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5,6-DIDEHYDRO-10-METHYLBENZOCYCLOOCTENE[1]

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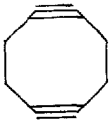
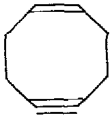
Summary. Treatment of 5-bromo-10-methylbenzocyclooctene (*11*) with potassium *tert*-butoxide gave 5-methyl-9-*tert*-butoxybenzocyclooctene (*14*), presumably via 5,6-didehydro-10-methylbenzocyclooctene (*13*). The cyclic acetylene (*13*) could be trapped by reaction with 1,3-diphenylisobenzofuran to give the adduct (*15*).

It has been reported that cycloocta-1,5-diyne (*1*)[3] is less reactive than cyclooct-1-en-5-yne (*2*)[4]. Similarly, we have shown that 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (*3*) is less reactive than 5,6-didehydrodibenzo[*a,e*]cyclooctene (*4*)[5]. We have recently demonstrated that


(*1*)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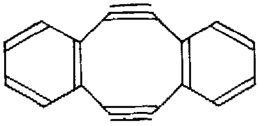
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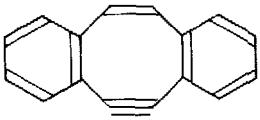
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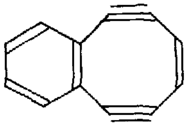
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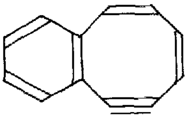
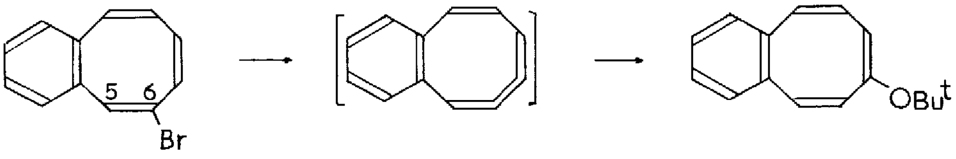

(*6*)

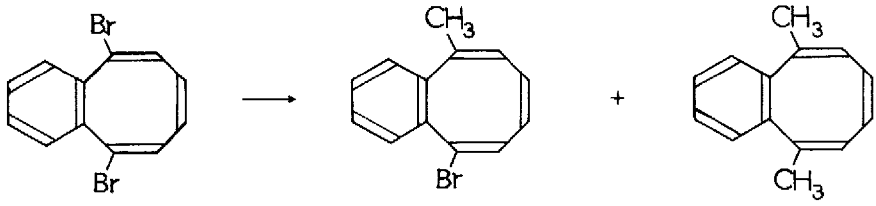
5,6,9,10-tetradehydrobenzocyclooctene (*5*) can be isolated, but is very unstable.[6] It was of interest to investigate whether 5,6-didehydrobenzocyclooctene (*6*) (or a simple derivative), which was expected to be even less stable than the corresponding diacetylene (*5*), could still be isolated.

It has been shown that treatment of 6-bromobenzocyclooctene (*7*) with potassium *tert*-butoxide leads to 7-*tert*-butoxybenzocyclooctene (*9*),[7] a reaction which presumably proceeded via the cyclic cumulene 6,7-didehydrobenzocyclooctene (*9*), and no evidence for the formation of 5,6-didehydrobenzocyclooctene (*6*) was obtained. It appeared that 5-bromobenzocyclooctene was a more suitable starting material than the 6-bromo isomer (*7*), since the primary dehydrobromination product of the 5-bromo isomer must be the required 5,6-didehydrobenzocyclooctene (*6*).



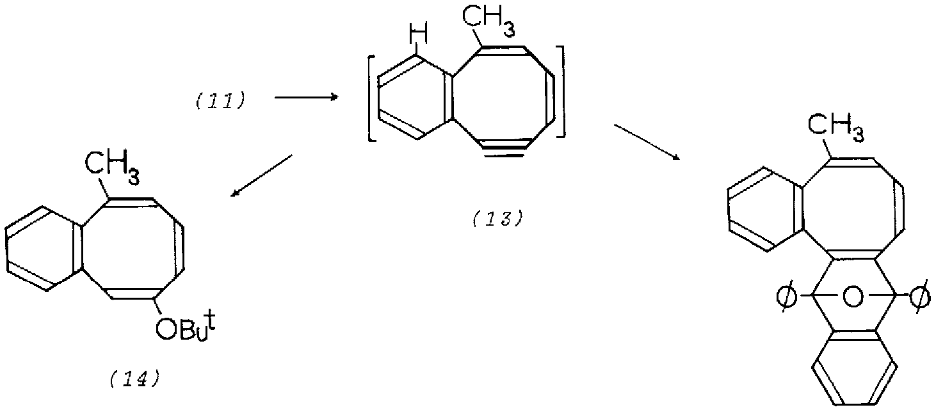
(*7*) (*8*) (*9*)

We decided to use 5-bromo-10-methylbenzocyclooctene (*11*) as the starting material, since this compound could be readily prepared, and the presence of the methyl group was expected to facilitate the recognition of any ring current in the product(s) by ^{1}H NMR spectrometry.[8] Treatment of 5,10-dibromobenzocyclooctene (*10*)[6,9] with one molar equivalent of lithium dimethylcuprate in ether for one hour led in 27% yield to compound (*11*) as a colorless oil; ^{1}H NMR (60 MHz,$CDCl_3$), δ2.21(d,3H,J=1.2Hz), 5.70-6.00(m,3H), 6.51-6.62(m,1H), 7.07-7.42(m,4H); MS (exact mass), calcd. for $C_{13}H_{11}Br$ 246.0045, measured: 246.0046. Use of HPLC (SiO_2,pentane) separated (*11*) from small amounts of unchanged dibromide (*10*) and 5,10-dimethylbenzocyclooctene (*12*); ^{1}H NMR (60 MHz,$CDCl_3$), δ2.15(s,6H), 5.77-6.00(m,4H,AA'BB'), 7.10-7.30(m,4H,AA'BB'); MS (exact mass), calcd. for $C_{14}H_{14}$: 182.1095, measured: 182.1091.



(*10*) (*11*) (*12*)

Dehydrobromination of the bromide (*11*) with one molar equivalent of potassium *tert*-butoxide in dry tetrahydrofuran for *ca* 5 minutes gave 5-methyl-9-*tert*-butoxybenzocyclooctene (*14*), a colorless oil, as the sole product to be isolated. The structure of (*14*) was established by the ^{1}H NMR spectrum [(60 MHz,$CDCl_3$), δ1.35(s,9H), 2.11(d,3H,*J*=0.5Hz), 5.75-6.02 (m,3H), 6.25(s,1H), 7.00-7.30(m,4H)] and by the mass spectrum [(exact mass), calcd. for $C_{17}H_{20}O$: 240.1514, measured: 240.1514]. Although there is little doubt that 5,6-didehydro-10-methylbenzocyclooctene (*13*) is an intermediate in the conversion of (*11*) to (*14*), it appears to be too unstable for isolation to be possible under the reaction conditions used. That (*13*) is an intermediate was confirmed through dehydrobromination of the bromide (*11*) with one molar equivalent of potassium *tert*-butoxide in dry tetrahydrofuran in the presence of a small excess of 1,3-diphenylisobenzofuran. This reaction led to 17% of the adduct (*15*) as a colorless solid, m.p. 75-79°; ^{1}H NMR (60 MHz,$CDCl_3$) δ1.45(s,3H), 7.10-8.00(m,21H); MS (exact mass), calcd. for $C_{33}H_{24}O$: 436.183, measured: 436.175.



(*13*) (*14*) (*15*)

The observed decreased stability of the benzannelated cyclooct-1-en-5-yne (*13*) as compared with the benzannelated cycloocta-1,5-diyne (*5*) is in keeping with the relative stabilities of (*1*) and (*2*), as well as (*3*) and (*4*). Although there may be some nonbonded H-H interaction in the presumably planar cyclic acetylene (*13*) due to the presence of the methyl group (see formula), we do not believe that this is of any particular significance for explaining the instability of (*13*).

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References and Notes

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