121 ml of glacial acetic acid was refluxed for 12 hr with 39.7 ml of concentrated HCl and 33 ml of water. The reaction mixture was poured into 300 ml of water and extracted with three 200-ml portions of ether. The ether solution was divided into two portions. Each portion was washed with 100-ml portions of 10% NaOH until basic, with another 50 ml of 10% NaOH, and with 50 ml of saturated NaCl solution. The ether was dried over $MgSO_4$ and removed in vacuo leaving a dark oil, which was fractionally distilled yielding 29.62 g of **5** (71% yield from the enamine **2**). Analytical samples were prepared by preparative VPC on a 6-ft 15% Apiezon L–Chromosorb P column (column temperature 134°, carrier flow rate 182 ml/min, retention time 21.0 min): bp 89.5–90° (6 mm); $n^{23}D$ 1.5244; uv λ_{max} (95% EtOH) 229.5 nm (ϵ 10060); NMR ($CDCl_3$, 100 MHz) δ 1.62 (m, 1, H_g), 1.95 (m, 5, H_h), 2.6 (m, 3, $H_c + H_d + H_e$), 2.98 (m, 1, H_f), 5.82 (d of d of d of d, 1, J_{ab} = 12.9, $J_{ad} = J_{ac} = J_{af}$ = 2.0 Hz, H_a), 6.21 (d of d of d of d, 1, J_{ab} = 12.9, J_{bc} = 4.7, J_{bd} = 3.4, J_{be} = 1.3 Hz, H_b); ir (neat) 3017, 2940, 2871, 1661, 1450, 1418, 1402, 1340, 1283, 1223, 1129, 898, 819 cm^{-1}.

Anal. Calcd mass for $C_9H_{12}O$: 136.0887. Measured mass: 136.0894.

Registry No.—**1**, 56533-25-6; **2**, 497-38-1; **3**, 41455-23-6; **4**, 56533-26-7; **5**, 56533-27-8; dimethylamine, 124-40-3.

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Molecular Design by Cycloaddition Reactions. XXIII.[1] Synthesis of Some Highly Strained Bridged Polycyclic Hydrocarbons

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Addition of dichlorocarbene (DCC) in aqueous medium to basketene, snoutene, and bullvalene gave the homobasketene, homosnoutene, and trishomobullvalene skeletons, respectively. Similar DCC addition of bicyclo[4.2.2]deca-2,4,7,9-tetraene afforded the formal 1:2 adduct of DCC to tetracyclodecadiene. Possible mechanisms for the reactions are also discussed.

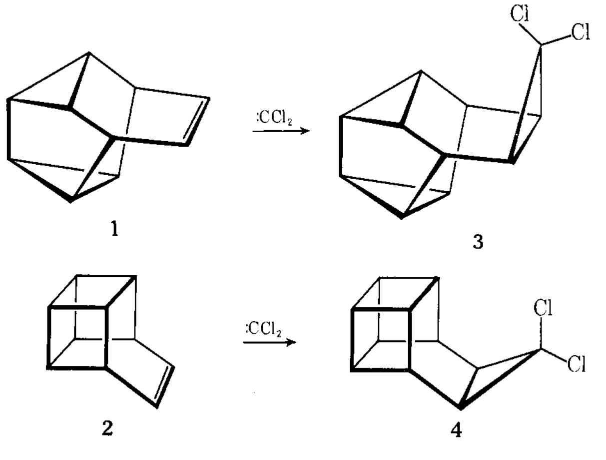
The synthesis of strained bridged polycyclic hydrocarbons is of considerable interest and continues to be a challenging objective to organic chemists.

As a continuation of our previous reports for providing a synthetic entry for new carbon-skeleton construction and further additional data for understanding the capability of a phase transfer catalyzed carbene addition[2] to some strained unsaturated compounds, we examined the carbene addition reactions of snoutene (**1**), basketene (**2**), bullvalene (**6**), and bicyclo[4.2.2]deca-2,4,7,9-tetraene (**11**), all of which are theoretically important $(CH)_{10}$ isomers connected on an energy surface with other $(CH)_{10}$ isomers.[3]

Results and Discussion

The reactions of snoutene (**1**)[4] and basketene (**2**)[5] with a 20-fold molar excess of dichlorocarbene (DCC) prepared at room temperature from chloroform in the presence of 50% aqueous sodium hydroxide–benzene with triethylbenzylammonium chloride (TEBA) as a catalyst afforded 1:1 adducts **3** and **4** in 45 and 60% yields, respectively (Scheme I). However, similar carbene addition reaction of **1** or **2** with excess phenyl(trichloromethyl)mercury gave only tarry materials and the 1:1 adduct could not be detected.

Scheme I



The NMR spectrum consisted of bridgehead protons at δ 2.87 (m, 2 H), cyclopropyl protons at δ 1.93 (m, 6 H), and characteristic dichlorocyclopropyl ring protons at δ 1.57 (s, 2 H) in compound **3**, and of two peaks of dichlorocyclopro-

Table I
DCC Addition to Bullvalene under Various Reagents

	Product distribution, % yield		
Reagent	1:1 (7)[a]	1:2 (8 + 9)	1:3 (10)
$CHCl_3$ + 50% NaOH in $PhCH_2\overset{+}{N}(Et)_3\ Cl^-$	0	50	10
$CHCl_3$ + $KOC(Me)_3$	60	0	0

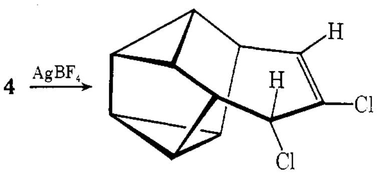
[a] See ref 9.

pyl ring protons as a singlet at δ 1.74 (2 H) and bridgehead protons as a broad singlet at δ 3.15 (8 H) in compound **4**.

These results indicate that the carbene addition reactions of **1** and **2** afforded the corresponding homosnoutene and homobasketene skeletons without skeletal rearrangement and insertion reaction. In this connection, cycloaddition reaction of basketene (**2**) with the skeletal rearrangement ($[{}_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2]$) is well known.[6]

The carbene addition to the polycyclic bridged hydrocarbons such as adamantane and adamantene gave the dichlorocarbene insertion products.[7,8] On the other hand, silver ion catalyzed skeletal rearrangement of basketene (**2**) into snoutene (**1**) is also reported.[4] Thus, the silver ion catalyzed rearrangement of **4** into **3** was carried out. When an acetone solution of **4** was refluxed with catalytic amounts of silver fluoroborate for several hours, compound **5** was obtained in a quantitative yield instead of an expected compound **3** (Scheme II).

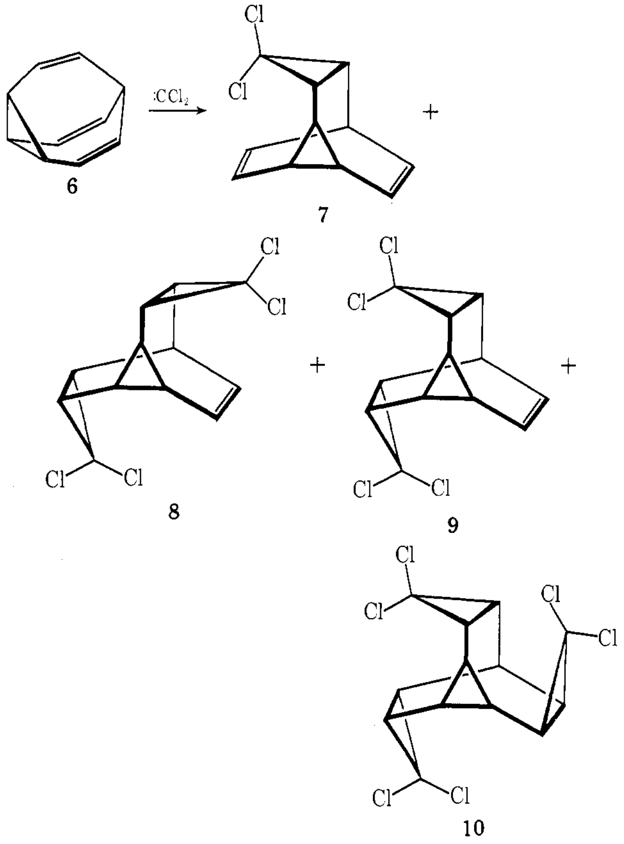
Scheme II



The NMR spectrum of **5** exhibits one olefinic proton at δ 6.28 (d, 1 H), an allylic methine proton at δ 4.61 (d, 1 H), and bridgehead protons at δ 2.87 (m, 2 H) and 2.0 (m, 6 H). Compound **5** was also identical with that of the thermal isomerization of **3** by GLC inspection (see Experimental Section).

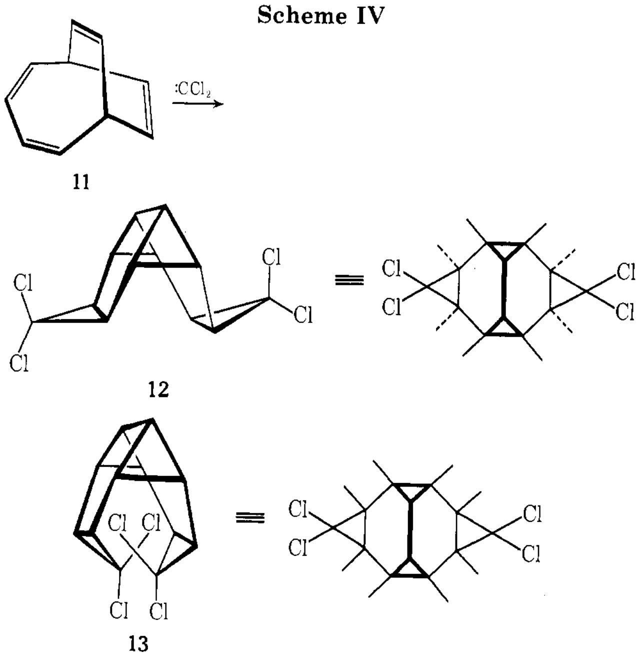
DCC addition to bullvalene (**6**)[9] under the same conditions gave a mixture of 1:2 isomers **8** and **9** (50% yield) together with a 1:3 adduct **10** (10% yield) (Table I). Further treatment of the 1:2 adducts with DCC afforded **10** mixed with recovered remaining isomeric adduct, but the mixture was difficult to purify (see Experimental Section). These results demonstrate that the reaction of **6** with DCC gave the 1:2 adducts **8** and **9** in a regioselective manner, and the formation of the 1:3 adduct **10** was only derived from the isomeric 1:2 adduct **9**, as suggested by an examination of molecular models. However, addition of bullvalene (**6**) to DCC prepared at room temperature from chloroform and potassium *tert*-butoxide afforded only a 1:1 adduct **7**,[9] from which no 1:2 and 1:3 adducts could be detected even with the use of excess DCC (Scheme III).

Scheme III



Similar DCC addition to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**11**)[10] in the dark gave compound **12** in 40% yield (Scheme IV). The structural assignment for **12** was made on the basis of the analytical and NMR data. Surprisingly, the NMR spectrum of **12** shows no olefinic proton signals and the appearance of a characteristic sharp singlet signal of four bridgehead protons in the dichlorocyclopropyl ring at δ 1.77, and of six equivalent cyclopropyl protons at δ 1.23 as a sharp singlet; the relevant dihedral angles in **12** are shown from molecular models to be approximately 80°, indicating the "extended" conformer rather than the "folded" counterpart **13** and, therefore, the spin–spin coupling constant in **12** should be 0 Hz.

Scheme IV

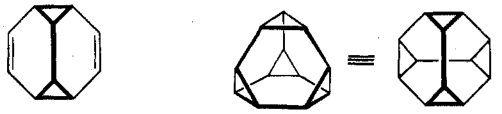


It is interesting that this intriguing structure **12** is the formal 1:2 adduct of DCC to tetracyclo$[4.4.0.0^{2,10}0^{5,7}]$deca-3,8-diene (**14**) (Chart I), an often-cited (but unisolated) key intermediate in some interconversions of $(CH)_{10}$ isomers,[3] which is easily interconverted with **6** and/or **11** under thermal and photochemical conditions.[3,11] However, compound **14** seems not to be the precursor of the 1:2 adduct **12**. To

Table II
NMR Data for Products

Compd	Chemical shifts, δ (*J*, Hz)
3	2.87 (m, 2 H, bridgehead), 1.93 (m, 6 H, cyclopropyl), 1.57 (s, 2 H, halocyclopropyl)
4	3.15 (broad s, 8 H), 1.74 (s, 2 H, halocyclopropyl)
5	6.28 (d, J = 8.0, 1 H, olefinic), 4.61 (d, J = 4.0, 1 H, allylic), 2.87 (m, 2 H, bridgehead), 2.0 (m, 6 H, cyclopropyl)
10	1.4–1.5 (m, 10 H)
12	1.77 (s, 4 H, halocyclopropyl), 1.23 (s, 6 H, cyclopropyl)
22	6.07 (dd, $J_{8,7}$ = 11.3, $J_{8,9}$ = 5.1, 1 H, H_8), 5.69 (dd, $J_{7,6}$ = 7.5, 1 H, H_7), 3.0–3.5 (m, 2 H, H_1, H_6), 2.4–2.9 (m, 3 H, H_2, H_5, H_9), 1.96 (s, 2 H, H_3, H_4), 1.85 (dd, $J_{10,9}$ = 9.8, $J_{10,1}$ = 2.0, 1 H, H_{10})
23	6.2–6.5 (m, 2 H, H_3, H_4), 6.10 (dd, $J_{8,7}$ = 12.0, $J_{8,9}$ = 6.0, 1 H, H_8), 5.63 (dd, $J_{7,6}$ = 8.0, 1 H, H_7), 3.2–3.8 (m, 2 H, H_1, H_6), 2.4–3.1 (m, 3 H, H_2, H_5, H_9), 1.1–2.4 (complex m, 5 H, H_{10}, 2 H_{11}, 2 H_{12})
24	6.12 (dd, $J_{8,7}$ = 11.7, $J_{8,9}$ = 5.7, 1 H, H_8), 5.55 (dd, $J_{7,6}$ = 7.5, 1 H, H_7), 3.4–3.9 (m, 2 H, H_1, H_6), 2.4–3.0 (m, 3 H, H_2, H_5, H_9), 1.92 (d, J = 2.0, 2 H, H_2, H_4), 1.8 (dd, 1 H, H_{10}), 1.8–2.4 (m, 4 H, 2 H_{11}, 2 H_{12})

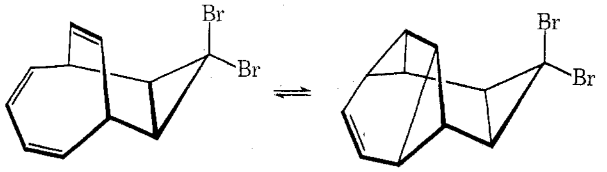
Chart I



14 **19**

our surprise, Schröder et al. have recently reported the isolation of 1:1 adduct **15** by the reaction of **11** with dibromocarbene (DBC) prepared at room temperature from bromoform and potassium *tert*-butoxide, which is shown to exist as an equilibrium mixture of **15** and **16** (Scheme V) in the ratios of 16:84 at 35° and 50:50 at 221.5° by NMR inspection.[12] Under the above conditions, no 1:2 adduct could be detected even with the use of excess DBC or DCC.

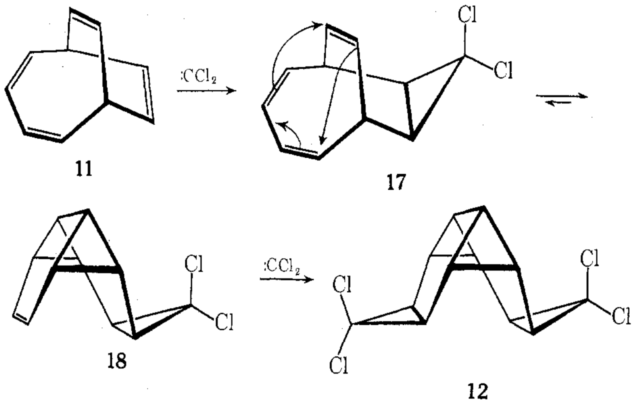
Scheme V



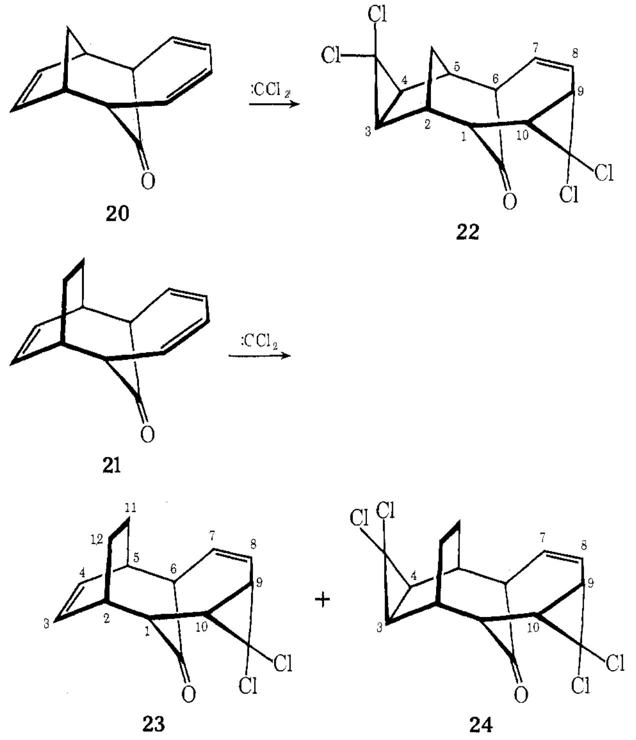
From the facts, it is concluded that the reaction of **11** with DCC by the phase transfer method initially afforded the 1:1 adduct **17** and successive DCC addition will occur after transformation by intramolecular [4 + 2] cycloaddition of **17** leading uniquely to **12**, quite close to truncated tetrahedran molecule **19** (Chart I). The reaction mechanism for **12** is shown in Scheme VI.

Finally, another type of compounds **20** and **21** was examined to the DCC additivity by the phase transfer method. DCC addition to **20**[13] and **21**[14] under the same conditions gave a 1:2 adducts in 40 and 5% yields, respectively (Scheme VII). However, further treatment of **23** even with the use of excess DCC gave only a small amount of **24**, suggesting a result of steric hindrance of the ethano bridge in **21**. The NMR spectra for these adducts are summarized in Table II.

Scheme VI



Scheme VII



As a conclusion, the generation of DCC by this catalytic method (phase transfer),[15] compared with other procedures,[16] is quite useful for the synthesis of the new highly strained bridged polycyclic hydrocarbons, which promised a synthetic approach to the truncated tetrahedran **19**[17] and will be the subject of further report.

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 elemental analyzer. The NMR spectra were taken with a Jeol C-60-XL recording spectrometer with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. GLC analyses were performed on a Varian gas chromatograph, Model 1400 (silicon SE-30). The ir spectra were taken with a Jasco Model IRA-1 grating infrared spectrophotometer.

General Procedure for Dichlorocarbene Addition Reactions in Aqueous Medium. In a 100-ml, three-necked flask fitted with a dropping funnel and a mechanical stirrer, a mixture of the unsaturated compound (0.01 mol), 50% (w/w) aqueous sodium hydroxide (0.4 mol, 21.3 ml), benzene (5–10 ml), and triethylbenzylammonium chloride (0.0005 mol, 0.114 g) was vigorously stirred at room temperature. Then the stirring was continued, and chloroform (0.2 mol, 16 ml) was added slowly to the mixture for several hours. The brown slurry was poured into water, and the mixture was extracted with chloroform or benzene. The extract was dried and evaporated to give a dark brownish oil. It was purified by silica gel chromatography and recrystallization.

Reaction of Snoutene (1) with DCC. Compound **3** was obtained as colorless needles in 45% yield, mp 95–97° (from MeOH).

Anal. Calcd for $C_{11}H_{10}Cl_2$: C, 62.00; H, 4.73. Found: C, 62.12; H, 4.93.

Reaction of Basketene (2) with DCC. Compound **4** was obtained as colorless needles in 60% yield, mp 87–89° (from MeOH).

Anal. Calcd for $C_{11}H_{10}Cl_2$: C, 62.00; H, 4.73. Found: C, 62.09; H, 4.80.

Silver Ion Induced Bond Rearrangement of Homobasketene (4). A solution of **4** (0.2 g) and catalytic amounts of silver fluoroborate in acetone (10 ml) was heated at reflux for several hours. The cooled solution was filtered to remove the silver salt; elution with acetone and recrystallization from EtOH gave **5** as colorless needles in a quantitative yield, mp 131–133°. This compound was identical with the thermal rearrangement product of **3**, which passed at 150° through GLC packed with 3% SE-30.

Anal. Calcd for $C_{11}H_{10}Cl_2$: C, 62.00; H, 4.73. Found: C, 62.08; H, 4.71.

Reaction of Bullvalene (6) with DCC.[18] Reaction products **8** and **9** were obtained as a mixture in 50% yield, and **10** in 10% yield.

A mixture of **8** and **9** had mp 116–119° (from EtOH). The NMR spectrum of the mixture exhibited complex signals in the region of δ 1.5–2.5 (m), centered at 3.6 (m) and 5.8 (m, olefinic protons). However, the mixture could not be purified.

Anal. Calcd for $C_{12}H_{10}Cl_4$: C, 48.69; H, 3.40. Found: C, 48.65; H, 3.32.

Compound **10** had mp 269–270° (from MeOH).

Anal. Calcd for $C_{13}H_{10}Cl_6$: C, 41.21; H, 2.66. Found: C, 41.41; H, 2.80.

Reaction of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (11) with DCC. Under the dark reaction conditions, compound **12** was obtained as colorless needles in 40% yield, mp 218–219° (from benzene–*n*-hexane).

Anal. Calcd for $C_{12}H_{10}Cl_4$: C, 48.69; H, 3.41. Found: C, 48.49; H, 3.32.

Reaction of Tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trien-11-one (20) with DCC. Compound **22** was obtained as colorless needles in 50% yield: mp 159–161° (from acetone); ir (KBr) 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{12}OCl_4$: C, 49.74; H, 3.58. Found: C, 49.61; H, 3.61.

Reaction of Tricyclo[4.4.1.2^{2,5}]trideca-3,7,9-trien-11-one (21) with DCC. Reaction products **23** and **24** were obtained as a mixture. The mixture was purified by silica gel chromatography with *n*-hexane–benzene as an eluent.

Compound **23** was obtained as colorless needles in 40% yield: mp 119–120° (from *n*-hexane); ir (KBr) 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{14}OCl_2$: C, 62.47; H, 5.24. Found: C, 62.37; H, 5.31.

Compound **24** was obtained as colorless needles in 5% yield: mp 220–223.5° (from *n*-hexane); ir (KBr) 1708 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{14}OCl_4$: C, 51.17; H, 4.01. Found: C, 51.21; H, 3.97.

Registry No.—**1,** 26934-61-2; **2,** 5603-34-9; **3,** 56571-98-3; **4,** 56571-99-4; **5,** 56572-00-0; **6,** 1005-51-2; **8,** 56572-01-1; **9,** 56613-91-3; **10,** 56572-02-2; **11,** 15677-13-1; **12,** 56572-03-3; **20,** 4668-70-6; **21,** 35522-47-5; **22,** 56572-04-4; **23,** 56572-05-5; **24,** 56572-06-6; dichlorocarbene, 1605-72-7; $AgBF_4$, 14104-20-2.

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(15) In the phase transfer reaction, DCC was generated by locally concentrated hydroxide ion in micellar surface and then quickly transferred to the organic layer. Therefore, the substrates such as polyolefins could consume stable DCC efficiently. The present synthesis of the strained bridged polycyclic hydrocarbons demonstrates that the phase transfer reaction will become more important in mild and regiospecific additions of polycyclic olefins.

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(18) By contrast, reaction of bullvalene with diazomethane in the presence of cuprous chloride gave homobullvalene (33%), two isomers of bishomobullvalene (15 and 27%), and trishomobullvalene (10%); see A. de Meijere and C. Weitemeyer, *Angew. Chem.*, **82**, 359 (1970).