Carbene Rearrangements, XXII[1]

Labelling Studies of the Reaction of 8,8-Dibromobicyclo[5.1.0]octa-2,4-diene with Methyllithium

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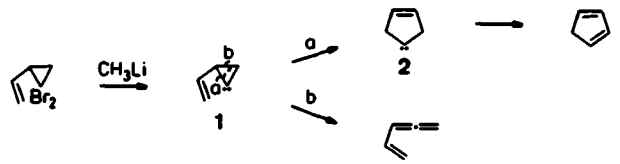
In the reaction of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (3) with methyllithium four dihydropentalenes are formed. In addition to the already described 1,6a-, 1,4-, and 1,5-dihydropentalenes (7, 8, 9), the 1,6-isomer 15 is detected. The dihydropentalenes were characterized by means of their perfluoro-2-butyne adducts. The mechanism of their formation has been elucidated by ^{12}C labelling. Cleavage of the lateral bond a in 4 induces a carbene-carbene rearrangement with 1,3-C migration (Skattebøl rearrangement) to give carbene 13. This stabilizes by a 1,2-vinyl shift to afford 1,6a-dihydropentalene (7). 1,4-, 1,5-, and 1,6-dihydropentalene (8, 9, 15) are formed by subsequent 1,5-H shifts.

Carben-Umlagerungen, XXII[1]. – Markierungsstudien der Reaktion von 8,8-Dibromobicyclo[5.1.0]octa-2,4-dien mit Methyllithium

In der Reaktion von 8,8-Dibrombicyclo[5.1.0]octa-2,4-dien (3) mit Methyllithium werden vier Dihydropentalene gebildet. Zusätzlich zu den bereits beschriebenen 1,6a-, 1,4- und 1,5-Dihydropentalenen (7, 8, 9) wurde das 1,6-Isomere 15 gefunden. Die Dihydropentalene wurden anhand ihrer Perfluor-2-butin-Addukte charakterisiert. Der Mechanismus ihrer Bildung wurde durch ^{12}C-Markierung aufgeklärt. Die Spaltung der lateralen Bindung a in 4 induziert eine Carben-Carben-Umlagerung mit 1,3-C-Wanderung (Skattebøl-Umlagerung) zum Carben 13. Dieses stabilisiert sich durch eine 1,2-Vinylverschiebung zu 1,6-Dihydropentalen (7). Die 1,4-, 1,5- und 1,6-Dihydropentalene (8, 9, 15) werden durch nachfolgende 1,5-H-Verschiebung gebildet.

Although the formation of cyclopentadienes from the reaction of 1,1-dibromo-2-vinylcyclopropanes with methyllithium has been known since 1962[2], the mechanism of the carbene-carbene rearrangement[3] of the type 1 → 2 (Skattebøl rearrangement) is still the subject of intensive studies[4].

Scheme 1

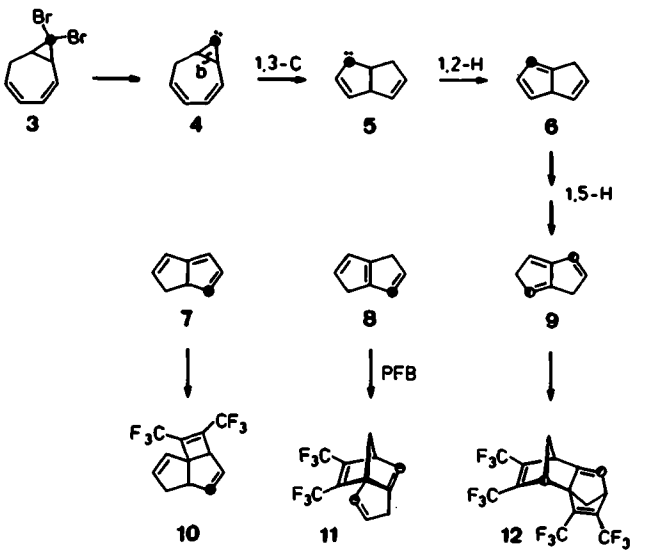


When investigating the reactions of *gem*-dibromovinylcyclopropanes with various substituents, special interest has been paid to the electronic and steric prerequisites of the rearrangement[5]. Systems in which the *gem*-dibromovinylcyclopropane unit is incorporated into a bicyclic structure have been studied thoroughly[6].

In 1970, van Vuuren treated 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (3) with methyllithium[7] and isolated 1,6a-, 1,4-, and 1,5-dihydropentalene (7, 8, 9) by means of the corresponding perfluoro-2-butyne (PFB) adducts 10, 11, and 12, respectively.

As a mechanism for the formation of the bicyclo[3.3.0] structure a carbene-carbene rearrangement of 4 to 5 was suggested. Opening of the distal bond b in 4 and 1,3-C and subsequent 1,2-H migration led primarily to 1,3a-dihydropentalene (6) which, due to its trisallylic hydrogen atom, isomerized readily to 7, 8, and 9 by 1,5-H shifts.

Scheme 2



● = ^{12}C-label (^{12}C ≥ 99.95%)
● = half labelled with ^{12}C

When Baird and Reese repeated the reaction of 3, only 1,6a- and 1,4-dihydropentalene (7, 8) were found and trapped as their dimethyl acetylenedicarboxylate adducts[8]. According to these experiments, 8 represents the thermal isomerization product of 7. 7 arises from a carbene-carbene rearrangement of 4 to bicyclo[3.2.1]octa-2,6-dien-8-ylidene (13) and a subsequent 1,2-vinyl shift of the C1 – C2 bond. The central rearrangement step 4 → 13 implies cleavage of the lateral bond a and 1,3-carbon migration to give the

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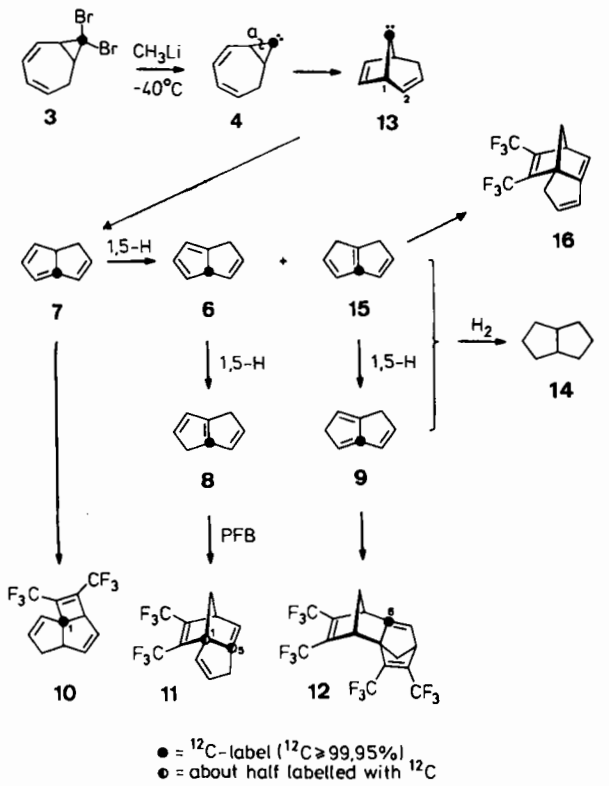
7-homonorbornadienylidene **13**[9]. In addition, **3** has also been treated with methyllithium for the construction of the 1,7-trimethylenenorbornane skeleton by a [4 + 2] cycloaddition of **7** and a ketene equivalent[10]. The corresponding adducts of **7** and **8** were obtained in a ratio of 9:1.

Scheme 3



In the course of our investigations on carbene rearrangements we have studied cyclopropylidene systems containing a 1,3-butadienyl substituent[4a,11]. Depending on the configuration of the central double bond a regiospecific rearrangement behavior has been observed[4a,11]. As **3** represents a model compound with a fixed geometry of the *cis*-1,3-butadienyl unit, we decided to reinvestigate its reaction with methyllithium. With regard to the above mentioned contradictory interpretations[7,8] emphasis was laid on the elucidation of the mechanism of the dihydropentalene formation.

Results

The reaction of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (**3**) with methyllithium (1.9 eq.) in ether at −40°C gave an unstable product mixture consisting of three main components according to gas chromatography. The ^{1}H-NMR spectrum revealed the presence of 1,5-dihydropentalene (**9**)[12].

Upon catalytic hydrogenation (H_2-Pt/C), *cis*-bicyclo[3.3.0]octane (**14**) was formed in 36% yield almost as the nearly exclusive product (95%). When the reaction mixture was allowed to react with an excess of perfluoro-2-butyne at −40°C prior to hydrolysis, the adducts of 1,6a-, 1,4-, 1,6-, and 1,5-dihydropentalene **10**, **11**, **16**, and **12** were isolated by VPC in 18%, 8%, 2%, and 4% yield, respectively. In addition to **10**, **11**, and **12** which have already been characterized by van Vuuren[7], **16**, the adduct of 1,6-dihydropentalene (**15**), was isolated. Recently, in another context, its structure has also been described independently by Klumpp[13].

The reaction of **3** with methyllithium and subsequent trapping with perfluoro-2-butyne was repeated using ^{12}C labelled starting material ($^{12}C \geq 99.95\%$)[4a,14]. [8-^{12}C]-**3** was synthesized from 1,3,5-cycloheptatriene and $^{12}CDBr_3$[14d]. After the reaction with methyllithium and PFB only three major products **10**, **11**, and **12** were isolated by preparative VPC. **16**, the component formed in lowest yield, had to be neglected this time.

Comparison of the ^{13}C-NMR spectra of the three labelled and the three unlabelled adducts revealed the absence of one signal each in the spectra of **10** and **12**. The assignment of the signals led to the conclusion that **10** is labelled at C-1 (signal at δ = 78.0) and **12** at C-6 (signal at δ = 159.9).

On the contrary, in the ^{13}C-NMR spectrum of the labelled adduct **11** no peak of unlabelled **11** was completely missing. Careful quantitative analysis[15], however, showed that the intensity of the signals for C-1 and C-5 (δ = 78.0 and 161.3) were reduced by about 48 and 44%, respectively.

From the distribution pattern of the ^{12}C label in the PFB adducts **10**, **11**, and **12** (Scheme 3) the following conclusions can be drawn with regard to the labelling of the corresponding dihydropentalenes, **7**, **8**, and **9**: 1,6a-dihydropentalene (**7**) (giving adduct **10**) bears the label in C-3a as does 1,5-dihydropentalene (**9**) (affording the 2:1 adduct **12**). 1,4-Dihydropentalene (**8**), the isomer with C_{2v}-symmetry, is also labelled in C-3a. Because of the two "crossed" diene units in the molecule, the Diels-Alder reaction gives rise to *two* adducts **11** in equal amounts differing only in the position of the ^{12}C label. Thus, there are just as many molecules labelled in C-1 as species labelled in C-5, i.e. **11** is, as expected, about 50% labelled in both positions.

Discussion

The introduction of the ^{12}C label in **3** clarifies the mechanism of the carbene-carbene rearrangement leading to the dihydropentalenes. It furthermore allows to distinguish between the reaction pathways proposed by van Vuuren[7] and Baird and Reese[8].

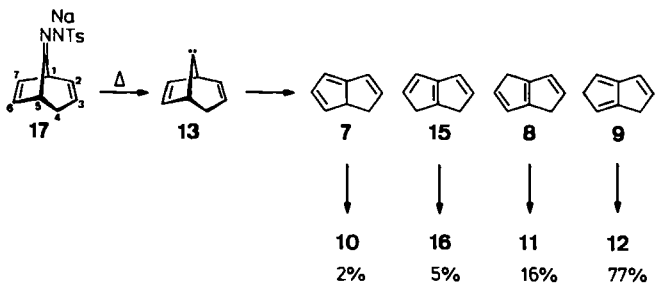
Cleavage of the distal bond b in [^{12}C]-**4** and 1,3-C migration would afford [^{12}C]-**5** which should result in the formation of the adducts **10**, **11**, and **12**. The ^{12}C positions to be expected are depicted in Scheme 2. However, this labelling pattern is not in agreement with our results described above.

In contrast to this, fission of the lateral bond in [^{12}C]-**4** and 1,3-C migration to the rearranged "foiled" carbene [^{12}C]-**13**[9] explains the observed distribution pattern. A 1,2-vinyl shift (cleavage of the C-1 − C-2-bond)[16] in **13** leads to 1,6a-dihydropentalene (**7**) which is partly trapped by PFB, but also isomerizes in part to 1,3a- and 1,6-dihydropentalene (**6** and **15**). An adduct of **6** could not be found because, under the conditions applied, **6** is rapidly converted to 1,4-dihydropentalene (**8**) by 1,5-H migration of its trisallylic hydro-

gen. The symmetrical isomer **8** and PFB afford the adduct **11** with the ^{12}C label distributed about equally between C-1 and C-5. **15** to some extent is trapped with PFB to give small amounts of **16**. The other portion isomerizes to 1,5-dihydropentalene (**9**) which undergoes a twofold Diels-Alder reaction with PFB to yield **12**.

This interpretation is supported by the known reactive behavior of bicyclo[3.2.1]octa-2,6-dien-8-ylidene (**13**) which has been generated by flash pyrolysis of the corresponding tosylhydrazone sodium salt at 250°C/0.03 Torr[9,17]. When the pyrolysate was allowed to react instantaneously with PFB at −30 to −40°C the same PFB adducts **10**, **11**, **12**, and **16** of the dihydropentalenes **7**, **8**, **9**, and **15** were isolated, however in different ratios (2:16:77:5). Here, there seems to exist a direct relationship between the thermal stability of the dihydropentalenes and the yields of the PFB adducts which make up ca. 85% of the total reaction mixture. Thus, the thermodynamically most stable 1,5-dihydropentalene[9,18] is the isomer which is formed by far most frequently.

Scheme 4



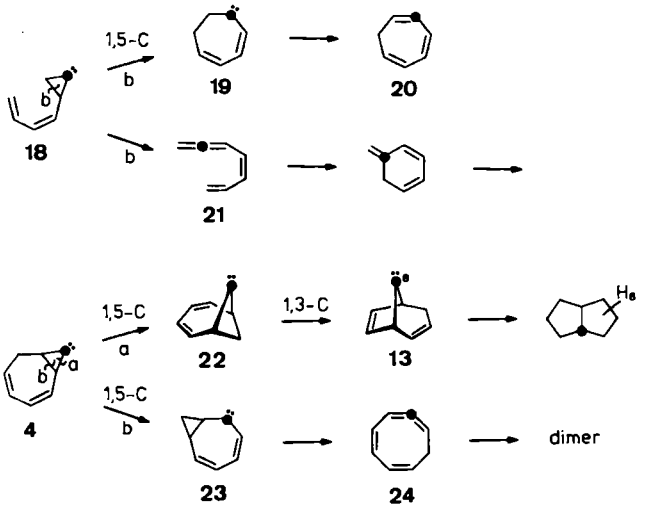
Since bicyclo[5.1.0]octa-2,4-dien-8-ylidene (**4**) contains a *cis*-2-(1,3-butadienyl)cyclopropylidene as a reactive substructure, the possibility of a carbene-carbene rearrangement with 1,5-C migration has to be discussed. As depicted in Scheme 5, fission of the lateral bond a in **4** ultimately also leads to dihydropentalenes. A prerequisite for this, however, is that another carbene-carbene rearrangement has to take place implying a 1,3-C migration in the vinylcyclobutylidene which is a structural subunit in the rearranged carbene **22**. We have recently demonstrated[17,19] that this pathway indeed is a mechanistic possibility. Thus, bicyclo-[4.1.1]oct-2-en-8-ylidene undergoes a carbene-carbene rearrangement with 1,3-C migration to bicyclo[3.2.1]octa-2-en-8-ylidene, however only to a minor extent (10−13%).

Through such a transformation the label in **22** would be also carried into the C-8 position of **13**.

Little is known about the reactive behavior of bicyclo-[4.1.1]octa-2,4-dien-8-ylidene (**22**) which has been generated[17] independently by the Bamford-Stevens reaction of the tosylhydrazone sodium salt of the corresponding ketone[20]. Due to the unusually low yield of monomeric hydrocarbons obtained in the flash pyrolysis (<10%), the study of this reaction was not pursued further.

Obviously, a priori a distinction between the two reaction mechanisms proposed, i.e. carbene-carbene rearrangement with 1,3-C migration **4** → **13** (Scheme 3) and a multiple carbene-carbene rearrangement with 1,5- and subsequent 1,3-C migration **4** → **22** → **13** (Scheme 5), is not possible. The last-mentioned rearrangement sequence, however, is not likely to occur. While the carbene-carbene rearrangement with 1,3-C shift **4** → **13** is expected to be strongly exothermic, the 1,5-C migration **4** → **22** might be isoenergetic[21].

Scheme 5



Finally, in **4** a second carbene-carbene rearrangement with a 1,5-C migration has to be discussed. In the parent *cis*-2-(1,3-butadienyl)cyclopropylidene (**18**) the rupture of the distal bond b has been shown by labelling experiments to be responsible for the formation of [2-^{12}C]-1,3,5-cycloheptatriene (**20**), which is thought to derive from **19** by 1,2-hydrogen migration. The cleavage of the distal bond b in **4**, preceeding the 1,5-C shift, leads to **23**. This carbene has been generated from the corresponding tosylhydrazone sodium salt[22] by photolysis and thermolysis to yield 1,2,4,6-cyclooctatetraene (**24**) which dimerizes.

24, however, is the product expected from the cyclopropylidene-allene rearrangement of **4**. This rearrangement, in general, is the typical reaction of cyclopropylidenes[23]. Thus, in the "open" parent system **18** this rearrangement to *cis*-1,2,4,6-heptatetraene (**21**) is the reaction competing efficiently with the 1,5-C shift to **19**. Interestingly enough, in **18** both competing reactions are induced by cleavage of the *same* bond, i.e. the distal bond b. This is in stark contrast to the reactive behavior of the vinylcyclopropylidene system **1** where the carbene-carbene rearrangement with 1,3-C migration proceeds through fission of the lateral bond a[14b], while the distal bond has to be broken in order to produce the vinylallene[24].

In the mechanistic studies[7,8] undertaken on **4**, which has been generated from the geminal dibromo compound **3** by action of methyllithium[7,8,10], the formation of the cyclic allene **24** has not been mentioned. This is also true for the deamination reaction of the bicyclo[5.1.0]octa-2,4-diene-8-diazonium ion in protic solvent in the presence of sodium

methoxide[25]. Here, the predominant formation of *syn*-8-methoxybicyclo[3.2.1]octa-2,6-diene was observed. This compound is thought to derive from the carbene-carbene rearrangement with 1,3-C migration, **4** → **13**, followed by protonation to the corresponding cation, which is trapped by methoxide ion. **24**, the product of a cyclopropylidene – allene rearrangement in **4**, could not be detected.

In conclusion, in contrast to the "unhampered" parent system **18** the fixed *cis*-1,3-butadienyl unit in **4** obviously does not allow a carbene-carbene rearrangement with 1,5-C shift to proceed. The 1,3-C migration **4** → **13** which takes place instead of this, is mechanistically analogous to the vinylcyclopropylidene-cyclopentenylidene rearrangement **1** → **2** discovered 25 years ago by Skattebøl.

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Experimental

^{1}H-NMR spectra: Bruker WP 80 and WM 250 spectrometers, 80 and 250 MHz, respectively, tetramethylsilane internal standard. Apparent coupling constants $J(\pm 1$ Hz), number of protons, and multiplicity are given. – ^{13}C-NMR spectra: FT mode, Bruker WM 250 spectrometer, 62.9 MHz [δ(ppm), multiplicity]. – IR spectra: Perkin-Elmer 257 and 325 spectrometers. – Mass spectra: Varian MAT CH 5 spectrometer, 70 eV. – VPC analysis and separations: Perkin-Elmer Model F 20 and Varian Fractometers 90-P and 920.

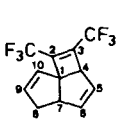
Reaction of 8,8-Dibromobicyclo[5.1.0]octa-2,4-diene (**3**) *with Methyllithium:* The solution of **3**[7] (264 mg, 1.0 mmol) in dry ether (15 ml) was cooled to −40°C (argon). An ethereal solution of methyllithium (1.2 ml, 1.9 mmol), was added via syringe within 15 min while stirring. The reaction mixture was stirred for another 30 min at −40°C and was then hydrolyzed by addition of ice/water (30 ml). The ether layer was separated, and the aqueous layer was extracted twice with small portions of cold ether. The combined organic extracts were washed with water and dried ($MgSO_4$). A few crystals of hydroquinone were added to the solution, and then it was carefully concentrated (≈10°C/100 Torr) until ca. 1 ml was left. Immediate ^{1}H-NMR analysis revealed the presence of 1,5-dihydropentalene (**9**) by showing signals at δ = 2.9, 5.8, and 6.3[12].

According to VPC analysis (glass capillary column, 85 m, silicone oil OV 101, 60°C, and 25 m, marlophen, 25°C) three compounds were formed in a ratio of 21:45:34.

Reaction of **3** *with Methyllithium and Subsequent Catalytic Hydrogenation:* The solution of **3** (710 mg, 2.7 mmol) in dry ether (25 ml) containing some crystals of hydroquinone was treated with an ethereal solution of methyllithium (3.7 ml, 4.1 mmol) as described above. After the work-up procedure ca. 80 mg of 10% platinum on charcoal was added to the undried ethereal solution of the reaction mixture. It was hydrogenated under atmospheric pressure. After 50 min, about 150 ml of H_2 had been consumed, and the catalyst was filtered off. The solution was dried ($MgSO_4$) and concentrated under reduced pressure (≈20°C/100 Torr) until ca. 2 ml were left. 3-Methylheptane (30 µl) was added as internal standard, and the solution was analyzed by VPC (glass capillary column, 80 m, OV 101, 60°C). The analysis revealed that *cis*-bicyclo[3.3.0]octane (**14**) was formed nearly as the sole product (95% relative; identification by comparison with the retention time of an authentic sample) in a yield of 36%.

Reaction of **3** *with Methyllithium and Subsequent Reaction with Perfluoro-2-butyne (PFB):* As described above, **3** (2.0 g, 7.6 mmol) in dry ether (30 ml) was treated at −40°C with an ethereal solution of methyllithium (8.7 ml, 11.3 mmol) containing a few crystals of hydroquinone. The reaction mixture was not hydrolyzed, however, some drops of acetic acid were added for neutralization. Then the cold solution was filled under argon into a precooled heavy-walled glass vessel (cooled to −40°C by partial immersion into a dry ice-acetone cooling bath). An excess of perfluoro-2-butyne (≈3 ml) was added, and the vessel was sealed. The reaction mixture was kept for 1.5 h at −40°C and then allowed to warm up to room temperature. After a total reaction time of 17 h the vessel was opened. The excess of perfluoro-2-butyne was allowed to evaporate. The ethereal solution was hydrolyzed, and the layers were separated. The aqueous layer was extracted twice with ether (30 ml), and the combined organic layers were dried ($MgSO_4$). The solution was concentrated under reduced pressure (≈20°C/20 Torr) up to ca. 3 ml. VPC analysis (glass capillary column, 80 m, OV 101, 90°C) revealed the presence of four compounds (rel. ratio: 47:23:6:12) besides some minor peaks. The reaction mixture was separated by preparative VPC (glass column, 2.5 m, SE 30, 105°C, flow rate: 95 ml He/min).

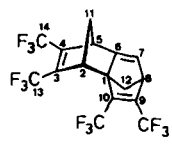
Fraction 1 (ret. time 24 min): 370 mg (18%) of *2,3-bis(trifluoromethyl)tricyclo[5.3.0.0^{1,4}]deca-2,5,9-triene* (**10**) (purity 99% according to VPC). – IR (CCl_4): 3090 cm^{-1}, 3040, 3000, 2940, 2890, 2840, 1670, 1525, 1435, 1340, 1325, 1280, 1260, 1240, 1160, 1135, 1120, 990, 945, 840, 710, 700. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.9–2.2 (m, 2H, 8-H), 2.65–2.95 (m, 1H, 7-H), 3.85 (br. s, 1H, 4-H), 5.95–6.15 (m, 1 olef. H), 6.35 (mc, 1 olef. H), 6.9–7.15 (m, 2 olef. H). – ^{13}C NMR (62.9 MHz, C_6D_6): δ = 30.8 (t, C-8), 51.1 (d, C-7), 78.0 (s, C-1), 88.1 (d, C-4), 122.5 (q* C-11, C-12, $J_{C,F} \simeq -270$ Hz), 129.5 (d, olef. C), 140.2 (d, 2 olef. C)[26], 148.5 (d, olef. C). (*This multiplicity refers to the C-F coupling). – MS: *m/z* (%) = 266 (52, M^+), 197 (76, $M^+ - CF_3$), 177 (100, $M^+ - CF_3$, – HF), 128 (55, $M^+ - 2CF_3$). – The data of the IR, ^{1}H NMR, and mass spectrum are in agreement with the reference data[7].



10

11

16



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Fraction 2 (ret. time 31 min): 230 mg (11%) of a mixture of *8,9-bis(trifluoromethyl)tricyclo[5.2.1.0^{1,5}]deca-2,5,8-triene* (**11**), *8,9-bis(trifluoromethyl)tricyclo[5.2.1.0^{1,5}]deca-3,5,8-triene* (**16**), and an unknown component X (ratio 66:17:9). By repeated VPC separation (glass column, 4.5 m, DC 200, 95°C, flow rate 110 ml He/min) **11** (ret. time 74 min) was obtained in 97% purity (yield 114 mg, 6%). – IR (CCl_4): 3050 cm^{-1}, 2970, 2930, 2860, 2810, 1670, 1640, 1450, 1420, 1355, 1335, 1290, 1275, 1260, 1235, 1170, 1130, 970, 895, 845, 715. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = AB-system: 1.95 (d, 1H, 10-H, $J_{10s,10a} = -7$ Hz) and 2.50 (dd, 1H, 10-H, $J_{7,10} = 2$ Hz), 3.05 (mc, 2H, 4-H), 4.05 (br. s, 1H, 7-H), 6.15 (mc, 2H, 2-, 3-H), 6.35 (mc, 1H, 6-H). The assignment was confirmed by decoupling

Table 1. Intensities of ^{13}C-NMR signals of **11** and [^{12}C]-**11**

Chemical shift	Signal intensities		Quotient of the relative signal intensities ([^{12}C]-**11**:**11**)							Relative standard deviation
[ppm]	**11**	[^{12}C]-**11**	(a)	(b)	(c)	(d)	(e)	(f)	mv	[%]
30.2	19.52	23.18	1	0.83	0.84	0.88	0.89	0.91	0.87	3.9
55.1	9.85	14.15	1.22	1	1.01	1.06	1.07	1.09	1.09	7.2
78.0	1.76	1.24	0.59	0.49	0.49	0.51	0.52	0.52	0.52	7.1
80.0	15.00	21.19	1.19	0.99	1	1.05	1.07	1.09	1.08	6.8
126.4	11.25	15.15	1.12	0.94	0.95	1	1.02	1.03	1.01	7.2
127.1	16.23	21.60	1.12	0.92	0.94	0.99	1	1.03	1.00	7.3
137.2	15.24	19.81	1.10	0.90	0.92	0.97	0.98	1	0.97	8.0
161.3	2.05	1.53	0.63	0.52	0.52	0.56	0.55	0.59	0.56	7.6

The columns (a)–(f) are referring to different signals of reference. This means that in each column the intensity of one signal was set 1. The intensities of all other signals were then related to this. The quotient of these relative intensities calculated for [^{12}C]-**11** and **11** are the values in columns (a)–(f). For determining the mean value (mv) the reference quotient 1 was not included.

experiments. – ^{13}C NMR (62.9 MHz, C_6D_6): δ = 30.2 (t, C-4), 55.1 (d, C-7), 78.0 (s, C-1), 80.0 (t, C-10), 122.6 (q*, C-11, -12, $J_{C,F} \simeq -270$ Hz), 126.4 (d, olef. C), 127.1 (d, olef. C), 137.2 (d, olef. C) (C-2, -3, -6), 161.3 (s, C-5). (*This multiplicity refers to the C-F coupling). – MS: *m/z* (%) = 266 (25, M^+), 197 (100, $M^+ - CF_3$), 177 (62, $M^+ - CF_3, - HF$), 128 (40, $M^+ - 2CF_3$), 104 (12, $C_8H_8^+$), 69 (26, CF_3^+). – The data of the IR, ^1H NMR, and mass spectrum are in agreement with the reference data[7,13].

16 was separated from compound X by preparative TLC (silica gel, 2 mm, eluent pentane). The yield was 20 mg (1%, purity 90%). – ^1H NMR (80 MHz, $CDCl_3$): δ = AB-system: 1.9 (d, 1H, 10-H, $J_{10s,10a} = -7$ Hz) and 2.4 (dd, 1H, 10-H, $J_{7,10} = 2$ Hz), AB-system: 2.5 (d, 1H, 2-H, $J_{2,2} = -19$ Hz) and 3.1 (d, 1H, 2-H), 4.15 (br. s, 1H, 7-H), 6.2 (dd, 1 olef. H, $J = 3$ and 1 Hz), 6.45 (s, 2 olef. H). The assignment and the coupling constants were confirmed by decoupling experiments. – MS: *m/z* (%) = 266 (47, M^+), 247 (11, $M^+ - F$), 197 (100, $M^+ - CF_3$), 177 (87, $M^+ - CF_3, - HF$), 128 (45, $M^+ - 2CF_3$). – The spectroscopic data are in accordance with the reference data of Klumpp[13].

Further efforts to purify **16** by VPC (glass column, 1.5 m, SE 30, 100°C, flow rate 120 ml He/min) resulted in a complete rearrangement of **16** to compound X which could be characterized as follows. – IR ($CDCl_3$): 1655 cm^{-1}, 1360, 1345, 1300, 1280, 1275, 1260, 1170, 1150, 1135. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.2 (d, 1H, $J = 9$ Hz), 2.15 (td, 1H, $J = 9$; 2 Hz), 2.3 (br. s, 1H), 2.65 (br. d, 1H, $J = 16$ Hz), 3.8 (mc, 1H), 6.15 (mc, 1H), 6.4–6.6 (m, 1H), 6.65 (dd, 1H, $J = 5$; 2 Hz). – MS: *m/z* (%) = 266 (26, M^+), 247 (7, $M^+ - F$), 197 (100, $M^+ - CF_3$), 177 (81, $M^+ - CF_3, - HF$), 128 (42, $M^+ - 2CF_3$).

Fraction 3 (ret. time 52 min): 150 mg (4%) of *3,4,9,10-tetrakis(trifluoromethyl)tetracyclo[6.2.1.1^{2,5}.0^{1,6}]dodeca-3,6,9-triene* (**12**) and two minor compounds (ratio 76:12:6). Further purification of **12** (purity 98%) was achieved by repeated preparative VPC (glass column, 2 m, carbowax, 100°C, flow rate 150 ml He/min, ret. time 20 min). – IR ($CDCl_3$): 2990 cm^{-1}, 2950, 2860, 1665, 1640, 1460, 1355, 1340, 1290, 1280, 1190, 1180, 1160, 1150, 1040, 985, 955, 940, 850, 815, 810, 785. – ^1H NMR (80 MHz, $CDCl_3$): δ = 2 AB-systems: 1.90 (d, 1H, $J_{gem} = -7$ Hz) and 2.25 (d, 1H, $J_{gem} = -10$ Hz) and 2.40 (ddd, 1H, $J_{gem} = -7$, $J_{vic} = 2$; 1 Hz) and 2.60 (td, 1H, $J_{gem} = -10$, $J_{vic} = 2$ Hz, 11-, 12-H), 3.80 (br. s, 1H), 3.90 (br. s, 2H, 2-, 5-, 8-H), 6.40 (dd, 1H, 7-H, $J = 3$; 1 Hz). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.0 (d, C-5), 45.5 (d, C-2), 53.1 (d, C-8), 54.0 (t, C-11), 73.0 (s, C-1), 76.6 (t, C-12), 120.4 (2 q*), 121.0 (q*), 121.9 (q*, C-13, -14, -15, -16, $J_{C,F} \simeq -275$ Hz), 127.0 (d, C-7), 141.3 (q*), 144.0 (q*), 151.7 (q*), 155.0 (q*, C-3, -4, -9, -10, $^3J_{C,F} \simeq 40$ Hz), 159.8 (s, C-6). (*This multiplicity refers to the C-F coupling). – MS: *m/z* (%) = 428 (65, M^+), 409 (30, $M^+ - F$), 359 (100, $M^+ - CF_3$), 339 (25, $M^+ - CF_3, - HF$), 319 (28, $M^+ - CF_3, - 2HF$), 290 (28, $M^+ - 2CF_3$), 227 (46), 226 (51, $M^+ - 2CF_3, - C_5H_4$), 177 (31). – Exact mass: 428.043 (calcd. for $C_{16}H_8F_{12}$ 428.0432). – The spectroscopic data are in agreement with the reference data[7,13].

Reaction of 8,8-Dibromo-[8-^{12}C]bicyclo[5.1.0]octa-2,4-diene ([8-^{12}C]-**3**) *with Methyllithium and Subsequent Reaction with Perfluoro-2-butyne (PFB):* The reaction was carried out in analogy to the reaction of unlabelled **3**. [8-^{12}C]-**3** (1.51 g, 5.7 mmol) – prepared from cycloheptatriene[7] and $^{12}CDBr_3$[14d,27] – was treated with methyllithium (6.1 ml, 8.6 mmol) and subsequently with PFB (ca. 2 ml). The reaction mixture was separated by preparative VPC to afford [^{12}C]-**10** (205 mg, 14%, purity: 98%), [^{12}C]-**11** (136 mg, 9%, purity 99%), and [^{12}C]-**12** (58 mg, 2%, purity 97%). [^{12}C]-**16** as a minor product was not isolated. ^{13}C-NMR spectra of [^{12}C]-**10**, [^{12}C]-**11**, and [^{12}C]-**12** were compared with those of **10**, **11**, and **12**, respectively.

[^{12}C]-**10**: ^{13}C NMR (62.9 MHz, C_6D_6): δ = 30.8 (t, C-8), 51.1 (d, C-7), 88.1 (d, C-4), 129.5 (d), 140.2 (d), 140.25 (d), 148.5 (d, C-5, -6, -9, -10). The signal at δ = 78.0 representing C-1 in **10** is totally missing.

[^{12}C]-**11**: ^{13}C NMR (62.9 MHz, C_6D_6): In Table 1 the intensities[15] of signals of **11** and [^{12}C]-**11** are compared.

[^{12}C]-**12**: ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.0 (d, C-5), 45.5 (d, C-2), 53.2 (d, C-8), 54.0 (t, C-11), 73.1 (s, C-1), 77.3 (t, C-12), 120.7 (2 q*), 121.4 (q*), 122.0 (q*, C-13, -14, -15, -16, $J_{C,F} \simeq -270$ Hz), 127.1 (d, C-7). (*This multiplicity refers to the C-F coupling). The signal at δ = 159.8, representing C-6 in unlabelled **12**, is totally missing.

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3: 34419-22-2 / **4**: 106435-82-9 / **7**: 61771-83-3 / **8**: 61771-84-4 / **9**: 33284-11-6 / **10**: 106435-81-8 / **11**: 75759-56-7 / **12**: 73286-14-3 / **13**: 65419-72-9 / **14**: 1755-05-1 / **15**: 89654-25-1 / **16**: 75759-57-8 / methyllithium: 917-54-4 / perfluoro-2-butyne: 692-50-2

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