}H	2.98	1.74	2.98	4.71		6.43	3.30	3.30	6.43		4.71
exo-4,5-*exo*-9,10-Tetrachlorotricyclo[5.4.0.0^{3,8}]undeca-5,10-diene (**9**)	^{13}C	40.49	36.29	45.27	66.24	131.35	132.63	38.39	47.18	63.44	130.05	135.93
	^{1}H	2.65	1.71 2.04	2.84	4.70		6.44	3.17	3.79	4.91		6.62
5-*exo*-6-*exo*-9,10-Tetrachlorotricyclo[5.4.0.0^{3,8}]undeca-4,10-diene (**10**)	^{13}C	38.36	43.40	38.36	138.63	129.73	63.09	48.20	48.20	63.09	129.73	138.63
	^{1}H	2.54	2.02	2.54	6.74		4.91	3.52	3.52	4.91		6.74

proton has only two spin-spin coupling constants (0.5 and 3.5 Hz), which indicates that the sp^2 hybridized C(5) atom should bear the bromine substituent. The *exo* position of the Br atom at C(4) in compound **7** is confirmed by the unusually low value of the chemical shift of the allyl H(8) proton (δ 3.02) due to the effect of the electronegative substituent through space.

Unlike the reaction with dibromocarbene, the reaction of diene **1** with dichlorocarbene yielded a mixture of three isomeric tetrachlorobicyclo[5.4.0.0^{3,8}]undecadienes (**8—10**) in a yield of 56% (Scheme 3). The NMR spectral data for compounds **8—10** are given in Table 1. After storage, the mixture yielded crystals of symmetrical tetrachloride **8**. The structure of **8** was established by X-ray structural analysis and is shown in Fig. 1.

Scheme 3



The local symmetry of the molecule is close to C_{2v}. The noncrystallographic twofold axis passes through the C(15) atom and the midpoint of the C(7)—C(10) bond. The ClCCCl torsion angles in the two halves of the molecule are −67.6 and −68.1°. The geometric parameters of the molecule are close to the standard values. The average C_{sp^2}—C_{sp^2} bond length is 1.315 Å. The average C_{sp^2}—Cl and C_{sp^3}—Cl bond lengths are 1.750 and 1.820 Å, respectively. The intermolecular distances correspond to the values of the van der Waals contacts except for three Cl···Cl contacts (3.260, 3.400, and 3.534 Å), which are substantially shorter than twice the van der Waals radius of the Cl atom (3.70 Å). This fact is consistent with the conclusions made previously.[7]

Column chromatography of the mother liquor on SiO$_2$ yielded a mixture of tetrachlorides **8—10** in a ratio of 2 : 4 : 1. As in the case of the addition of dihalocarbenes to derivatives of norbornene, we also failed to isolate or detect 5,5-dichlorotetracyclo[5.3.0.0^{4,6}.0^{3,8}]decene (**11**) when diene **1** was used as a substrate.

The *exo* orientations of the chlorine atoms in product **8** were established by X-ray structural data. Unfortunately, we failed to confirm *exo* orientations of the chlorine atoms in tetrachlorides **9** and **10** by NMR spectroscopy because of the noncharacteristic spin-spin coupling constants ($J_{3,4}$ = $J_{1,11}$ = 3.1 Hz for **8**; $J_{3,4}$ = 3.3 and $J_{8,9}$ = 1.6 Hz for **9**; and $J_{6,7}$ = $J_{8,9}$ = 1.0 Hz for **10**). According to the published data,[8] for the analogous products of addition of :CCl$_2$ to benzonorbornadiene, the spin-spin coupling constants are 5 and 1.5 Hz for *endo* and *exo* chlorides, respectively. An *exo* orientation of the substituent also cannot be judged from the values of the chemical shifts of the C(2) atoms (δ 30.32, 36.29,

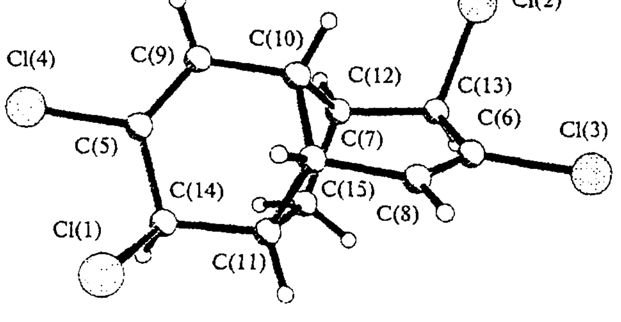


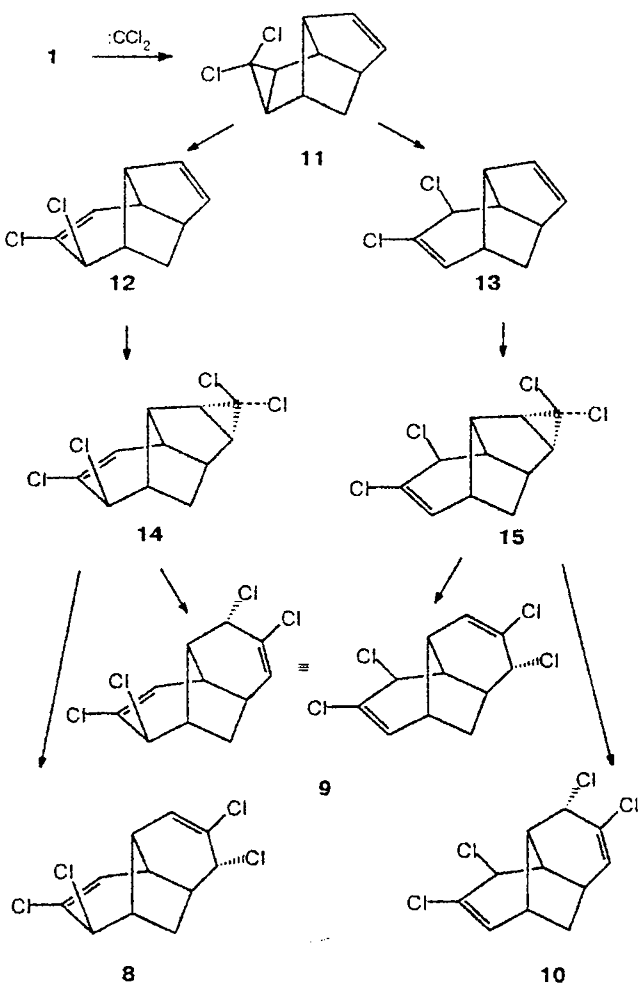
Fig. 1. Structure of compound **8** according to X-ray structural data.

and 43.40 for compound **8**—**10**, respectively) because the downfield shift of this signal in going **10**→**9**→**8** can also be caused by the homoallyl effect of the double bond. Unfortunately, the ^{13}C NMR spectrum only of a saturated compound, tricyclo[5.4.0.0^{3,8}]undecane, has been reported in the literature.[9] The data on unsaturated hydrocarbons with analogous structures are unavailable.

It is known that solvolytic rearrangement of cyclopropanes with the leaving group occurs as heterolysis of the C—X bond accompanied by disrotatory ring opening to form an allyl cation—X anion ionic pair followed by "collapse" of this ionic pair. In the case of condensed bicyclic systems, this course of the reaction is possible only when the orientation of the leaving X group is identical to that of a three-membered ring,[10] while in dihalocyclopropanes, only one C—X bond is ionized. The direction of the attack of carbene (*exo* or *endo*) can be judged from the *exo* or *endo* orientation of the allyl substituent.

In our opinion, intermediate dichlorides **12** and **13** as well as tetrachlorides **8**—**10** are formed from the same precursors (**11**, **14**, and **15**, respectively). Tetrachlorides **9** and **10** as well as **8** have a di-*exo* configuration (Scheme 4).

Scheme 4



Therefore, both double bonds of the hydrocarbon are involved in the reaction of dichlorocarbene with diene **1** under the conditions of phase transfer catalysis in the presence of excess haloform. In this case, all three possible tetrachlorides **8**—**10** are formed. Dibromocarbene adds to diene **1** to form only one tetrabromide with the structure of tricycloundecadiene. This regioselectivity of opening of dihalocyclopropanes has been observed previously only in the series of alkoxy-substituted dihalocyclopropanes.[11]

Table 2. Atomic coordinates and thermal parameters B_{iso}/B_{eq} in molecule **8**

Atom	x	y	z	B_{iso}/B_{eq}
Cl(1)	0.2538(1)	0.0918(1)	0.3234(0)	4.18(3)
Cl(2)	0.5500(1)	0.8743(1)	0.4540(0)	5.31(3)
Cl(3)	0.7102(1)	0.5072(2)	0.4673(0)	4.69(3)
Cl(4)	0.1103(1)	0.4799(2)	0.2911(0)	5.25(3)
C(5)	0.2351(2)	0.4677(5)	0.3283(2)	3.45(9)
C(6)	0.5843(3)	0.5150(5)	0.4321(1)	3.17(8)
C(7)	0.4154(3)	0.3764(5)	0.4002(1)	2.90(8)
C(8)	0.5242(3)	0.3696(5)	0.4304(1)	3.36(9)
C(9)	0.2672(3)	0.5838(5)	0.3685(2)	3.7(1)
C(10)	0.3745(3)	0.5755(5)	0.3995(1)	3.15(8)
C(11)	0.4107(2)	0.3460(5)	0.3386(1)	2.96(8)
C(12)	0.4480(3)	0.6720(5)	0.3670(1)	3.22(9)
C(13)	0.5525(3)	0.6927(5)	0.4039(1)	3.22(9)
C(14)	0.2998(3)	0.3221(5)	0.3095(1)	3.25(9)
C(15)	0.4526(2)	0.5326(5)	0.3209(1)	3.42(9)
H(7A)	0.3730(2)	0.2899(5)	0.4148(1)	6.3165
H(8A)	0.5500(2)	0.2573(5)	0.4488(1)	6.3165
H(9A)	0.2214(2)	0.6750(5)	0.3781(1)	6.3165
H(10A)	0.3809(2)	0.6256(5)	0.4357(1)	6.3165
H(11A)	0.4519(2)	0.2426(5)	0.3320(1)	6.3165
H(12A)	0.4218(2)	0.7900(5)	0.3528(1)	6.3165
H(13A)	0.6011(2)	0.7258(5)	0.3818(1)	6.3165
H(14A)	0.2960(2)	0.3351(5)	0.2709(1)	6.3165
H(15A)	0.4119(2)	0.5752(5)	0.2873(1)	6.3165
H(15B)	0.5213(2)	0.5176(5)	0.3159(1)	6.3165

Table 3. Bond lengths (d) in molecule **8**

Bond	d/Å	Bond	d/Å
Cl(1)—C(14)	1.825(4)	Cl(2)—C(13)	1.815(4)
Cl(3)—C(6)	1.748(3)	Cl(4)—C(5)	1.752(4)
C(5)—C(9)	1.314(5)	C(5)—C(14)	1.494(5)
C(6)—C(8)	1.317(5)	C(6)—C(13)	1.483(5)
C(7)—C(8)	1.509(5)	C(7)—C(10)	1.533(5)
C(7)—C(11)	1.544(5)	C(7)—H(7A)	0.960(5)
C(8)—H(8A)	0.961(5)	C(9)—C(10)	1.499(5)
C(9)—H(9A)	0.960(5)	C(10)—C(12)	1.557(5)
C(10)—H(10A)	0.961(5)	C(11)—C(14)	1.533(5)
C(11)—C(15)	1.553(5)	C(11)—H(11A)	0.960(5)
C(12)—C(13)	1.529(5)	C(12)—C(15)	1.537(5)
C(12)—H(12A)	0.960(5)	C(13)—H(13A)	0.960(5)
C(14)—H(14A)	0.960(5)	C(15)—H(15A)	0.960(5)
C(15)—H(15B)	0.960(5)		

Table 4. Bond angles (ω) in molecule **8**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Cl(4)—C(5)—C(9)	120.9(3)	Cl(2)—C(13)—C(6)	109.5(2)	C(7)—C(10)—C(12)	99.3(3)
C(9)—C(5)—C(14)	124.2(3)	Cl(2)—C(13)—H(13A)	108.8(3)	C(9)—C(10)—C(12)	110.6(3)
Cl(3)—C(6)—C(13)	115.4(3)	C(6)—C(13)—H(13A)	108.8(4)	C(12)—C(10)—H(10A)	112.0(4)
C(8)—C(7)—C(10)	110.1(3)	Cl(1)—C(14)—C(5)	109.7(3)	C(7)—C(11)—C(15)	102.4(3)
C(8)—C(7)—H(7A)	111.9(4)	Cl(1)—C(14)—H(14A)	109.0(3)	C(14)—C(11)—C(15)	109.4(3)
C(10)—C(7)—H(7A)	111.9(4)	C(5)—C(14)—H(14A)	109.0(4)	C(15)—C(11)—H(11A)	111.6(4)
C(6)—C(8)—C(7)	121.2(3)	C(11)—C(15)—C(12)	106.4(3)	C(10)—C(12)—C(15)	102.8(3)
C(7)—C(8)—H(8A)	119.4(4)	C(11)—C(15)—H(15B)	110.5(4)	C(13)—C(12)—C(15)	110.5(3)
C(5)—C(9)—H(9A)	119.6(4)	C(12)—C(15)—H(15B)	110.4(4)	C(15)—C(12)—H(12A)	111.4(4)
C(7)—C(10)—C(9)	110.3(3)	Cl(4)—C(5)—C(14)	114.9(3)	Cl(2)—C(13)—C(12)	110.5(2)
C(7)—C(10)—H(10A)	112.0(4)	Cl(3)—C(6)—C(8)	121.1(3)	C(6)—C(13)—C(12)	110.4(3)
C(9)—C(10)—H(10A)	112.0(4)	C(8)—C(6)—C(13)	123.5(3)	C(12)—C(13)—H(13A)	108.8(4)
C(7)—C(11)—C(14)	109.8(3)	C(8)—C(7)—C(11)	110.1(3)	Cl(1)—C(14)—C(11)	110.1(2)
C(7)—C(11)—H(11A)	111.6(4)	C(10)—C(7)—C(11)	100.2(3)	C(5)—C(14)—C(11)	109.9(3)
C(14)—C(11)—H(11A)	111.6(4)	C(11)—C(7)—H(7A)	111.9(4)	C(11)—C(14)—H(14A)	109.0(4)
C(10)—C(12)—C(13)	109.1(3)	C(6)—C(8)—H(8A)	119.4(4)	C(11)—C(15)—H(15A)	110.4(4)
C(10)—C(12)—H(12A)	111.4(4)	C(5)—C(9)—C(10)	120.8(3)	C(12)—C(15)—H(15A)	110.5(4)
C(13)—C(12)—H(12A)	111.4(4)	C(10)—C(9)—H(9A)	119.6(4)	H(15A)—C(15)—H(15B	108.6(4)

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-500 instrument (500.17 and 125.77 MHz, respectively). The mass spectra were obtained on a Finnigan MAT-112S instrument. X-ray structural analysis was carried out on an automated Syntex-P2$_1$ diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.71069 Å, $\theta/2\theta$ scanning technique, $2\theta \leq 60°$). The reaction products were separated on silica gel (Chemapol 40—100 μm).

Addition of dichlorocarbene. Addition of dichlorocarbene was carried out according to the procedure reported previously.[12] Diene **1** (0.5 g, 4.3 mmol) was added to a mixture of $CHCl_3$ (1.4 mL, 2.0 g, 17 mmol), CH_2Cl_2 (1.7 mL), and triethylbenzylammonium bromide (0.1 mmol). A 50% NaOH solution (0.9 mL, 0.68 g of NaOH, 17 mmol) was added to the reaction mixture with ice-cooling. The mixture was stirred with cooling for 20 min and then at ~20 °C for 7 h. The mixture was poured into water (50 mL) and extracted with CH_2Cl_2. The extracts were washed with water until the reaction mixture became neutral. Evaporation gave a mixture of chlorides in a yield of 0.66 g (56%) from which crystals of tetrachloride **8** precipitated (50 mg, m.p. 191—193 °C, yield 4%). Compound **8** was studied by X-ray structural analysis. Crystals of **8** are orthorhombic, space group $C2/c$, a = 13.407(3), b = 7.195(1), c = 25.003(1) Å, β = 101.12(1)°, V = 2366.6(7) Å^3, d = 1.600 g cm^{-3}, Z = 8. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic temperature factors for nonhydrogen atoms. The final value of R_f was 0.037 for 2043 F_{hkl} with $I > 4\sigma$.

Chromatography of the mother liquor on a column packed with SiO_2 (a hexane—chloroform mixture as the eluent) gave a mixture of tetrachlorides **8**—**10** (360 mg, yield 30%) in a ratio of 2 : 4 : 1 (according to the NMR spectral data). Mass spectra of compounds **8**—**10** (EI, 70 eV), m/z (I_{rel} (%)): 288 $[M]^+$ (2.6), 286 $[M]^+$ (13.3), 284 $[M]^+$ (32), 282 $[M]^+$ (24), 251 $[M-Cl]^+$ (8), 249 $[M-Cl]^+$ (24), 247 $[M-Cl]^+$ (23), 215 $[M-HCl-Cl]^+$ (4), 213 $[M-HCl-Cl]^+$ (17), 211 $[M-HCl-Cl]^+$ (33), 177 $[M-2\ HCl-Cl]^+$ (53), 175 $[M-2\ HCl-Cl]^+$ (72), 149 (94), 147 (45), 141 (100), 139 (39), 137 (41), 135 (55), 125 (27), 115 (64), 113 (84).

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