Strained Hydrocarbon Skeletons: Pentacyclo[6.4.0.$0^{2,4}$.$0^{3,10}$.$0^{7,9}$]dodecanes by [2+2+2]Cycloadditions to Substituted Dihydrobullvalenes

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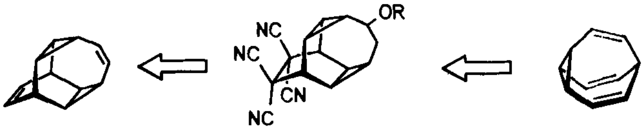
The preparation of some pentacyclo[6.4.0.$0^{2,4}$.$0^{3,10}$.$0^{7,9}$]dodecane derivatives 2 by [2+2+2] cycloaddition of tetracyanoethylene (TCNE) to dihydrobullvalene derivatives 6 is described. Upon pyrolysis of the acetate 2d and the xanthate 2e a [2+2+2] cycloreversion is observed instead of an elimination.

Pentacyclo[6.4.0.$0^{2,4}$.$0^{3,10}$.$0^{7,9}$]dodeca-5,11-diene (**1**), was conceived as the key intermediate in our new strategy for an entry onto the $(CH)_{12}$ energy surface[1]. One of the possible strategies towards **1** utilizes the 1,5-cycloaddition of the 1,4-diene subunit bullvalene **3** with a dienophile. Unlike tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dienes ("barbaralanes")[2,3], bullvalenes react only with dienophiles of extreme reactivity. Presently only two examples are known, in which a dienophile adds to a molecule with a bullvalene carbon skeleton to give the 1,5-adduct[2,4]. Since **3** itself cannot be utilized due to rearrangement of the dipolar intermediates[2,5], we strove for suitably substituted dihydrobullvalenes and their adducts in order to introduce necessary double bonds in a later step.

The ketone **4** yields bicyclo[4.2.2]deca-2,4,7-trien-9-one (**5**) upon heating with TCNE. To avoid this cationic rearrangement[6], **4** was reduced to the alcohol **6a** with $NaBH_4$[7] and silylated with *tert*-butylchlorodimethylsilane. When the silyl ether **6b** was refluxed with an equimolar amount of TCNE in toluene for three hours, a crystalline product was obtained in 44–67% yield, the spectroscopic properties of which were consistent with the constitution **2b**.



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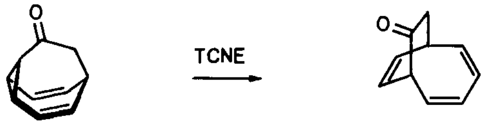

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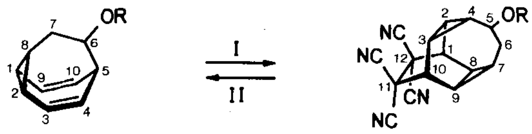

6 2

a: R = H
b: R = $SiMe_2tBu$
c: R = THP
d: R = Ac
e: R = C(S)SCH_3

I: For **6b**, **d**, **e**: TCNE, toluene, reflux. – II: 550°C for **2d**; 250°C for **2e**.

The tetrahydropyranyl ether (THP ether) **6c** of the alcohol **6a** was not stable under the conditions necessary for the cycloaddition of TCNE.

Since **2b** decomposed upon any attempted desilylation under various conditions[8,9], TCNE was added to the acetate **6d**[7] and the xanthate **6e** in order to facilitate the introduction of a $C^5 = C^6$ double bond via a pyrolytic *cis* elimination. **2d** and **2e** were obtained in moderate yields.

2d was pyrolyzed by sublimation into a quartz tube kept at 550°C. Due to its limited volatility, a major fraction of the educt decomposed upon heating before subliming into the quartz tube. Surprisingly, the product consisted mainly of **6d**. When the xanthate **2e** was pyrolyzed, product formation occurred at 250°C, and **6e** was isolated in 70% yield.

Obviously, in **2** the σ bonds in the α position of the nitrile groups are weakened, so that a cycloreversion takes place at the relatively low temperature of 250°C. At this point, however, it is not clear, whether this bondweakening is due mainly to the electron withdrawing effect or the steric and the angle strain incorporated in the skeleton of **2**. Anyhow, the tendency of **2** towards cycloreversion corresponds to a low reactivity of **6** towards cycloaddition, because neither maleic anhydride, fumaroyl dichloride, *N*-phenyltriazolinedione nor dicyanoacetylene added to **6b**, the least sensitive derivative of **6**, even under vigorous conditions.

In contrast to an argument put forward by Fickes and Metz[10], who correlated the reactivity of 1,4-dienes in [2+2+2] cycloadditions with the distance between the two double bonds in the diene system, we feel that the reactivity mainly depends on the increase of strain energy upon going to the cycloadduct. According to molecular mechanics calculations with the Allinger method[11], the geometry of the 1,4-diene unit in dihydrobullvalene (distance between double bonds d = 309 pm) does not differ significantly from that of barbaralane (d = 308 pm), but dihydrobullvalene **6** reacts about two orders of magnitude more slowly with TCNE than barbaralane derivatives.

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Experimental

^1H NMR: Bruker WH 270; δ = 0 for tetramethylsilane, δ = 7.26 for chloroform, δ = 7.15 for $[D_5]$benzene. – ^{13}C NMR: Bruker WM 400; the DEPT spectrum was recorded with an editing pulse of 135°, + = signal positive, – = signal negative, 0 = signal disappeared under these conditions[12]. – IR: Perkin-Elmer 297 and 399. – MS: Varian MAT CH-7, MAT 112 with Varian Aerograph 1400. – GLC: Siemens Sichromat 3. – Melting points (uncorrected): Wagner and Münz Melting Point Apparatus. – Column chromatography: Merck silica gel 60, 70–230 mesh and Woelm alumina.

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5-(tert-Butyldimethylsiloxy)pentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{7,9}]dodecane-11,11,12,12-tetracarbonitrile (**2b**): A mixture of 222 mg (1.50 mmol) of **6a**, 271 mg (1.80 mmol) of *tert*-butylchlorodimethylsilane, 254 mg (3.75 mmol) of imidazole, and 2 ml of dry DMF was stirred over night at room temperature. After addition of 30 ml of ether the mixture was poured into water, extracted three times with 5 ml of ether, the organic phase was washed with 5 ml of water and 5 ml of brine, dried over magnesium sulfate, and the solvent was evaporated. The residue was chromatographed over silica gel with ether/pentane (1:4) to yield 325 mg (82%) of *6-(tert-butyldimethylsiloxy)-tricyclo[3.3.2.0^{2,8}]deca-3,9-diene* (**6b**). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.00 (2s; 2 $SiCH_3$), 0.85 [s; $C(CH_3)_3$], 1.84 (ddt, ^3J_t = 8.3 Hz, ^3J_d = 7.0 Hz, ^3J_d = 1.2 Hz; 1-H), 2.02 (ddd, ^2J = 14.1 Hz, ^3J = 9.1 Hz, ^3J = 1.2 Hz; 7-H), 2.30 (dt, ^3J_t = 9.0 Hz, ^3J_d = 0.5 Hz; 5-H), 2.38 (ddd; ^2J = 14.1 Hz, ^3J = 7.6 Hz, ^3J = 7.5 Hz; 7-H), 2.51 [m; 2(8)-H], 3.87 (ddd, ^3J = 9.0 Hz, ^3J = 7.6 Hz, ^3J = 1.5 Hz, 6-H), 5.02 (tm, ^3J ca. 9.5 Hz) and 5.17 (tm, ^3J ca. 9.5 Hz) [4(10)-H], 5.83 [m, 3(9)-H].

A mixture of 115 mg (0.44 mmol) of **6b**, 56 mg (0.44 mmol) of TCNE, and 1 ml of dry toluene was stirred for 5 h at 100°C. After addition of 5 ml of pentane the precipitate was filtered off, washed with 5 ml of pentane, and dried in vacuo. The residue (106 mg) was chromatographed over silica gel with dichloromethane and recrystallized from toluene to yield 114 mg (67%) of **2b**, m.p. 157–159°C (dec.). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.08 (2s; 2 $SiCH_3$), 0.90 [s; $C(CH_3)_3$], 1.21 (tt, ^3J = 9.0 Hz, ^3J = 5.4 Hz; 7-H), 1.39–1.58 [m; 2(3,4,8,9)-H], 2.20 (m; 2H, 6-H), 3.64 [m; 1(10)-H], 4.33 (dt, ^3J_d = 6.8 Hz, ^3J_t = 4.5 Hz; 5-H). – ^{13}C NMR (100.62 MHz, $CDCl_3$; BB, DEPT): δ = – 4.76 (0; $SiCH_3$), – 4.68 (0; $SiCH_3$), 15.81, 15.96, 16.00, 16.60, and 17.08 [+; C-2 (3,7,8,9)], 18.03 [0; $C(CH_3)_3$], 25.76 [+; $C(CH_3)_3$], 29.54 (+; C-4), 33.28 (–; C-6), 39.79 and 40.41 [+; C-1 (10)], 44.82 [0; C-11(12)], 67.32 (+; C-5), 111.99 (0; CN). – IR (KBr): 2980 cm^{-1}, 2960, 2918, 2885, 2280 (CN), 1480, 1403, 1376, 1097 (C–O, Si–O), 1049, 1020. – MS (70 eV): *m/z* (%) = 390 (0.3, M$^+$), 333 [56, M$^+$ – $C(CH_3)_3$], 75 [100, $(H_3C)_2SiOH^+$].

$C_{22}H_{26}N_4OSi$ (390.6) Calcd. C 67.66 H 6.71 N 14.35
Found C 67.83 H 6.67 N 14.39

6-(Tetrahydro-2H-pyran-2-yloxy)tricyclo[3.3.2.0^{2,8}]deca-3,9-diene (**6c**): A mixture of 400 mg (2.70 mmol) of **6a**, 340 mg (4.05 mmol) of dihydropyran, 68 mg (0.27 mmol) of pyridinium *p*-toluenesulfonate, and 20 ml of dichloromethane was stirred at room temperature for 15 h. After addition of 70 ml of ether the mixture was washed twice with 20 ml of half saturated brine, dried over magnesium sulfate, and the solvent was evaporated. The residue was chromatographed over 10 g of basic alumina containing 7% of water with ether/pentane (1:4) to yield 494 mg (79%) of **6c** as colourless oil with a small impurity (3%) of **6a**. – ^{1}H NMR (270 MHz, [D$_6$]benzene): δ = 1.22 (m; 4H), 1.50 (m; 3H), 1.57–1.76 (m; 2H), 2.14 (ddd, ^2J = 14.2 Hz, ^3J = 10.7 Hz, ^3J = 1.7 Hz, 7-H), 2.31 (m; 1H), 2.37 (m; 1H), 3.33 (m; 2H), 3.78 (dddd, ^2J = 18.8 Hz, ^3J = 9.0 Hz, ^3J = 7.8 Hz, ^3J = 1.8 Hz; 1H), 4.00 (dt, ^3J_d = 6.6 Hz; ^3J_t = 3.6 Hz; O_2CHCH_2), 4.91 (tm, ^3J = 9.4 Hz; 1H) and 5.14 (tm, ^3J = 9.4 Hz; 1H) [4(10)-H], 5.77 [m; 3(9)-H]. – IR (film): 3015 cm^{-1}, 2920, 2850, 2835, 1638, 1619, 1458, 1441, 1430, 1380, 1342, 1102, 1068, 1043, 1010. – MS (70 eV): *m/z* (%) = 144 (0.3, highest mass peak), 131 (0.6, $C_{10}H_{11}^+$), 101 (1.4, $OTHP^{+\cdot}$), 85 (100, THP^+).

$C_{15}H_{20}O_2$ (232.2) Calcd. C 77.55 H 8.68
Found C 77.34 H 8.84

5-Acetoxypentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{7,9}]dodecane-11,11,12,12-tetracarbonitrile (**2d**): A mixture of 108 mg (0.57 mmol) of **6d**, 72 mg (0.57 mmol) of TCNE, and 1 ml of toluene was allowed to react and was worked up as described for **2b** to yield 91 mg (51%) of **2d**, dec.p. 172°C (hexane/toluene, 1:2). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.30 (m; 7-H); 1.46–1.64 (m; 4H), 1.72 (dd, ^3J = 8.8 Hz, ^3J = 6.1 Hz; 1H), 2.11 (s; $COCH_3$), 2.34 (m; 2H, 6-H), 3.67 [qm, ^3J = 4.4 Hz; 1(10)-H], 5.33 (dt, ^3J_t = 5.7 Hz, ^3J_d = 4.7 Hz; 5-H). – IR (KBr): 3070 cm^{-1}, 2960, 2250 (CN), 1725 (CO), 1375, 1057, 1018. – MS (70 eV): *m/z* (%) = 276 (0.1, M$^+$ – CH_2CO), 259 (0.2, M$^+$ – $OCOCH_3$), 232 (0.4, M$^+$ – HCN), 43 (100, H_3CCO^+).

$C_{18}H_{14}N_4O_2$ (318.3) Calcd. C 67.92 H 4.43 N 17.60
Found C 68.03 H 4.41 N 17.43

S-Methyl O-(11,11,12,12-Tetracyanopentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{7,9}]-dodec-5-yl) Dithiocarbonate (**2e**): In a dry atmosphere of argon 300 mg (2.02 mmol) of **6a**, 91 mg (3.03 mmol) of 80% sodium hydride, and 10 ml of dry toluene were stirred for 1 h. 307 mg (4.04 mmol) of carbon disulfide was added dropwise, the mixture was stirred for 1 h, and 573 mg (0.404 mmol) of methyl iodide was added. After 1 h stirring and the usual workup (cf. **2b**) the residue was chromatographed over 20 g silica gel (1 × 20 cm) with ether/pentane (4:1) to yield 105 mg (35%) of unreacted **6a** (R_f = 0.38, ethyl acetate/hexane 1:1) and 193 mg (61%, calcd. for reacted **6a**) *S-methyl O-(tricyclo[3.3.2.0^{2,8}]deca-3,9-dien-6-yl) dithiocarbonate* (**6e**) (R_f = 0.63, ethyl acetate/hexane, 1:1) as colourless oil. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.31 (m; 2H), 2.07 (m; 1H), 2.11 (s; SCH_3), 2.14 (m; 1H), 2.42 (m; 1H), 2.49 (m; 1H), 4.86 [m; 4(10)-H], 5.67 [m; 3(9)-H], 5.84 (dt; ^3J_t = 7.7 Hz, ^3J_d = 3.2 Hz; 6-H). – IR (film): 3040 cm^{-1}, 2960, 2930, 2860, 1647, 1222 (C=S), 1055 (C–O), 1027.

A mixture of 193 mg (0.81 mmol) of **6e**, 114 mg (0.89 mmol) of TCNE and 2 ml of toluene was refluxed for 5 h and worked up as described for **2b** to yield 127 mg (43%) of crystalline **2e**, dec.p. 155°C. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.40 (m; 7-H), 1.50–1.67 [m; 2(3,8,9)-H], 1.86 (dt, ^3J_t = 8.6 Hz, ^3J_d = 7.6 Hz; 4-H), 2.39 (ddd, ^2J = 15.2 Hz, ^3J = 7.6 Hz, ^3J = 4.7 Hz; 6-H), 2.45 (s; SCH_3), 2.55 (ddd, ^2J = 15.2 Hz, ^3J = 4.8 Hz, ^3J = 2.8 Hz; 6-H), 3.67 (m; 1H) and 3.74 (m; 1H) [1(10)-H], 4.48 (dt; ^3J_d = 7.4 Hz, ^3J_t = 4.7 Hz; 5-H). – IR (KBr): 3020 cm^{-1}, 2990, 2250 (CN), 1641, 1445, 1378, 1040. – MS (70 eV): *m/z* (%) = 338 (1.0 M$^+$ – CO), 319 (2.4, M$^+$ – SCH_3), 291 (11, M$^+$ – $COSCH_3$), 75 (100, $COSCH_3^+$).

$C_{18}H_{14}N_4OS_2$ (366.5) Calcd. C 59.00 H 3.85 N 15.29
Found C 59.32 H 3.87 N 15.22

Pyrolysis of **2d**: 50 mg (0.16 mmol) of **2d** was sublimed at a pressure of 0.01 Torr into a quartz tube heated to 550°C, which had previously been deactivated with hexamethyldisilazane. The temperature of the evaporation bulb was increased from 100°C to 160°C in steps of 10°C/10 min by means of a small oven. After 3 h/160°C the pyrolysis was terminated, as the remaining contents (39 mg) of the evaporating bulb had turned into a black substance, insoluble in dichloromethane. The trapped product was washed with dichloromethane into a flask, the solvent was evaporated to yield 3 mg (10%) of **6d** as a yellow oil. – On the basis of TLC, GLC, and IR the substance was identical with an authentic sample.

Pyrolysis of **2e**: 62 mg (0.17 mmol) of **2e** was heated in a short path distillation apparatus (kugelrohr) with a dry ice cooled receiver at a pressure of 0.1 Torr from 100°C to 250°C in steps of 10°C/5 min. At 250°C a yellow oil condensed in the receiver. After 2 h the pyrolysis was terminated. The contents of the receiver yielded 28 mg (70%) of **6e**. – On the basis of TLC, GLC, and ^{1}H NMR the substance was identical with an authentic sample.

CAS Registry Numbers

2b: 110318-76-8 / **2d**: 110318-78-0 / **2e**: 110318-80-4 / **6a**: 17340-86-2 / **6b**: 110318-75-7 / **6c**: 110330-28-4 / **6d**: 110318-77-9 / **6e**: 110318-79-1

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