# Cycloallenes, 13[+]

# Cyclohexa-1,2,4-triene from 1-Bromocyclohexa-1,4-diene

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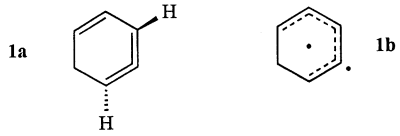
*Dedicated to Dr. Karl Peters on the occasion of his 60th birthday with warm thanks for a very prolific collaboration over many years*

**Keywords:** Cycloallenes / Cycloadditions / Eliminations / Strained molecules / Rearrangements

1-Bromocyclohexa-1,4-diene (**3**) was prepared from *trans*-4,5-dibromocyclohexene by elimination of hydrogen bromide. Treatment of a solution of **3** in furan or 2,5-dimethylfuran with KO*t*Bu afforded the tetrahydroepoxynaphthalenes **4** and **5**, respectively. The structure of these products is evidence for the title cycloallene (isobenzene **1**) being the reactive intermediate. The compounds **4** and **5** were dehydrogenated by DDQ to the known dihydroepoxynaphthalenes **6** and **7**, respectively. These conversions unambiguously confirm the structures of **4** and **5**. In pure styrene, **3** was not attacked by KO*t*Bu, and only upon the addition of 18-crown-6 did a reaction occur. This reaction did not, however, furnish the known [2+2] cycloadduct **9** of styrene and **1**, but, instead, a small amount of 1,2-diphenylethane (**8**) was formed. In agreement with this finding, the conjecture that **1** was deprotonated to give the phenyl anion was confirmed by the treatment of a solution of **3** and benzophenone in THF with KO*t*Bu, which resulted in the formation of triphenylmethanol.

## Introduction

In spite of their extremely short lifetime, numerous six-membered cyclic allenes including cyclohexa-1,2,4-triene (**1**) can be trapped by addition and cycloaddition reactions.[1−10] For a number of years, derivatives of **1** have been considered to be formed initially as Diels−Alder adducts in reactions of vinylacetylenes with acetylenes.[1,11,12,13] Furthermore, two rearrangement reactions are believed to proceed via derivatives of **1**.[14,15] Conclusive evidence for the parent isobenzene **1** was provided by the isolation of interception products after *exo*-6-bromo-*endo*-6-fluoro- or 6,6-dibromobicyclo[3.1.0]hex-2-ene had been treated with methyllithium in the presence of an activated olefin.[3,7] Another route to **1** is the electrocyclisation of hexa-1,3-diene-5-yne.[16,17] A kinetic investigation of this reaction in the presence of molecular oxygen gave the heat of formation of **1** as 105 kcal·mol$^{-1}$.[16] As this value is 85 kcal·mol$^{-1}$ greater than that of benzene, a comparison with the value estimated from group equivalents indicates that **1** is more likely to be the diradical **1b** than the allene **1a** (Scheme 1).




Scheme 1

A quantum chemical study using the AM1 method[18] found **1b** to be less stable than **1a** by 2 kcal·mol$^{-1}$, which is only a slight deviation from the above result. However, the heat of formation of **1a** was computed to be considerably different to the experimental value, i.e. only 72 kcal·mol$^{-1}$ above that of benzene.[18] Later, a high level ab initio calculation failed to get significantly closer to the experimental value, although it also favoured the allenic structure **1a**.[19]

Here, we present a third access to the reactive intermediate **1**, namely a β-elimination route, which allows us to address the question of whether **1** is amenable to deprotonation with formation of the phenyl anion. In the use of the Doering−Moore−Skattebøl pathway to **1**, this deprotonation is not apparent although methyllithium, a very strong base, is the reagent.[3,7]

## Results and Discussion

By treatment of 1-bromocyclohexene with potassium *tert*-butoxide (KO*t*Bu), Wittig and Fritze[20] generated cyclohexa-1,2-diene and thus clearly demonstrated for the first time the existence of a six-membered cyclic allene. Later, such a β-elimination of hydrogen bromide was used to access other six-membered cyclic allenes,[1,5,6,10] especially 1-oxacyclohexa-2,3-diene[5,6] and 3δ$^2$-chromene (2,3-didehydro-2*H*-1-benzopyran).[10] In the latter case, the Doering−Moore−Skattebøl approach is unsuccessful and, thus, the β-elimination pathway provides the only route to the reactive intermediate.[10]

Following the previous strategy,[20] we chose 1-bromocyclohexa-1,4-diene (**3**) as the precursor for **1** and prepared **3**

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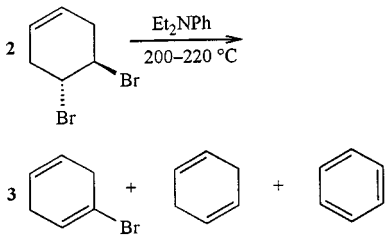
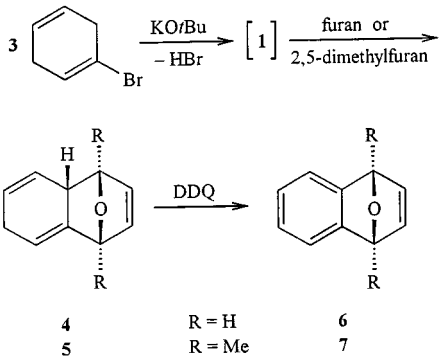



Scheme 2

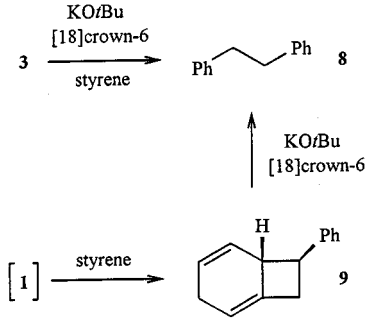
by heating of a mixture of *trans*-4,5-dibromocyclohexene (**2**) and *N*,*N*-diethylaniline at 200−220 °C (Scheme 2). In addition to **3** (11−27% yield), benzene and cyclohexa-1,4-diene were also formed. Whereas the latter is the result of a reductive elimination,[21] benzene is formed from a two-fold *anti* elimination and **3** from a *syn* elimination. This outcome clearly demonstrates that, in this case, the *syn* elimination is not as strongly disfavoured relative to the *anti* elimination as textbooks try to make the reader believe.[22] Our result is essentially analogous to the formation of 1-bromocyclohexene, cyclohexa-1,3-diene, cyclohexene and benzene on heating of *trans*-1,2-dibromocyclohexane with quinoline.[20b]




Scheme 3

Treatment of **3**, dissolved in pure furan, with KO*t*Bu afforded a 30% yield of the tetrahydroepoxynaphthalene **4** (Scheme 3), which had been prepared previously in low yield from 6,6-dibromobicyclo[3.1.0]hex-2-ene. Apparently, in the Doering−Moore−Skattebøl reaction and the β-elimination of hydrogen bromide from **3**, the same intermediate is generated, namely **1**. Analogously, use of 2,5-dimethylfuran instead of furan resulted in the formation of **5** (13%). The configuration of **4** as *endo*-substituted 7-oxanorbonene derivative is revealed by the magnitude of the coupling constant $J_{4,4a} \approx 4$ Hz in the $^1$H NMR spectrum.[7] Because of a torsional angle of ca. 90 °, a value close to 0 Hz has to be expected for the *exo*-isomer. Based on the similarity of the NMR spectroscopic data of **4** and **5**, the *endo*-configuration of **5** seems highly probable. In support of the constitutions of **4** and **5**, these compounds were converted into the known dihydroepoxynaphthalenes **6** and **7**, respectively, on treatment with DDQ (Scheme 3).

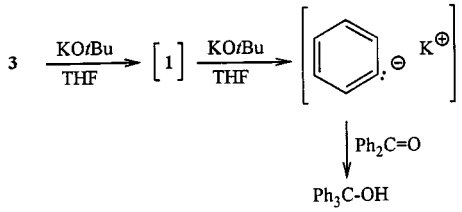
Our attempt to trap the isobenzene **1** generated from **3** by styrene had an unexpected result. At first it turned out that **3**, dissolved in pure styrene, did not react with KO*t*Bu. Whereas furan and its 2,5-dimethyl derivative obviously solvate the potassium cation sufficiently to make *tert*-butoxide a strong enough base for the β-elimination of HBr from **3**, styrene, as a pure hydrocarbon, cannot do this. Therefore, we added 18-crown-6 as a fourth component in order to complex the potassium cation. The immediate darkening of the mixture indicated the start of the reaction. However, the expected [2+2] cycloadduct **9**[7] of **1** to styrene, previously obtained by employing the Doering−Moore−Skattebøl route to **1**, was not observed. Instead, we isolated 1,2-diphenylethane (**8**), albeit in only 10% yield (Scheme 4).




Scheme 4

It is assumed that, under these reaction conditions, **3** is converted into **1**, from which two pathways to **8** are conceivable. One of them involves the deprotonation of **1** by *tert*-butoxide with formation of the phenyl anion, which could add to the β-carbon atom of styrene as in the anionic polymerisation of styrene.[23] Thus generated, the corresponding anion of **8** would be protonated by *tert*-butyl alcohol to give **8**. Alternatively, the isobenzene **1** could undergo the known [2+2] cycloaddition with styrene with production of **9**,[7] which would have to be isomerised to **8** by the action of the base, i.e. by deprotonation of the methylene group of the cyclohexa-1,4-diene subunit, opening of the four-membered ring, resulting in the anion of **8** mentioned above, and its protonation. We have examined this possibility by a control experiment. Indeed, the treatment of **9** with KO*t*Bu in the presence of 18-crown-6 gave rise to **8** in 76% yield. This high yield militates against the formation of **9** as the major pathway in the reaction of **3** with KO*t*Bu in styrene, since the yield of **8** should be much larger than 10% in this case.

In order to test whether the deprotonation of **1** can proceed under the reaction conditions, we tried to intercept the suspected phenyl anion with an electrophile other than styrene. For this purpose, we added KO*t*Bu to a solution of **3** and benzophenone in THF and, indeed, obtained triphenylmethanol (Scheme 5). The low yield (5%) may have its origin in the possible protonation of the phenyl anion by *tert*-butyl alcohol with formation of benzene, which was not looked for. Thus, the route by which **8** is formed from **3** remains unclear.




Scheme 5

## Conclusion

In the presence of furan, the treatment of 6,6-dibromobicyclo[3.1.0]hex-2-ene with methyllithium[7] and the β-elimination of hydrogen bromide from 1-bromocyclohexa-1,4-diene (**3**) described here furnish the same product. This is good evidence for the same intermediate in both reactions, i.e. the isobenzene **1** is unassociated with fragments of the precursors. In addition, the reaction conditions offer a test as to whether **1** can be transformed to the phenyl anion by deprotonation. The finding that performing the reaction in the presence of benzophenone gives rise to triphenylmethanol provides an unequivocally positive answer. For the preparation of cycloadducts of **1** in quantity, the use of **3** is inferior to the one-pot procedure starting from cyclopentadiene,[7] in particular because of the low yield in the synthesis of **3**. Moreover, the possibility of the cycloadducts being isomerised under the influence of KO*t*Bu/18-crown-6 limits the scope of the method, as shown by the styrene adduct **9** of **1**.

## Experimental Section

**Instrumentation**: See ref.[24]

***trans*-4,5-Dibromocyclohexene (2):** This compound was obtained according to a literature procedure.[25] Thus, cyclohexa-1,4-diene (15.21 g, 189.8 mmol, containing 1.29 g benzene, as obtained by the Birch reduction of benzene[26]) was dissolved in 50 mL of anhydrous chloroform. The stirred solution was cooled to −78 °C and bromine (32.9 g, 206 mmol) was added slowly so that the temperature did not exceed −75 °C. The solvent was then evaporated at 20 °C in vacuo and the remaining colourless solid was subjected to distillation. The product **2** (28.04 g, 62%; ref.[25] 90%) was obtained at 112 °C/8−10 mbar and solidified rapidly in the receiver, m.p. 37 °C (ref.[27] b.p. 119 °C/20 Torr; ref.[25] m.p. 34−37 °C). The solid residue (15.7 g, 21%) was shown to be a 93:7 mixture of 1*r*,2*t*,4*c*,5*t*- and 1*r*,2*t*,4*t*,5*c*-tetrabromocyclohexane[27] by NMR spectroscopy.
**2:** $^1$H NMR ($CDCl_3$): δ = 2.60, 3.20 (2 × dm, $J_{gem} \approx 19$ Hz, 3-$H_2$), 4.52 (m, 4-H), 5.66 (m, 1-H). − $^{13}$C NMR ($CDCl_3$): δ = 30.9 (t, C-3), 48.4 (d, C-4), 122.0 (d, C-1).
1*r*,2*t*,4*c*,5*t*-Tetrabromocyclohexane: $^1$H NMR: δ = 2.88 (br. s, $CH_2$), 4.51 (m, CH). − $^{13}$C NMR ($CDCl_3$): δ = 39.7 ($CH_2$), 50.6 (CH).
1*r*,2*t*,4*t*,5*c*-Tetrabromocyclohexane: $^1$H NMR: δ = 2.46, (m, $J_{gem}$ = −14.0 Hz, $J_{vic}$ = +12.0 Hz, 3-$H_{ax}$), 3.14 (dm, $J_{vic}$ = +4.6 Hz, 3-$H_{eq}$), 3.95 (m, $J_{1,2}$ = +10.5 Hz, 1-H); the coupling constants were determined by simulation. − $^{13}$C NMR ($CDCl_3$): δ = 46.8 ($CH_2$), 51.6 (CH).

**1-Bromocyclohexa-1,4-diene (3):** A flask, equipped with a reflux condenser and containing a mixture of **2** (2.00 g, 8.33 mmol) and *N*,*N*-diethylaniline (2.49 g, 16.7 mmol) under nitrogen, was heated with an electric mantle to 200−220 °C within 10 min and kept at that temperature for 5 min. Then, the heater was turned off and the flask was allowed to cool within the mantle. The mixture was treated with water and diethyl ether until two layers resulted, which were then separated. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with 2 M hydrochloric acid (3 × 5 mL) and water (5 mL), dried with $MgSO_4$, and concentrated in vacuo. From the residue, analytically pure **3** (150−357 mg, 11−27% in several experiments) was obtained by distillation, b.p. 50 °C/10 mbar m. p. 23−25 °C. − IR (film): $\tilde{\nu}$ = 3034 $cm^{-1}$, 2880, 2822, 1678, 1428, 1350, 964, 929, 661, 633. − $^1$H NMR ($CDCl_3$): δ = 2.77 ("ttd", line distances 8.7, 3.5, 1.8 Hz, 3-$H_2$), 3.04 ("tdt", line distances 8.7, 3.2, 1.8 Hz, 6-$H_2$), 5.59 (dtt, $J_{4,5}$ = 10.1, $J_{5,6}$ = 3.2, $J_{3,5}$ = 1.8 Hz, 5-H), 5.70 (dttd, $J_{3,4}$ = 3.2, $J_{4,6}$ = 2.0, $J_{2,4}$ = 1.3 Hz, 4-H), 6.05 (tq, $J_{2,3}$ = 3.7, $J_{2,6}$ = 1.6 Hz, 2-H); the assignment is based on a NOESY experiment. − $^{13}$C NMR ($CDCl_3$): δ = 28.9 (C-3), 35.4 (C-6), 119.6 (C-1), 123.0 (C-4), 123.9 (C-5), 126.1 (C-2); the assignment is based on a C,H-COSY spectrum. − $C_6H_7Br$ (159.0): calcd. C 45.31, H 4.44; found C 45.63, H 4.70.

**(1α,4α,4aα)-1,4,4a,7-Tetrahydro-1,4-epoxynaphthalene (4):** Under nitrogen, potassium *tert*-butoxide (767 mg, 6.84 mmol) was added in small portions to a stirred solution of **3** (543 mg, 3.41 mmol) in freshly distilled furan (15 mL) over a period of 10 min at room temperature. The mixture was stirred vigorously for 1 h and then treated with water (5 mL). After separation of the layers, the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography ($SiO_2$, light petroleum for the first 200 mL of eluate, light petroleum/diethyl ether, 20:1 for the next 400 mL and 15:1 finally) to give **4** (150 mg, 30%) as a pale yellow liquid, which was shown by $^1$H NMR spectroscopy to contain a few per cent of the dehydrogenation product **6**. − $^1$H, $^{13}$C NMR: ref.[7] − MS (70 eV): *m*/*z* (%) = 146 (16) [$M^+$], 145 (95), 131 (36), 128 (32), 127 (36), 117 (61), 116 (30), 115 (100), 91 (71), 78 (20), 77 (23), 68 (44), 65 (20), 51 (25), 39 (65). − HRMS ($C_{10}H_9O$ [$M^+$ − H]): calcd. 145.0653; found 145.0653. − $C_{10}H_{10}O$ (146.2): calcd. C 82.16, H 6.90; found C 81.59, H 6.78.

**(1α,4α,4aα)-1,4,4a,7-Tetrahydro-1,4-dimethyl-1,4-epoxynaphthalene (5):** According to the procedure described for the preparation of **4**, from **3** (300 mg, 1.88 mmol) in 2,5-dimethylfuran (15 mL), **5** (43 mg, 13%) was obtained as a colourless oil after flash chromatography ($SiO_2$, light petroleum/diethyl ether 10:1). − $^1$H NMR ($CDCl_3$): δ = 1.63, 1.70 (2 × s, 2 × Me), 2.62−2.70 (m, 4a-H, 7-$H_2$), 5.44 (m, 8-H), 5.76−5.81 (m, 5-, 6-H), 5.87, 6.16 (2 × d, $J_{2,3}$ = 5.4 Hz, 2-, 3-H). − $^{13}$C NMR ($CDCl_3$): δ = 15.2, 17.7 (2 × Me), 27.9 (C-7), 48.0 (C-4a), 87.0 (double intensity, C-1, C-4), 111.0 (C-8), 126.7, 128.0 (C-5, C-6), 133.9 (C-3), 139.9 (C-2), 148.4 (C-8a). − MS (70 eV): *m*/*z* (%) = 174 (13) [$M^+$], 159 (26), 132 (12), 131 (100), 130 (17), 129 (28), 128 (17), 116 (19), 115 (32), 91 (52), 77 (11), 43 (49). − HRMS ($C_{12}H_{13}O$ [$M^+$ − H]): calcd. 173.0966; found 173.0965.

**1,4-Dihydro-1,4-epoxynaphthalene (6):** To a solution of **4** (10.0 mg, 0.0684 mmol) in benzene (0.7 mL) was added DDQ (18.6 mg, 0.0819 mmol) at room temperature. The mixture was shaken until the DDQ had dissolved and then left at 25 °C for 24 h. The precipitate formed was removed by filtration and the filtrate was concentrated in vacuo. The residue was shown to be virtually pure **6** by the $^1$H and $^{13}$C NMR spectra on comparison with literature data.[28]

**1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene (7):** According to the procedure described for the reaction of **4**, compound **5** (22.0 mg, 0.126 mmol) was treated with DDQ. The precipitate formed was removed by filtration through basic $Al_2O_3$ (activity IV) with benzene as eluant. The filtrate was concentrated in vacuo and the remaining colourless oil (20 mg, 92%) was shown to be virtually pure **7** by NMR spectroscopy. The $^1$H NMR chemical shifts ($CDCl_3$) reported in ref.[29] deviate somewhat from our values: δ = 1.90 (s, Me), 6.78 (s, 2-H ), 6.98, 7.12 ( 2 × m, 5-, 6-H). − $^{13}$C

NMR ($CDCl_3$): δ = 15.2 (Me), 88.6 (C-1), 118.3 (C-5), 124.7 (C-6), 146.8 (C-2), 152.7 (C-4a).

**Treatment of 3 with KO*t*Bu in the Presence of 18-Crown-6 and Styrene:** At room temperature, KO*t*Bu (695 mg, 6.19 mmol) was added over a period of 30 min in small portions to a stirred solution of **3** (500 mg, 3.15 mmol) and 18-crown-6 (830 mg, 3.14 mmol) in styrene (20 mL), kept under nitrogen. Stirring was continued for 2 h and water (5 mL) was then added to the mixture. After separation of the layers, the aqueous layer was extracted with diethyl ether (3 × 10 mL); the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. From the residue, 1,2-diphenylethane (**8**, 55 mg, 10%) was obtained as a colourless oil by distillation at 100 °C (kugelrohr)/0.15 mbar. The NMR spectra are in agreement with literature data.[30]

**Treatment of *exo*-7-Phenylbicyclo[4.2.0]octa-1,4-diene (9) with KO*t*Bu in the Presence of 18-Crown-6:** KO*t*Bu (616 mg, 5.49 mmol) was added in small portions to a stirred solution of **9** (500 mg, 2.74 mmol) in anhydrous THF (20 mL), kept under nitrogen, at room temperature. Since no reaction occurred within 1 h, 18-crown-6 (728 mg, 2.75 mmol) was added. This caused the mixture to turn from almost colourless to a deep brownish red instantaneously. Stirring was continued for 1 h, after which the solvent was removed in vacuo. The residue was treated with light petroleum (10 mL) and water (5 mL) and the layers were separated. The aqueous layer was extracted with light petroleum (3 × 15 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. From the residue, 1,2-diphenylethane (**8**, 380 mg, 76%) was obtained by distillation at 100 °C (kugelrohr)/0.15 mbar as a colourless oil, which solidified, m.p. 45−47 °C (ref.[30] 45−50 °C, ref.[31] 52 °C). The NMR spectra were the same as those of the product of the above experiment.

**Reaction of 3 with KO*t*Bu in the Presence of Benzophenone:** To a solution of **3** (685 mg, 4.30 mmol) and benzophenone (3.13 g, 17.2 mmol) in anhydrous THF (10 mL), kept under nitrogen, was added KO*t*Bu (2.24 g, 20.0 mmol). The mixture was stirred at room temperature for 1 h and then treated with water (5 mL) and diethyl ether, until two layers resulted. These were separated and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography ($SiO_2$, light petroleum/diethyl ether, 10:1 for the first 300 mL of eluate and then 5:1) to give triphenylmethanol (55 mg, 5%) as colourless crystals, m.p. 166 °C (ref.[31] m.p. 164 °C). $^1H$ and $^{13}C$ NMR spectra were identical with those of an authentic sample.

## Acknowledgments

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