4 indicate a HOMO–LUMO separation of 1.25 eV (slightly larger than that in **2**), so that at the short Co–Co separation a singlet ground state seems more likely than a triplet ground state. In **6**, the four hydride ligands interact strongly with one of the Co–Co δ and both Co–Co π orbitals, leading to significant destabilization of these metal-based orbitals, much as we saw for [CpReH)$_2$(μ-H)$_4$].[15] As a result of these interactions, the HOMO's of **6** are the half-filled, doubly degenerate Co–Co π* orbitals [Figure 1 (right)], and the molecule is expected to possess a triplet ground state.

Complex **6** has strong precedent in the literature. An analogous Group 8 complex, [(Cp*Ru)$_2$(μ-H)$_4$] (**9**), which has two fewer valence electrons than **6** and is diamagnetic, possesses a Ru–Ru bond length of 2.463 Å consistent with its formulation as a hydride-supported metal–metal triple bond.[16] In addition, we have recently demonstrated that [Cp*$_2$Re$_2$(CO)$_4$] (**10**), which contains a Re–Re double bond supported by two semibridging carbonyls, reacts with H$_2$ at −80 °C to yield [Cp*$_2$Re$_2$(CO)$_4$(μ-H)$_2$].[3] Compound **10** is more sterically congested than [Cp*$_2$Co$_2$], suggesting that the latter would also undergo facile addition of hydrogen (an expected by-product of the reaction of Co atoms with Cp*H) to the Co–Co bond.

In summary, we believe that the electronic structure of **2** together with the reactivity exhibited by **1** casts some doubt on whether the latter is truly [Cp*$_2$Co$_2$], and feel that there may be additional hydride ligands present in the observed structure. The presence of one, three, or four bridging hydride ligands could explain the observed magnetic behavior of **1**, and compounds with such supporting ligands would be less reactive than one containing an unsupported Co–Co double bond. We are currently undertaking higher level electronic structure calculations on compounds **2–6**, and we hope these comments stimulate further experimental studies of compound **1**.

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[Cp*Co$_2$]: Co 30.35, C 61.86, H 7.79%;
[Cp*Co$_2$H$_2$]: Co 30.19, C 61.54, H 8.26%;
[Cp*Co$_2$H$_4$]: Co 30.04, C 61.22, H 8.73%;
[Cp*Co$_2$]: Co 22.51, C 68.82, H 8.66%.
The last compound is included because **1** is cocrystallized with [Cp*Co$_2$], and reference is made to repeated recrystallizations in order to provide analytically pure **1**. Chronically high hydrogen analyses might be interpreted as [Cp*Co$_2$] in [Cp*Co$_2$], but the actual values for the analytically pure sample were not stated in [1].
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1,2,4-Cyclohexatriene, an Isobenzene, and Bicyclo[4.4.0]deca-1,3,5,7,8-pentaene, an Isonaphthalene: Generation and Trapping Reactions**

By Manfred Christl,* Martin Braun, and Germar Müller

After Miller and Shi[11] had generated the isomer **1** of dimethylnaphthalene by β elimination of HBr and had trapped it with potassium tert-butoxide as well as diphenylisobenzofuran, we asked ourselves whether the isonaphthalene **2** and the isobenzene **3** could also be prepared and subjected to trapping reactions. Two further isobenzenes, namely 1,2,3-cyclohexatriene and cyclohex-1-en-3-yne, were recently generated and intercepted.[2]

1   **2**   **3**
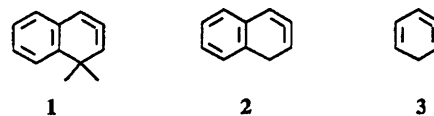
In connection with our work[3] concerning 1,2-cyclohexadiene and its derivatives,[4] we wanted to liberate **2** and **3** using the Doering–Moore–Skattebøl method. At first, the dibromocyclopropanes **13** and **14** were considered as unsuitable starting materials, since the addition of dibromocarbene, generated from bromoform and a base, to indene and cyclopentadiene only yields 2-bromonaphthalene[5] and bromobenzene, respectively, because of the rapid rearrangement of **13** and **14**.

Therefore, as previously for a precursor of 1-oxacyclohexa-2,3-diene,[6] we used the high energy of the C–F bond and added bromofluorocarbene (CHBr$_2$F, 50% NaOH, PhCH$_2$NEt$_3$Cl, CH$_2$Cl$_2$, ice bath) to indene and cyclopentadiene. We obtained **6**[7, 8] and **10**[7] in 16 and 20% yields,
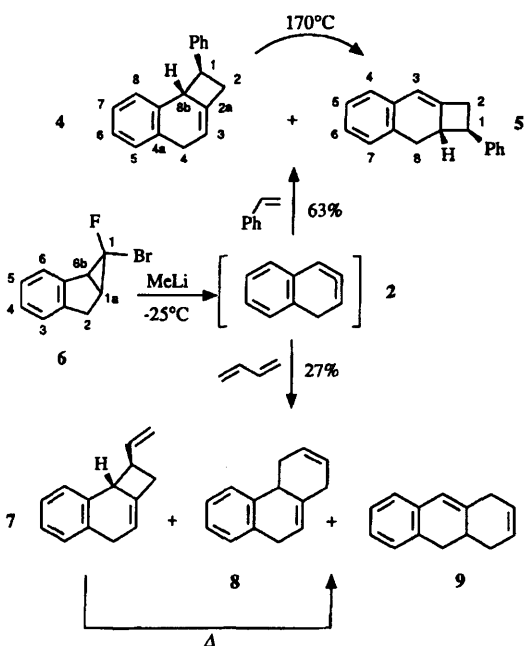
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Institut für Organische Chemie der Universität
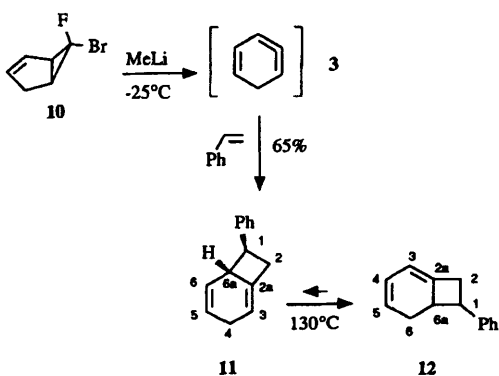Am Hubland, D-W-8700 Würzburg (FRG)

respectively. Only upon heating, the compounds **6** (130 °C, 3.5 h) and **10** (70 °C, 2 h) decompose to give 2-bromonaphthalene and bromobenzene, respectively.

As hoped, methyllithium causes the Br–Li exchange in **6** and **10**, followed by the loss of LiF. This leads, with ring expansion, to the cyclic allenes **2** and **3**, respectively, as the products of trapping reactions suggest.

Thus, a 14:1 mixture of the [2+2]cycloadducts **4**[7] and **5**[7] of the isonaphthalene **2** was formed by the reaction of **6** in styrene with MeLi in ether at −25 °C in 63% yield. Analogous products were obtained with α-methylstyrene. The use of butadiene as the trapping reagent afforded a 4:2:1 mixture of the [2+2]cycloadduct **7**,[7] and the [4+2]cycloadducts **8**[7] and **9**[7] in 27% yield. In the case of 2,3-dimethylbutadiene, the amount of the [2+2]cycloadduct was significantly larger than that of the [4+2]cycloadducts.
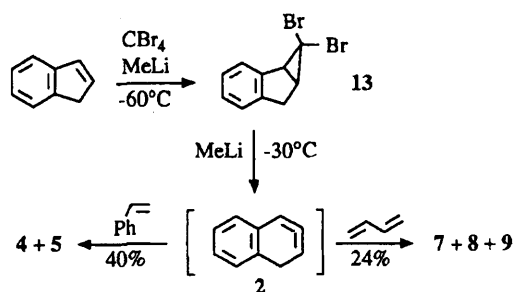
spectively, were also stable enough for preparative purposes. Produced from indene and cyclopentadiene, respectively, and tetrabromomethane in ether with MeLi[9] at −60 °C, they are actually stable in solution up to 0 °C as proved by the ¹H NMR spectra. We have used these findings to synthesize the cycloadducts of **2** and **3** in one-pot reactions.

Treatment of **13**, prepared at −60 °C, with MeLi in the presence of styrene at −30 °C furnishes the same mixture of **4** and **5** as from the use of **6**. With butadiene instead of styrene, **7–9** were again formed. The yields based on indene were, with 40 and 24%, respectively, considerably higher than from the method via **6** (10 to 4%, respectively).

If **10** is allowed to react with MeLi in the presence of styrene, then the [2+2]cycloadduct **11**[7] of **3** and probably its diastereomer are obtained as a 19:1 mixture in 65% yield. The trapping reaction of **3** with α-methylstyrene proceeded analogously.
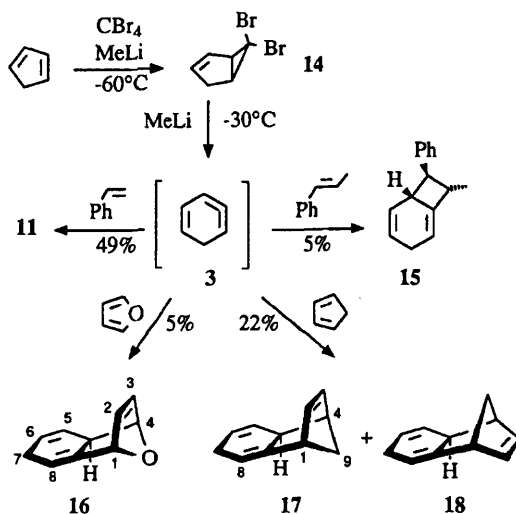
The cycloadducts **11** (49% compared with 13% via **10**), **17**[7] (14%) and **18**[7] (8%), **15**[7] (5%), and **16**[7] (5%), were formed analogously from cyclopentadiene, tetrabromomethane, MeLi, and the trapping reagents styrene and cyclopentadiene (see *Experimental Procedure*) as well as (E)-β-methylstyrene and furan, respectively. The 1,4-cyclohexadiene subunits of these compounds and their configurations are proved unequivocally by NMR spectroscopy (cf. Table 1).

We then investigated whether the dibromocarbene adducts of indene and cyclopentadiene, namely **13** and **14**, re-

Noteworthy are the reactivities of the different allene π bonds in **2** and **3**. The [4+2]cycloaddition of **2** with butadiene appears to lead, with little selectivity, to a 2:1 mixture of the tetrahydrophenanthrene **8** and the tetrahydroanthracene **9**. Due to the readily occurring thermal rearrangement of the [2+2]cycloadduct **7**, formed at the same time, into **8** and **9** in the ratio 2:1, this result must be confirmed by further investigations. The exclusive participation of the conjugated allene π bond in the [4+2]cycloadditions of **3** results in the

formation of **16–18**. We explain this by the more favorable frontier orbital energies in comparison to those of the non-conjugated allene π bond. This is based on the assumption of a one-step mechanism in the sense of the Diels–Alder reaction. In the [2 + 2]cycloadditions those allene π bonds react which are conjugated with the benzene unit in **2** and the ethylene unit in **3**, respectively. On the basis of previous

Table 1. Selected physical data of **4–18**; ¹H NMR (200 or 400 MHz) and ¹³C NMR (50 or 100 MHz) spectra measured in CDCl₃ if not stated otherwise.

4: Mp = 45–47 °C. ¹H NMR (C₆D₆): δ = 2.87 (m, 2H; H2), 3.09 (ddd, J(4,4) = 18.8, J(3,4) = 6.3, J(4,8b) = 2.3 Hz, 1 H; H4), 3.25 (dm, J(3,4) = 2.9 Hz, 1 H; H4), 3.27 (q, mean J(1,2) = J(1,8b) = 8.3 Hz; H1), 3.95 (m; H8b), 5.58 (ddq, mean J(2,3) = J(3,8b) = 1.9 Hz; H3), 6.90–7.90 (m, 9H; H-arene); ¹³C NMR: δ = 30.6 (t; C4), 38.1 (t; C2), 46.9, 51.7 (each d; C1,8b), 113.7 (d; C3), 125.4, 126.0, 126.1, 126.4, 128.2 (each d; C5,6,7,8, p-C), 126.9 (d; o-C), 128.6 (d; m-C), 136.4, 139.1, 139.4 (each s; C2a,4a,8a), 144.2 (s; ipso-C)

5: ¹H NMR: δ = 2.77–3.34 (m; 6H), 6.22 (t, line width 2.0 Hz; H3), 6.96–7.38 (m; 9 H-arene); ¹³C NMR: δ = 34.7 (t; C8), 37.7 (t; C2), 45.08, 45.13 (each d; C1,8a), 115.8 (d; C3), 125.7, 125.8, 126.2, 126.7, 128.2 (each d; C4,5,6,7, p-C), 126.5 (d; o-C), 128.4 (d; m-C), 134.3, 135.4 (each s; C3a,7a), 141.8 (s; C2a), 144.1 (s; ipso-C)

6: Mp = 71–72 °C. ¹H NMR: δ = 2.51 (m, 1 H), 3.18 (m, 3 H), 7.08–7.22 (m, 3 H), 7.32 (m, 1 H); ¹³C NMR: δ = 32.2 (td, J(C,F) = 3.5 Hz; C2), 34.0 (dd, J(C,F) = 12.6 Hz; C1a), 41.3 (dd, J(C,F) = 12.1 Hz; C6b), 82.6 (d, J(C,F) = 315.0 Hz; C1), 124.3, 125.2, 126.7, 127.3 (each d; C3,4,5,6), 137.0 (d, J(C,F) = 2.5 Hz), 143.5 (s; C2a,6a)

7: ¹³C NMR: δ = 30.4 (t; C4), 36.0 (t; C2), 45.7, 49.8 (each d; C1,8b), 113.0 (d; C3), 113.8 (t), 141.8 (d) (CH = CH₂), 125.3, 126.1 (double intensity), 128.1 (each d; C5,6,7,8), 136.3, 139.0, 139.6 (each s; C2a,4a,8a)

8: ¹³C NMR: δ = 29.5, 34.9, 36.9 (each t; C1,4,9), 38.0 (d; C4a), 116.4 (d; C10), 125.8, 126.0, 126.6, 126.9, 127.7, 128.3 (each d; C2,3,5,6,7,8), 133.2, 134.8, 137.7 (each s; C4b,8a,10a)

9: ¹³C NMR: δ = 33.1, 33.5, 33.8 (each t; C1,4,10), 34.3 (d; C4a), 120.7 (d; C9), 125.3, 126.32, 126.34, 126.4, 126.8, 127.5 (each d; C2,3,5,6,7,8); the signals of C4a,8a,10a could not be located precisely because of the low intensity.

10: ¹H NMR: δ = 2.31 (ddddd, J = 7.6, 6.5, 2.5, 1.8, 0.7 Hz; H5), 2.60 (br dquin, J = 16.0, 2.4 Hz, 1 H; H4), 2.66 (dm, 1 H; H4), 2.73 (dtdd, J = 7.6, 2.4, 1.0, 0.4 Hz; H1), 5.64 (dq, J = 5.6, 2.1 Hz), 5.78 (dtd, J = 5.6, 2.2, 0.8 Hz) (H2,3); ¹³C NMR: δ = 33.3 (td, J(C,F) = 3.0 Hz; C4), 33.5 (dd, J(C,F) = 13.3 Hz), 41.6 (dd, J(C,F) = 12.4 Hz) (C1,5), 82.5 (d, J(C,F) = 316.0 Hz; C6), 124.5 (d; C3), 133.6 (dd, J(C,F) = 1.7 Hz; C2)

11: ¹H NMR [a]: δ = 2.66 (m, 2H; H4), 2.91 (ddquin, J(2,2) = 12.5, J(1,2) = 9.0, J(2,3) ≈ mean J(2,4) ≈ J(2,6a) ≈ 1.9 Hz, 1 H; H2), 2.98 (ddquin, J(1,2) = 7.2, J(2,3) ≈ mean J(2,4) ≈ J(2,6a) ≈ 1.4 Hz, 1 H; H2), 3.19 (≈q, J(1,6a) = 8.3 Hz; H1), 3.35 (≈qtq, mean J(4,6a) = 8.2, J(3,6a) ≈ J(5,6a) ≈ 3.0, J(6,6a) = 1.8 Hz; H6a), 5.44 (m; H3), 5.83 (≈dqd, J(5,6) ≈ 9.4, mean J(4,5) ≈ 3.1, J(3,5) ≈ 0.9 Hz; H5), 5.91 (dq, mean J(4,6) = 1.9 Hz; H6), 7.17–7.33 (m; C₆H₅); ¹³C NMR: δ = 26.4 (t; C4), 38.4 (t; C2), 46.9 (d; C6a), 50.6 (d; C1), 112.0 (d; C3), 126.2 (d, p-C), 126.6 (d; o-C), 127.2, 127.3 (each d; C5,6), 128.4 (d; m-C), 138.5 (s; C2a), 144.0 (s; ipso-C)

12: ¹H NMR: δ = 2.18 (ddm, J(6,6) = 17.5, J(6endo,6a) = 14.0 Hz; endo-H6), 2.40 (dddm, J(6exo,6a) = 9.7, J(5,6exo) = 6.0 Hz; exo-H6), 2.90–3.06 (m, 2H), 3.08–3.30 (m, 2H), 5.55–5.70 (m, 2H), 5.94 (m, 1H), 7.15–7.37 (m; C₆H₅); ¹³C NMR: δ = 27.8 (t; C6), 38.4 (t; C2), 43.4, 45.9 (each d; C1,6a), 123.0, 125.1, 125.9, 126.1 (each d; C3,4,5, p-C), 126.4 (d; o-C), 128.5 (d; m-C), 138.4 (s; C2a), 144.4 (s; ipso-C)

13: ¹H NMR (CDCl₃/ether): δ = 2.57 (br t, J(1a,2exo) ≈ J(1a,6b) ≈ 7.0 Hz; H1a), 2.97 (br d, J(2,2) = 17.7 Hz; endo-H2), 3.17 (dd; exo-H2), 3.26 (br d; H6b), 7.05–7.17 (m, 3 H), 7.28 (br d, J = 7.3 Hz; 1 H)

14: ¹H NMR (CDCl₃/ether): δ = 2.29 (dm; endo-4-H), 2.30 (br t; H5), 2.55 (ddt, J(4,4) = 18.6, J(4exo,5) = 7.6, J(2,4exo) ≈ J(3,4exo) ≈ 2.0 Hz; exo-H4), 2.73 (≈ dt, J(1,5) = 7.2, J(1,4endo) = 3.0, J(1,2) = 2.4 Hz; H1), 5.58 (dq, J(2,3) = 5.5, J(2,4endo) = 2.2 Hz; H2), 5.77 (dtd, J(3,4endo) = 2.2, J(3,5) = 0.8 Hz; H3)

15: ¹³C NMR: δ = 17.0 (q; CH₃), 26.1 (t; C4), 47.3, 47.6 (each d; C2,6a), 55.6 (d; C1), 109.7 (d; C3), 126.3 (d; p-C), 126.7 (d; o-C), 127.2, 127.3 (each d; C5,6), 128.4 (d; m-C), 143.2, 145.0 (each s; C2a, ipso-C)

16: ¹H NMR [a]: δ = 2.64–2.73 (m, 2 H; H7), 2.90 (m; H4a), 5.18 (m; H1), 5.19 (dm, J(4,4a) ≈ 4.0 Hz; H4), 5.59 (qm; J(4a,8) ≈ mean J(7,8) ≈ 3.5 Hz; H8), 5.80 (br s; H5,6), 6.09 (dd, J(2,3) = 5.7, J(3,4) = 1.6 Hz; H3), 6.43 (br dd, J(1,2) = 1.6 Hz; H2); ¹³C NMR: δ = 28.0 (t; C7), 40.6 (d; C4a), 80.1, 80.7 (each d; C1,4), 112.9 (d; C8), 126.7, 128.4, 129.9 (each d; C3,5,6), 136.1 (d; C2), 141.7 (s; C8a)

Table 1. (continued)

17: ¹³C NMR: δ = 28.1 (t; C7), 41.9 (d; C4a), 45.5, 47.4 (each d; C1,4), 50.4 (t; C9), 112.3 (d; C8), 127.4, 130.3, 131.0 (each d; C3,5,6), 136.4 (d; C2), 146.2 (s; C8a)

18 [a]: ¹H NMR: δ = 1.30 (dtt, J(9,9) = 8.1, J(1,9syn) = J(4,9syn) = 1.6, J(2,9syn) = J(3,9syn) = 0.6 Hz; syn-H9), 1.67 (dq, J(1,9anti) = J(4,9anti) = J(4a,9anti) ≈ 2.0 Hz; anti-H9), 2.11 (dm; H4a), 2.54 (dddt, J(7,7) = 20.0, J(4a,7endo) = 11.0, J(5,7endo) = 3.0, J(6,7endo) = J(7endo,8) = 1.7 Hz; endo-H7), 2.70 (dddd, J(7exo,8) = 6.2, J(6,7exo) = 5.2, J(4a,7exo) = 4.0 Hz; exo-H7), 2.81 (br s; H4), 3.34 (br s; H1), 5.71 (dm; H8), 5.85 (br dd, J(5,6) = 9.0, J(4a,5) = 1.3 Hz; H5), 5.88 (ddddd, J(4a,6) = 3.1, J(6,8) = 0.9 Hz; H6), 6.10 (br dd, J(2,3) = 5.6, J(1,2) = 2.9 Hz; H2), 6.39 (br dd, J(3,4) = 3.1 Hz; H3); ¹³C NMR: δ = 28.4 (t; C7), 42.6 (d; C4a), 45.2, 48.9 (each d; C1,4), 50.8 (t; C9), 114.7 (d; C8), 129.7, 131.1, 133.0 (each d; C3,5,6), 139.0 (d; C2), 145.2 (s; C8a)

[a] The assignment is based on decoupling and NOE experiments.

results,[10] we assume that two-step processes occur with diradical intermediates such as **19** and **20** when styrene is used as the trapping reagent. Apparently, the ring closures of **19** and **20** yield **4** and **11**, respectively, with high selectivity under kinetic control. These are thermodynamically less stable than their conjugated isomers **5** and **12**, respectively.
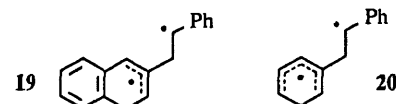
The latter is supported by the thermolyses of **4** and **11**, which lead mainly to **5** (81 %)[7] and a 1 : 3 mixture (64 %) of **11** and **12**,[7] respectively. Here, the diradicals **19** and **20** should again be intermediates, because the ring closures **19** → **4** and **20** → **11** are probably reversible above 100 °C. The preferred pathways of **19** and **20** to the nonconjugated products **4** and **11**, respectively, are attributed to the absolute spin density maximum in the benzyl position of the allyl radical moiety of **19**, and in the center of the pentadienyl radical part of **20**, respectively. In the case of **20**, this is the result of a theoretical study, which also describes the nature of the isobenzene **3** (see following communication[11]).

Experimental Procedure

11: To a stirred solution of 1,3-cyclopentadiene (2.25 g, 34.0 mmol) and tetra-bromomethane (11.3 g, 34.1 mmol) in ether (50 mL), MeLi (34.0 mmol, 34 mL, 1.0 M in ether) was added dropwise at −60 °C under N₂ during 1 h. Then the mixture was warmed to −30 °C, and styrene (20 g, 192 mmol) was added. A further 34.0 mmol of MeLi was then added dropwise over 30 min. The mixture was stirred continually and allowed to warm to 0 °C over a 4 h period. Then water (30 mL) was added and the phases were separated. The aqueous phase was extracted with ether (3 × 30 mL). The combined ether layers were dried with Na₂SO₄, concentrated at 20 °C/20 torr, and the excess styrene was distilled off at 20 °C/0.1 torr. From the residue, colorless **11** (3.04 g, 49 %) was distilled at 100 °C (kugelrohr)/0.1 torr, which probably contained ca. 5 % of its diastereomer.

17 and **18**: As described above, to a solution of 1,3-cyclopentadiene (8.0 g, 121 mmol) and tetrabromomethane (4.14 g, 12.5 mmol) in ether (10 mL), MeLi (13.1 mmol and 14.6 mmol) was added at −60 and −30 °C, respectively. The final distillation at 60 °C (kugelrohr)/0.1 torr yielded a yellowish liquid (1.56 g). Purification by flash chromatography (SiO₂, pentane) afforded firstly dicyclopentadiene, then **18** (145 mg, 8 %), and finally 307 mg of a 5.7 : 1.0 mixture of **17** (14 %) and benzonorbornadiene (2 %). Pure **17** was obtained by preparative gas chromatography (column length: 1.5 m, 20 % ethylene glycol adipate (EGA) on Volaspher®, 100 °C). A mixture of **17** and **18** was dehydrogenated with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) which yielded benzonorbornadiene (38 %).

CAS Registry numbers:
2, 139407-87-7; 3, 124869-33-6; cis-4, 139407-88-8; cis-5, 139407-89-9; 6, 139407-90-2; cis-7, 139407-91-3; 8, 139407-92-4; 9, 139407-93-5; 10, 139407-94-6; cis-11, 139244-61-4; trans-11, 139408-00-7; 12, 139407-95-7; 13, 139407-96-8; 14, 88472-16-6; 15, 139407-97-9; , 16, 139407-98-0; 17, 139407-99-1; 18, 139492-53-8; PhCH=CH₂, 100-42-5; H₂C=CHCH=CH₂, 106-99-0; PhCMe=CH₂, 98-83-9; (E)-PhCH=CHMe, 873-66-5; CHBr₃, 75-25-2; CHBr₂F, 1868-53-7; CBr₄, 558-13-4; indene, 95-13-6; cyclopentadiene, 542-92-7; furan, 110-00-9.

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[7] The proposed structures of the new compounds are in agreement with the analytical and spectroscopic data (cf. Table 1). The isolation of the compounds was achieved by kugelrohr distillation at 0.1 torr (5, 8–12, 16–18), flash chromatography on SiO₂ with pentane (4, 7–9, 15–18) or crystallization (6, from methanol).

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1,2,4-Cyclohexatriene, an Isobenzene, and its [2+2] Cycloaddition with Styrene: A Theoretical Study**

By Rudolf Janoschek*

Only a fraction of the 217 constitutional isomers with the general formula C_6H_6 are known. In the preceding communication Christl et al. describe their successful generation of the isobenzene 1,2,4-cyclohexatriene (1), which was proven by subsequent trapping reactions.[11] The identification of this interesting compound raises a number of questions. Where does isobenzene fit into the series of C_6H_6 isomers with regard to its heat of formation? What is its equilibrium geometry? Is this a chiral compound, and if so, how high is the barrier to racemization? What evidence is there for a possible diradical character of 1? Questions arise concerning the chemoselectivity in its [2+2] cycloaddition with styrene. The amount of information in the respective answers can be increased by the comparison of this isobenzene with related known compounds, primarily with 1,2-cyclohexadiene (2) which has been investigated experimentally[2] and theoretically.[3]
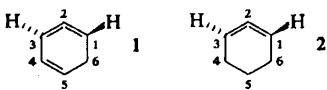
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To answer these questions we employed the semiempirical AM1 method.[4] This computational method provides especially reliable results for hydrocarbons; another advantage is the speed with which answers for our list of complicated questions may be obtained. The calculations were conducted with the MOPAC6 program[5] on a STARDENT computer.[6] The bent and twisted allene fragments in 1 and 2 give rise to diradical character which requires a multiconfigurational wave function for its correct description.[7] The calculations were thus carried out with the configuration interaction (CI) formalism, in which all electronic configurations arising from the distribution of two electrons in two orbitals are taken into account. The restricted Hartree–Fock (RHF) open-shell orbitals served in the construction of the configurations. On the energy hypersurfaces numerous stationary points, discussed later in this communication, were characterized either as minima or saddle points (transition structures) by their complete sets of harmonic vibrational frequencies.

The calculated heat of formation of 1, 93.7 kcal mol⁻¹, is considerably higher than that of benzene (22.0 kcal mol⁻¹). This increase in energy relative to benzene can be understood as arising from three contributions: loss of the stabilization of benzene, ring strain (bent allene), and rehybridization of the C6 center ($sp^2 \rightarrow sp^3$). The heat of formation of 1 correlates well with the values of the known C_6H_6 isomers like fulvene (62.6 kcal mol⁻¹) and Dewar benzene (116.7 kcal mol⁻¹).

A "planar or chiral allene fragment" are the two possible structural alternatives for 1. Significant calculated structural data are listed in Table 1. The local energy minimum corre-

Table 1. Structural data for 1 and 2 (bond lengths in Å, angles in degrees), for the energy minima (C_1 and C_2), and for the transition structures (C_s) of the racemizations.

	1		2	
	C_1	C_s	C_2	C_s
C1-C2	1.334	1.335	1.329	1.347
C2-C3	1.348	1.377	1.329	1.347
C3-C4	1.456	1.424	1.497	1.488
C4-C5	1.354	1.364	1.538	1.526
C5-C6	1.502	1.486	1.538	1.526
C1-C6	1.493	1.488	1.497	1.488
C1-C2-C3	132.4	131.9	133.7	133.3
H-C1-C2-C3	−159.0	180.0	−154.3	−178.5
H-C3-C2-C1	−163.1	180.0	−154.3	178.5
C5-C4-C3-C2	−23.8	0.0	−29.8	−21.9
C4-C3-C2-C1	12.1	0.0	21.2	0.2

sponds to a chiral structure with C_1 symmetry. The dihedral angles H-C1-C2-C3 and H-C3-C2-C1 with an average value of −161° are characteristic (−180° corresponds to a planar orientation). The C1-C2-C3 angle of 132.4° is indicative of considerable ring strain. Optical activity for the calculated chiral structure of 1 can be expected only if the energy barrier (activation enthalpy) to racemization is high enough. The corresponding transition structure has C_s symmetry and is only 2 kcal mol⁻¹ higher in energy than the C_1 minimum (Fig. 1). The resulting high rate of racemization rules out the observation of optical activity. Isobenzene can thus be designated as dynamically chiral.

The predictive value of the calculated properties of the new compound 1 can be understood better if the related known 1,2-cyclohexadiene (2) is referred to. Significant structural data for both 1 and 2 are provided in Table 1. In the minimum energy structure of 2 (C_2 symmetry) the expanded dihedral angle H-C1-C2-C3 (−154°) relative to that