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CARBENE–CARBENE REARRANGEMENTS AS A ROUTE TO 1,5-DIHYDROPENTALENE[1]

UDO H. BRINKER* and ILONA FLEISCHHAUER
Abteilung für Chemie der Ruhr-Universität, 4630 Bochum, West Germany

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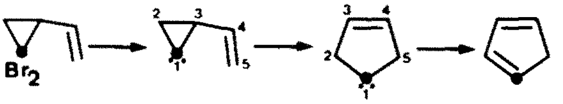
Abstract—1,5-Dihydropentalene (**4**) is formed as the main product on treatment of *trans*-1,2-bis(2,2-dibromocyclopropyl)ethene **3** with methyllithium at −40°. In addition the reaction affords 1- and 2-propadienylcyclopentadienes (**5a**) and (**5b**), and *trans*-1,2,4,6,7-octapentaene (**6**), new C_8H_8 isomers. Diels–Alder adducts of **4**, **5a** and **5b** were obtained in the reaction with perfluorobut-2-yne. The formation of 1,5-dihydropentalene **4** is explained by a double ring expansion sequence involving consecutive carbene–carbene rearrangements with 1,3-carbon and subsequent 1,2-hydrogen shifts, supported by the reaction of double labelled (^{13}C-depleted) **3**. From readily available **3** at low temperatures formation and fusion of two 5-membered rings are achieved in one step.

Compounds comprising structures based on the fusion of two or more cyclopentane rings continue to fascinate chemists. The recognition of some biologically active natural products possessing polyquinane skeletons[2] is responsible for the current interest as are the efforts towards the construction of dodecahedrane,[2–4] a platonic solid consisting of twelve cyclopentane rings. A great number of diverse methods for the synthesis of polyfused cyclopentanoid rings have been developed.[2] However, an approach to polyquinanes involving carbene–carbene rearrangements[5] as the decisive steps has not yet been reported so far.

We now provide details[6] of a simple new synthetic entry to the bicyclo[3.3.0]-ring system by sequential vinylcyclopropylidene-3-cyclopentenylidene rearrangements **1**→**2** (tandem carbene–carbene rearrangement) by which a twofold 3-carbon annulation is achieved in one step.



1 **2**

Fig. 1.

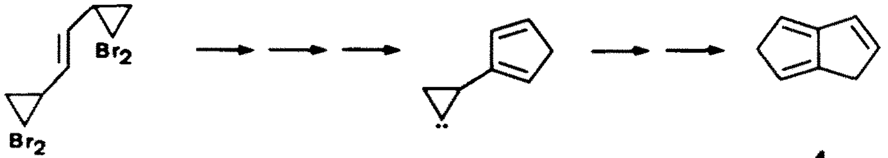
Skattebøl discovered in 1962[5a] that vinylcyclopropylidenes when generated from geminal dibromocyclopropanes with methyllithium[7–9] at −78° rearrange to cyclopentadienes. The mechanism for the formation of cyclopentadienes was established 15 years later, by using as starting material a specifically substituted and ^{12}C-labelled geminal dibromovinylcyclopropane,[5g] in combination with examination by ^{13}C NMR spectroscopy[10] of the cyclopentadiene formed. Hence, vinylcyclopropylidene (**1**) rearranges to 3-cyclopentenylidene (**2**) by cleavage of bond C-1–C-3.[5g] A subsequent 1,2-hydrogen shift in **2** affords cyclopentadiene. We anticipated that, in principle, two consecutive carbene–carbene rearrangements of this type could proceed in a compound comprising two geminal dibromocyclopropane moieties separated by a double bond. For example, reaction of the bifunctional model compound **3** with alkyllithium could initiate a sequence of carbene–carbene rearrangements and 1,2-hydrogen migrations.

The first carbene–carbene rearrangement followed by a 1,2-hydrogen shift and reaction of the second equivalent of alkyllithium could lead to a compound containing a new vinylcyclopropylidene system. Further ring expansion could be achieved by a second carbene–carbene rearrangement whereupon, subsequent to a final 1,2-hydrogen shift, ultimately 1,5-dihydropentalene (**4**) could be formed.

RESULTS AND DISCUSSION

The starting material *trans* - 1,2 - bis(2,2 - dibromocyclopropyl)ethene (**3**) was readily available from pure *trans*-1,3,5-hexatriene as well as from the mixture of the stereoisomers (*cis*:*trans* = 30:70) by twofold dibromocarbene addition ($CHBr_3$, K-t-butoxide).[11] The crystalline bisadduct was isolated in 15 and 10% yield, respectively.

Reaction of **3** in ether at −40° under argon with methyllithium (molar ratio 1:2.5) afforded four compounds in a total yield of 32% as was determined by immediate vpc analysis using an internal standard. The ratio of the four components found was 51:21:18:7. Attempts to separate them from the reaction mixture by preparative vpc failed. However, the comparison with the retention times of an authentical sample showed 1,5-dihydropentalene (**4**) to be the main component formed in 51%. On concentrating the solvent, polymerization



3 **4**

Fig. 2.

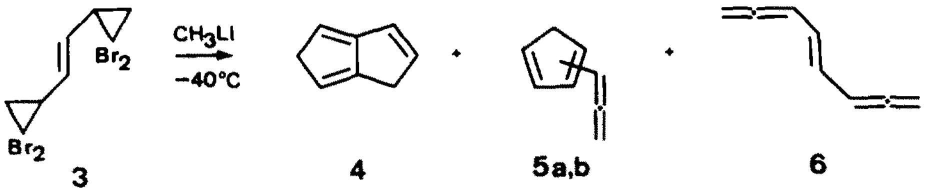


Fig. 3.

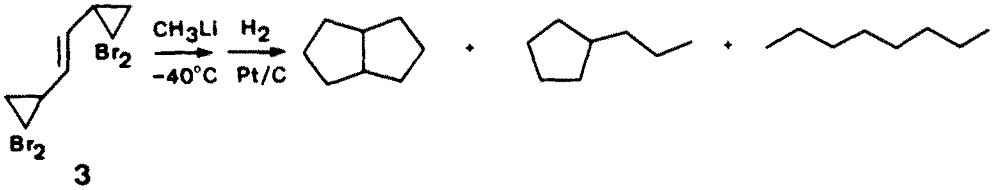


Fig. 4.

started. The ^{1}H NMR spectrum of the crude reaction mixture, however, revealed the characteristic signals of 1,5-dihydropentalene (4).[12] Furthermore, when directly recorded, the IR-spectrum of the same mixture showed a strong absorbance at 1935–1940 cm^{-1} pointing to the presence of allenes **5a, b** and (or) **6**. **6** represents the unknown parent system of diallenes[13] containing allene units connected via a double bond. Next, the crude reaction mixture was directly hydrogenated at 20° after immediate work up in which the temperature was kept below 15°. Vpc analysis with an internal standard showed the formation of only three compounds in the ratio of 53:40:6 (total yield 24%), which were identified as *cis*-bicyclo[3.3.0]octane, n-propylcyclopentane, and n-octane, respectively. The close agreement of the ratios of the saturated and unsaturated products suggests that the three unsaturated hydrocarbons, which due to their instability could not yet be isolated, are 1- and 2-propadienylcyclopentadiene (**5a, b**) (40%), and *trans*-1,2,4,6,7-octapentaene (**6**) (6%).

In order to trap **4** and **5a, b** we chose perfluorobut-2-yne as dienophile, since the adducts with the hydrocarbons were expected to be liquids which would permit their separation by preparative vpc. Thus, **3** was treated with methyllithium (molar ratio 1:2.5) at −40°. After immediate work up (<15°) excess of perfluorobut-2-yne (PFB) was added at −40°. Vpc analysis of the reaction mixture showed the formation of five components (4:2:10:15:65). The two compounds formed in *ca.* 1% yield each could not be identified by preparative vpc due to their instability. However, we succeeded in isolating the Diels–Alder adducts **7, 8** and **9** in 4, 5 and 17% yields, respectively. **7**, containing a vinylallene as a subunit, proved to be relatively unstable. The 1:2-adduct **9** had already been synthesized by independent routes.[14,15]

Reaction pathways leading from **3** to **4, 5a, b** and **6** are depicted in Scheme 1. *trans*-1,2,4,6,7-Octapentaene (**6**) can be regarded as the result of a twofold cyclopropylidene–allene rearrangement. Propadienylcyclopentadienes (**5a, b**) could be formed by a carbene–carbene rearrangement involving a 1,3-carbon shift followed by a 1,2-hydrogen shift and an additional cyclopropylidene–allene conversion. The sequence of these competing rearrangements, however, cannot be established.

1,5-Dihydropentalene (**4**) can be conceived as the product of a double ring expansion sequence involving sequential carbene–carbene rearrangements and 1,2-hydrogen shifts. Thus, the first equivalent of methyllithium generates carbene **10**, which rearranges to carbene **11** followed by subsequent 1,2-hydrogen shift to give **12**. Reaction of **12** with the second equivalent of methyllithium affords **13** containing again a vinylcyclopropylidene system, a prerequisite for the second carbene–carbene rearrangement to **14** to proceed. A final 1,2-hydrogen shift completes the transformation **3**→**4**. The term tandem carbene–carbene rearrangement was proposed for consecutive rearrangements of this type.[6]

A closely related thermal rearrangement sequence has been reported by Ketley *et al.*[16] to occur in a hydrocarbon comprising two 3-membered rings attached to one carbon of a double bond. However, the conversion of **15** into **16** by a twofold vinylcyclopropane–cyclopentene rearrangement requires temperatures of about 400°.

According to the reaction sequence depicted in Scheme 1, 1,5-dihydropentalene (**4**) is formed directly from the rearranged carbene **14** by 1,2-hydrogen shift. In case, however, a different isomeric dihydropentalene would result from the reaction of **3** with methyllithium, it could, like **4**, be partially converted to a dihydropen-

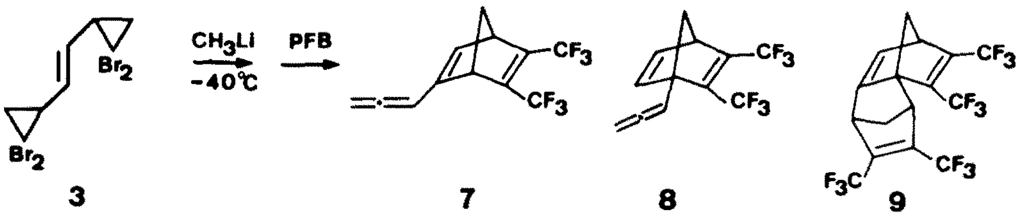
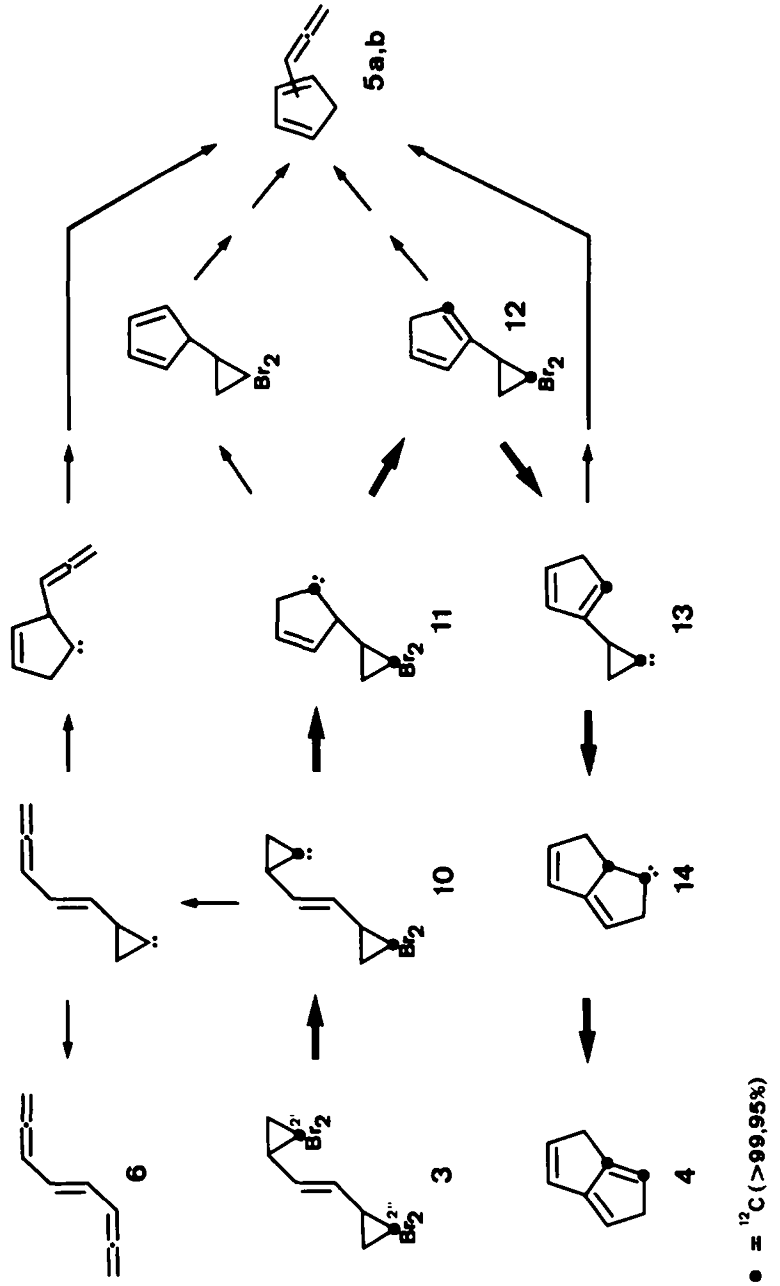


Fig. 5.



Scheme 1.

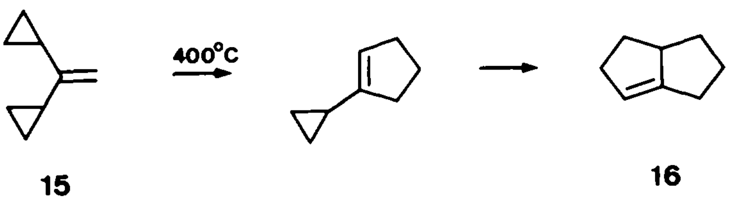


Fig. 6.

talenyl anion or (and) the pentalenyl dianion[12] due to the 0.5 molar excess of methyllithium present. With the assumption that 1,5-hydrogen migrations of secondary hydrogens do not proceed to a significant extent under the conditions given[17] (< 15°), by quenching of the anion or (and) the dianion with water, always formation of **4**, probably the thermodynamically most stable dihydropentalene, could be expected.[18] The isolation of diadduct **9** from the double stepwise addition of perfluorobut-2-yne is clear evidence for the existence of **4**. The total amount of unidentified compounds in the reaction of **3** with methyllithium and perfluorobut-2-yne made up only 4%. In order to find out whether perfluorobut-2-yne-adducts of isomeric dihydropentalenes **17** and **18** could be found among them, **19** and **20** were synthesized according to the literature.[14] The reaction leading from **21** at first to dihydropentalene **17**, has been explained in 1976 by Baird and Reese[5e] to proceed via carbene–carbene rearrangement **22**→**23**. These authors, however, used dimethyl acetylenedicarboxylate as trapping agent for the dihydropentalenes **17** and **18**. A diadduct corresponding to **9** was not found. Comparison of retention times of **19** and **20** revealed these compounds not to be formed in the reaction of **3**.

In order to further support the mechanism for the formation of 1,5-dihydropentalene (**4**) from **3** outlined in Scheme 1, the reaction was carried out with labelled starting material. **3**, containing a ^{12}C-label (^{12}C-content > 99.95%) at C-2′ and C-2″ was readily available by reaction of ^{12}CDBr$_3$ and K-t-butoxide with *trans*-1,3,5-hexatriene. ^{12}CDBr$_3$[5g] was prepared by the method of Soroos and Hinkamp.[19]

After treatment of labelled **3** with methyllithium followed by addition of perfluorobut-2-yne under the given conditions, 1:2-adduct **9** was isolated. Comparison of the ^{13}C NMR spectra of labelled and unlabelled **9** disclosed the absence of two signals at $\delta = 73.0$ and 45.5 ppm.

In **9** with natural isotope distribution the signal at $\delta = 73.0$ ppm could be assigned unambiguosly to the aliphatic quaternary carbon C-1 due to the appearance of a singlet in the off-resonance experiment (Table 1). However, two carbons (C-2 and C-5; f and h in Table 1) came into question for the signal at $\delta = 45.5$ ppm due to similar resonance frequencies (44.0 ppm) and identical multiplicities (doublets). Nonetheless, the signal in question could be assigned to C-2 as follows.

As was already shown, the formation of **9** from the reaction of **3** with methyllithium in the presence of perfluorobut-2-yne can be explained to proceed via a reaction sequence involving consecutive carbene–carbene rearrangements with 1,3-carbon and subsequent 1,2-hydrogen shifts. Additionally, 1,5-hydrogen shifts had to be taken into account, which could already take place to some extent (vide supra) in dihydropentalenes at the temperatures employed (< 15°) in the reaction of **3**. By all combinations of these three types of reactions, the double-labelled starting material **3** is converted into four 1,5-, two 1,3a-, and two 1,6a-dihydropentalenes. These eight dihydropentalenes exhibit only labelling patterns **24** and **25** (Fig. 9).

Only the four labelled 1,5-dihydropentalenes in Fig. 10 can undergo the twofold Diels–Alder addition to labelled **9**. Of these four, only **4** and **26** place a label at a quaternary carbon in **27** and **9**, respectively. From this it is obvious that the assignment of the signal at $\delta = 73.0$ ppm to the aliphatic quaternary carbon C-1 is of decisive importance in order to locate the second ^{13}C-depleted carbon. Thus, only the labelling pattern depicted in **9** is compatible with our findings. Furthermore, Fig. 8 reveals an isotopic labelling at C-2 and C-5 of at least 95%, as can be seen from the complete absence of

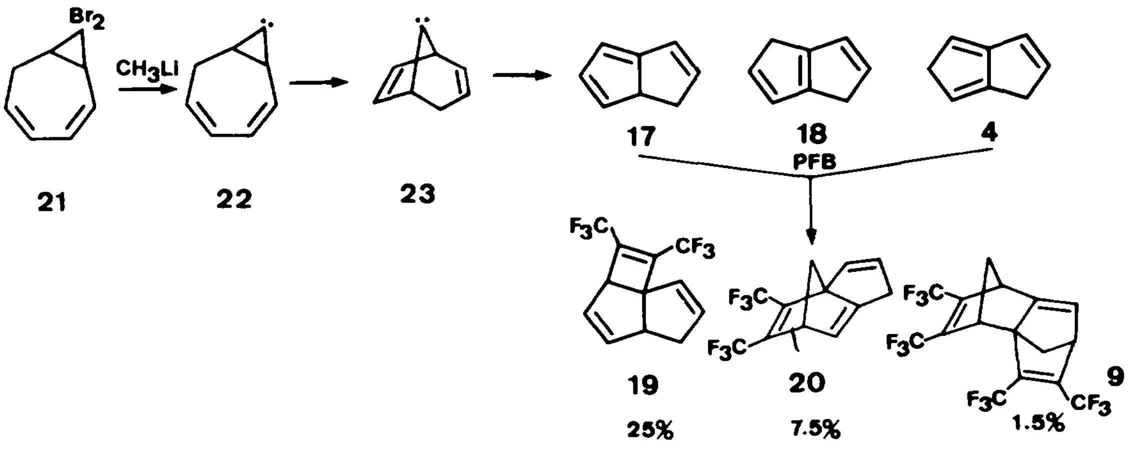


Fig. 7.

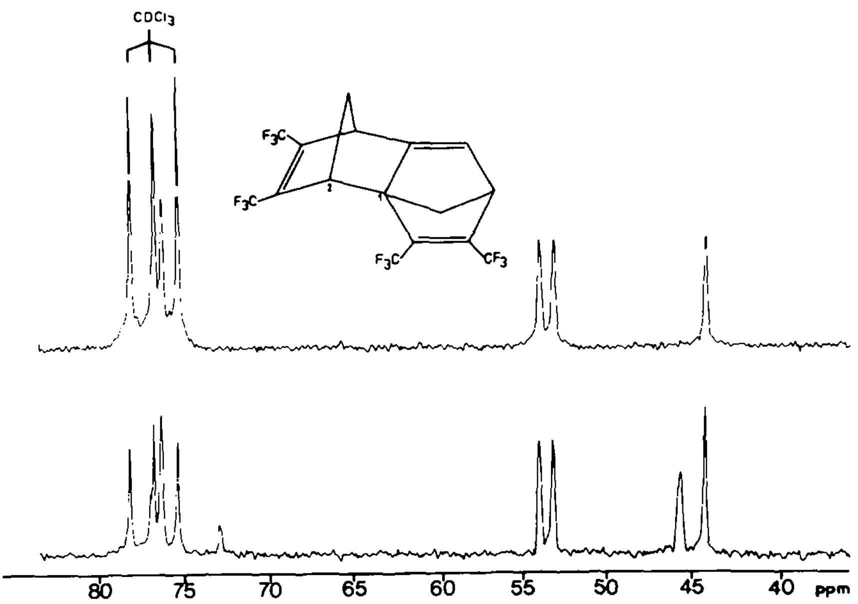
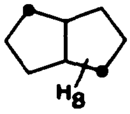
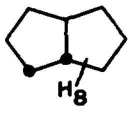


Fig. 8. Partial ^{13}C NMR spectra (62.9 MHz, $CDCl_3$) of labelled and unlabelled **9**.



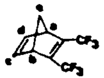
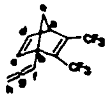
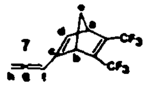
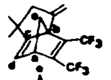
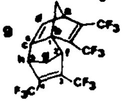
24



25

Fig. 9.

Table 1. Selected δ (^{13}C NMR) data (62.9 MHz) of 7, 8, 9 and of model compounds[a,b]

	a	b	c	d	e	f	g	h	ref.
	52.5 d	52.5 d	142.2 d	142.2 d	73.4 t				c
	50.4 d	50.4 d	143.2 d	143.2 d	75.2 t				20
8 	51.5 d	63.8 s	(142.5)d (144.2)	(144.2)d (142.5)	(76.6)t (77.4)	87.8 d	209.1 s	(77.4)t (76.6)	c d
7 	(52.9)d (53.3)	(53.3)d (52.9)	150.4 s	133.5 d	(77.2)t (70.5)	89.4 d	211.0 s	(70.5)t (77.2)	c
	54.3 d	75.0 s	173.8 s	125.2 d	81.0 t				22
9 	53.1 d	73.0 s	159.8 s	127.0 d	76.6 t	45.5 d	54.0 t	44.0 d	c

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a) All values in ppm; multiplicity; solvent $CDCl_3$. Alternative possible assignments are given in parentheses.
b) See also ref. 21
c) This work.
d) solvent C_6D_6

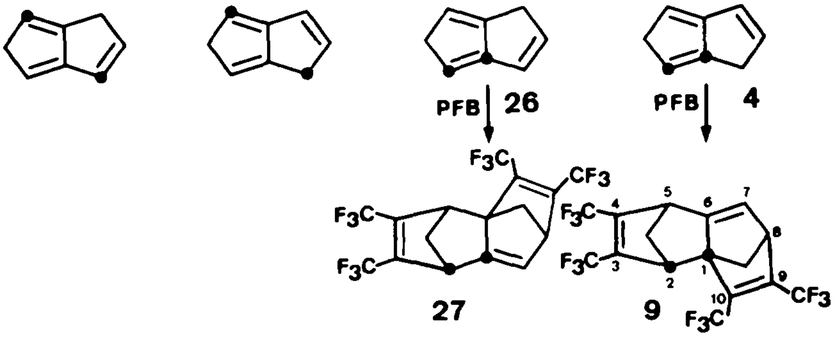

Fig. 10.

the signals at $\delta = 73.0$ and 45.5 ppm. C-2′ and C-2″ separated by five carbon–carbon bonds in 3 (Scheme 1), are hence directly connected in 1,5-dihydropentalene (4) after two consecutive carbene–carbene rearrangements. Appropriate model compounds can be imagined which contain suitably arranged geminal dibromocyclopropanes and double bonds, in order to achieve multiple skeletal conversion by tandem-carbene–carbene rearrangement leading to even higher fused cyclopentanoid rings.

EXPERIMENTAL

^{1}H NMR spectra were obtained with Varian A-60 D and Bruker WP 80 and WM 250 spectrometers at 60, 80 and 250 MHz, respectively. ^{1}H chemical shifts (δ) are in parts per million (positive downfield) from internal tetramethylsilane. Apparent coupling constants J (±1 Hz), number of protons, and multiplicity (s, singlet; br, broad; d, doublet; t, triplet; qa, quartet; m, multiplet) are given in all cases. ^{13}C NMR spectra were recorded in the FT mode on a Bruker WM 250 spectrometer at 62.9 MHz (δ[ppm], multiplicity). UV spectra (λ[nm]ϵ) were obtained with a Varian Cary 17 spectrophotometer. IR spectra (ν, cm^{-1}) were taken on Perkin–Elmer 257 and 325 spectrometers. Mass spectra were recorded on a Varian MAT CH 5 spectrometer at an ionization potential of 70 eV [*m/e* (% of base peak)]. Vpc analysis and separations were carried out on Perkin–Elmer Model F20 and Varian Fractometers 90-P and 920 with the following columns: A: glass capillary column, 41 m, silicone oil OV 101; B: glass capillary column, 85 m, silicone oil OV 101; C: glass capillary column, 80 m, silicone oil OV 101; D: glass column, 4.5 m × 9 mm, 20% silicone oil SE 52 on 45/60 mesh Chromosorb P; E: glass column, 1.5 m × 9 mm, 20% silicone oil SE 30 on 45/60 mesh Chromosorb P.

The quantitative analyses were carried out by adding a weighed amount of standard to the product mixture. The relative peak areas of product and standard were measured with an electronic integrator. Microanalysis were performed by Laboratorium I. Beetz, 8640 Kronach, Germany. Melting points are uncorrected.

^{12}C-*Deuteriobromoform from* ^{12}C-*Deuteriochloroform*

$^{12}CDCl_3$ (^{12}C-content > 99.95%, E. Merck, Darmstadt, Germany) (6.4 g, 53.1 mmol), ethylbromide (38 g, 0.35 mol) and aluminum trichloride (1.1 g, 8.3 mmol) were heated under gentle reflux (50°) for 6 hr. After the excess of ethylbromide was distilled off at 50°, the residue was diluted with methylenechloride (10 mL) and washed extensively with water (4 × 20 mL) and saturated aqueous sodium bicarbonate solution (20 mL) prior to drying ($MgSO_4$). Evaporation left 9.7 g of crude product. Vpc analysis (column A, column temp.: 90°) showed the ratio of $^{12}CDCl_2Br$, $^{12}CDClBr_2$ and $^{12}CDBr_3$ to be about 1:14:85. Separation by preparative vpc (column D, column temp.: 120°, flow rate: 100 mL helium/min) afforded 6.8 g (50%) $^{12}CDBr_3$ (99.5% of purity by vpc, column A, column temp.: 90°). The IR spectrum showed an essentially identical absorption at $\nu_{C-D} = 2258\ cm^{-1}$, as reported.[23]

trans-1,2-*Bis(2,2-dibromocyclopropyl)ethene* (3)

A. *From* trans-1,3,5-*hexatriene.* In a 2-necked 250 mL flask equipped with a magnetic stirring bar, a low temperature thermometer and an addition funnel with side arm, which was used as inlet for argon, were placed *trans*-1,3,5-hexatriene (4.5 g, 56.3 mmol) (98% of purity by vpc, column B, column temp.: 50°; stabilized with hydroquinone) and 150 mL of dry pentane. Through the apparatus a slow stream of argon was passed. To the solution was added potassium-t-butoxide (E. Merck) (19 g, 0.17 mol) while vigorously stirring. The suspension was cooled to −40 (±5)° (dry ice–acetone bath), and bromoform (E. Merck) (43 g, 0.17 mol) was added dropwise over a period of 2–3 hr. The solution gradually darkened and became more viscous. After completion of the addition the cooling bath was removed. The reaction mixture was allowed to warm up to about −5° and then hydrolyzed with water (300 mL). The layers were separated, and the aqueous phase was extracted with ether (2 × 80 mL). The combined organic layers were washed with water (3 × 100 mL), dried ($MgSO_4$) and evaporated (water aspirator). The dark brown oily residue was distilled in a Zincke-apparatus by applying oil pump vacuum. After the excess of bromoform was removed, 2.8–4.2 g (20–30%) *trans*-1,1-dibromo-2(1,3-butadienyl)cyclopropane was isolated (b.p.: 40–45°/0.01 mm; 90–95% of purity by vpc; column B, column temp.: 120°). The analytical sample was obtained by renewed distillation in vacuo (purity: 99% by vpc). IR (CCl_4): 3080, 3010, 2940, 2875, 1645, 1600, 1415, 1250, 1100, 995, 945, 910 cm^{-1}; UV (n-hexane): 229.5 nm (ϵ 22500); ^{1}H NMR (60 MHz, CCl_4): δ 1.4–2.55 (m, 3H), 4.85–5.7 (m, 3H), 6.0–6.7 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 28.5 (s), 30.1 (t), 33.6 (d), 117.3 (t), 131.4 (d), 134.7 (d), 136.1 (d); MS: *m/e* 252 (1), 173, 171 (11, 11), 92 (75), 91 (100), 65 (25), 39 (35). Found: C, 33.24; H, 3.31. Calc. for $C_7H_8Br_2$: C, 33.37; H, 3.20%.

The third fraction (b.p.: *ca.* 120°/0.01 mm) contained 8.3–9.5 g (35–40%) of crude *trans*-1,2-bis(2,2-dibromocyclopropyl)ethene (3) as a yellow oil. Crystallization and renewed recrystallization from methanol furnished 2.4–3.6 g (10–15%) of 3 as colorless crystals: m.p.: 92–93°; IR (CCl_4): 3080, 3000, 1430, 1220, 1100, 1045, 1020, 960 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ 5.45–5.7 (dd, 2H, $J_{1,1'} = J_{1'',2} = 5$ Hz; $J_{1',2} = J_{1,1''} = 2.5$ Hz), 1.45–2.6 (m, 6H); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.64 ("t", dd, 2H, H-$3'_s$, H-$3''_s$); 2.03 (dd, 2H, H-$3'_a$, H-$3''_a$); 2.35 ("undecett", 2H, H-1′, H-1″, $J_{1',3'} = J_{1'',3''_s} = 10.5$ Hz, $J_{1',3'_a} = J_{1'',3''_a} = 7.5$ Hz, $J_{3'_a,3'_s} = J_{3''_a,3''_s} = -7.5$ Hz); 5.52 (dd, 2H, H-1, H-2, $J_{1,1'} = J_{1'',2} = 5$ Hz, $J_{1',2} = J_{1,1''} = 2.5$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 27.8 (s), 29.9 (t), 33.5 (d), 132.3 (d); MS: *m/e* 345, 343 (5, 5), 264 (12), 185, 183 (40, 47), 104 (100), 103 (61), 77 (41), 51 (80). Found: C, 22.65; H, 1.96. Calc. for $C_8H_8Br_4$: C, 22.67; H, 1.90%.

B. *From* cis- *and* trans-1,3,5-*hexatriene. Cis*- and *trans*-hexatriene (ratio: 30:70) (5.0 g, 62.5 mmol) stabilized with hydroquinone and 150 mL of dry pentane were given in the flask as described above (method A). Potassium-t-butoxide (21.0 g, 0.19 mol) and bromoform (47.4 g, 0.19 mol) were introduced to the solution in a manner described above. Reaction time and work up procedure were kept identical. The distillation in vacuo of the crude reaction mixture gave, besides excess of bromoform, 1,1-dibromo-2(1,3-butadienyl)cyclopropanes (3.0 g, 19%) (b.p.: 40–45°/0.01 mm; ratio: *cis* : *trans* = 25:75 from vpc, column

C, column temp.: 100°, ret. time: 45 (*cis*) and 48 (*trans*) min). The third fraction afforded 9.3 g (35%) of crude *cis*- and *trans*-1,2-bis(2,2-dibromocyclopropyl)ethenes (b.p.: *ca.* 120°/0.01 mm). Isolation of 3 could be affected by crystallization and subsequent recrystallization from methanol to yield 1.3 g (5% based on *cis*- and *trans*-hexatriene; 7% based on pure *trans*-hexatriene) of 3 (m.p.: 91–93°). The yield could be improved by filtration of the crystals which had precipitated by keeping the crude reaction mixture overnight at −30° prior to distillation. By subsequent threefold recrystallization from methanol the yield of 3 was raised to 10% (based on *cis*- and *trans*-hexatriene) and 15% (based on *trans*-hexatriene), respectively.

Reaction of trans - 1,2 - *bis*(2,2 - *dibromocyclopropyl*)*ethene* (3) *with methyllithium*

A 50 mL three-necked flask equipped with a magnetic stirring bar, low temperature thermometer, an argon inlet with exit bubbler and a rubber septum was charged with *trans*-1,2-bis(2,2-dibromocyclopropyl)ethene (3) (470 mg, 1.1 mmol), dry ether (25 mL) and a few crystals of hydroquinone. At −40° (dry ice–acetone bath) an ethereal solution of methyllithium (2.3 mL, 2.8 mmol†) was added dropwise via syringe within 30 min, while stirring. The reaction mixture was allowed to stir for another 20–30 min at −40° and was then hydrolyzed at that temperature by addition of 20 mL of water. The ether layer was separated while the aqueous phase was extracted twice with cold (*ca.* 10°) ether (2 × 20 mL). The combined organic layers were washed neutral with ice water.

An exact amount of the internal standard (1-octene) and a few crystals of hydroquinone were added to the solution immediately prior to vpc analysis. The yield did not change significantly when the ethereal solution was dried (*ca.* 8°) for 10 min over anhydrous magnesium sulfate and concentrated (*ca.* 10°, 100 mm Hg) up to *ca.* 3 mL prior to vpc analysis (column A, column temp.: 50°). The analysis revealed 4 compounds in a ratio of 21 : 18 : 51 : 7 with retention times of 18.0, 18.8, 20.6 and 24.8 min, respectively. Based on the added internal standard the yield of the 4 compounds was 32%.

Reaction of trans - 1,2 - *bis*(2,2 - *dibromocyclopropyl*)*ethene* (3) *with methyllithium and subsequent catalytic hydrogenation*

The solution of *trans* - 1,2 - bis(2,2 - dibromocyclopropyl)ethene (3) (500 mg, 1.2 mmol) in 25 mL of dry ether containing a few crystals of hydroquinone was treated at −40° under argon with an ethereal solution of methyllithium (2.5 mL, 3.0 mmol) in the same way as described above, followed by an identical work-up procedure. To the undried ethereal solution of the reaction mixture *ca.* 70 mg of 10% platinium on charcoal was added immediately prior to hydrogenation under atmospheric pressure. After 1–1.5 hr *ca.* 60 mL of H_2 were consumed, and the catalyst was filtered off. The solution was dried over anhydrous magnesium sulfate, and the ether was cautiously removed under reduced pressure (100 mm Hg, Vigreux column) until *ca.* 2–3 mL were left. As internal standard 3-methylheptane was added, and the solution was analyzed by vpc (column A and C, column temp.: 50° and 60°, respectively). The following data were obtained: n-octane (retention time, A: 10.5, C: 21.2 min), n-propylcyclopentane (A: 12.2, C: 24.5 min), and *cis*-bicyclo[3.3.0]octane (A: 14.5, C: 29.2 min) with a ratio of 6 : 40 : 53 and with a total yield of 24%. The products were identified by comparison of vpc retention times with those of samples synthesized by alternative routes or purchased commercially.

Reaction of trans - 1,2 - *bis*(2,2 - *dibromocyclopropyl*)*ethene* (3) *with methyllithium and subsequent reaction with perfluorobut - 2 - yne*

trans - 1,2 - Bis(2,2 - dibromocyclopropyl)ethene (3) (1.85 g, 4.4 mmol) in 70 mL dry ether was reacted with an ethereal solution of methyllithium (8.9 mL, 11.1 mmol) containing a few crystals of hydroquinone at −40 (±5)° according to the procedure described above. After immediate work-up of the reaction mixture (*ca.* < 15°) the ethereal solution was dried over anhydrous magnesium sulfate (10 min, 0°). The filtrate (*ca.* 60 mL) was filled under argon into a 250 mL precooled heavywalled glass vessel (cooled to −40° by partial immersion into a dry ice–acetone cooling bath). An excess of perfluorobut-2-yne (*ca.* 3 mL) (PCR Research Chemical, Inc., Gainesville, Florida) was added, and the vessel was sealed. The reaction mixture was kept 1 hr at −40° and then was allowed to warm up to room temperature. After a total reaction time of 2 hr the pressure vessel was opened at −30°. Excess of perfluorobut-2-yne was allowed to evaporate, and the ethereal solution of the crude product mixture was concentrated up to *ca.* 3 mL. Vpc analysis (column A and C, column temp.: 90° and 100°, respectively) showed it to consist of two unknown components (4% with retention times, A: 8.4 and C: 19.8 min, and 5%, A: 9.7 and C: 23.1 min), 1-propadienyl-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta - 2,5 - diene (8) (13%, A: 10.9 and C: 26.2 min), 5-propadienyl - 2,3 - bis(trifluoromethyl)bicyclo[2.2.1]hepta - 2,5 - diene (7) (16%, A: 13.6 and C: 33.1 min), and 3,4,9,10 - tetrakis(trifluoromethyl) - tetracyclo[6.2.1.1^{2,5}.0^{1,6}]dodeca - 3,6,9 - triene (9) (52%, A: 18.7 and C: 45.7 min).

After preparative vpc (column E, column temp.: 90°, flow rate: 90 mL He/min) 17 mg (1.5%) of the two unknown components with the shortest retention time (19–30 min) which already polymerized in the vpc-trap, 51 mg 8 (4.4%, 32 min), 53 mg 8 (4.6%, 46 min), and 316 mg 9 (17%, 73 min) were isolated. The total yield amounted to 27.5%. 7 proved to be relatively unstable. In order to receive an analytical sample 7 had to be purified again by vpc which led to substantial losses.

1 - *Propadienyl* - 2,3 - *bis*(*trifluoromethyl*)*bicyclo*[2.2.1]*hepta* - 2,5 - *diene* (8)

IR ($CDCl_3$): 3010, 2990, 2940, 2870, 1955, 1675, 1560, 1340, 1290, 1170, 1150, 850, 790 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.05–2.45 (AB, 2H, H-7a, H-7s, $J_{7a,7s} = -7$ Hz, $J_{4,7} = 2$ Hz); 3.90 (br s, 1H, H-4); 4.90 (d, 2H, H-10, $J_{8,10} = -7$ Hz); 5.65 (t, 1H, H-8, $J_{8,10} = -7$ Hz); 6.75–7.00 [AB, 2H, H-5, H-6, $J_{5,6} = 5$ Hz, $J_{4,5} =$ 3 Hz (1 Hz ?), $J_{4,6} = 1$ Hz (3 Hz ?)]; ^{13}C NMR (62.9 MHz, C_6D_6): δ 51.5 (d), 63.8 (s), 76.6 (t), 77.4 (t), 87.8 (d), 123 (q, $J_{C-F} \approx 260$ Hz), 142.5 (d), 144.2 (d), 209.1 (s); MS: *m/e* 266 (7), 197 (100), 177 (42), 171 (22), 151 (27), 128 (33); exact mass 266.052 (calc. for $C_{12}H_8F_6$, 266.0528).

5 - *Propadienyl* - 2,3 - *bis*(*trifluoromethyl*)*bicyclo*[2.2.1]*hepta* - 2,5 - *diene* (7)

IR ($CDCl_3$): 3010, 2980, 2950, 2880, 1935, 1675, 1640, 1425, 1345, 1290, 1170, 1150, 1000, 860 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.05–2.40 (AB, 2H, H-7a, H-7s, $J_{7a,7s} = -7$ Hz, $J_{1,7} = J_{4,7} = 2$ Hz); 3.95 (br s, 2H, H-1, H-4); 5.10 (dd, 2H, H-10, $J_{8,10} = -7$ Hz, $J_{6,10} = 2$ Hz); 6.05 (t, 1H, H-8, $J_{8,10} = -7$ Hz); 6.55 (br s, (dt), 1H, H-6, $J_{1,6} = 3$ Hz, $J_{6,10} = 2$ Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 52.9 (d), 53.3 (d), 70.5 (t), 77.2 (t), 89.4 (d), 133.5 (d), 150.4 (s), 211.0 (s); MS: *m/e* 267 (7), 266 (44), 227 (11), 197 (51), 177 (28), 128 (24), 64 (88).

3,4,9,10 - *Tetrakis*(*trifluoromethyl*)*tetracyclo*[6.2.1.1^{2,5}.0^{1,6}] - *dodeca* - 3,6,9 - *triene* (9)

IR ($CDCl_3$): 2990, 2950, 2860, 1665, 1640, 1460, 1355, 1340, 1290, 1280, 1190, 1180, 1160, 1150, 1040, 985, 955, 940, 850, 815, 810, 785 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4): δ 1.90 (d, 1H, J = −7 Hz); 2.15–2.75 (m, 3H); 3.90 (br s, 3H, H-2, H-5, H-8); 6.45 (d, 1H, H-7, J = 3 Hz); ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.90 (d, 1H, $J_{gem} = -7$ Hz); 2.25 (d, 1H, $J_{gem} = -10$ Hz); 2.40 (ddd, 1H, $J_{gem} = -7$ Hz, $J_{vic} = 2$ Hz and 1 Hz); 2.60 (dt, 1H, $J_{gem} = -10$ Hz, $J_{vic} =$ 2 Hz) 2 AB systems; 3.80 (br s, 1H); 3.90 (br s, 2H); 6.40 (dd, 1H, J = 3 Hz, J = 1 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 44.0 (d), 45.5 (d), 53.1 (d), 54.0 (t), 73.0 (s), 76.6 (t), 127.0 (d), 159.8 (s), 120.4 (q), 121.0 (q), 121.9 (q), 141.3, 144.0, 151.7, 155.0, $J_{C-F} \approx 275$ Hz, $^3J_{C-F} \approx 40$ Hz; MS: *m/e* 428 (65), 409 (30), 359 (100), 339 (25), 319

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†Methyllithium was obtained as an ethereal solution (*ca.* 1.0–1.3 molar) from E. Merck (Darmstadt) containing lithiumbromide. It was titrated in benzene under nitrogen with a standard solution of sec-butanol in xylene by using 1,10-phenanthroline as indicator.[24]

(28), 290 (28), 227 (46), 226 (51), 177 (31); exact mass 428.043 (calc. for $C_{16}H_8F_{12}$, 428.0432).

On an analytical scale the reaction was run under conditions identical to those described above with **3** (500 mg, 1.2 mmol), ether (25 mL), ethereal solution of methyllithium (2.3 mL, 3.0 mmol), and perfluorobut-2-yne (*ca.* 1 mL). The product ratio and the yield were determined by vpc (column A, column temp.: 90°) with 2,3-bis(trifluoromethyl)tricyclo[$5.3.0^{1,4}.0^{1,7}$]deca-2,5,9-triene (**19**) as internal standard. The unknown components were formed in 4% and 2%, **8**, **7**, and **9** in 10, 15 and 65%, respectively (retention times as above) with a total yield of 21%.

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