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THE STEREOCHEMISTRY OF THE [2+2]-CYCLOADDITIONS OF CYCLOPENTYNE - EVIDENCE FOR AN ANTISYMMETRICAL SINGLET GROUND STATE[1)]

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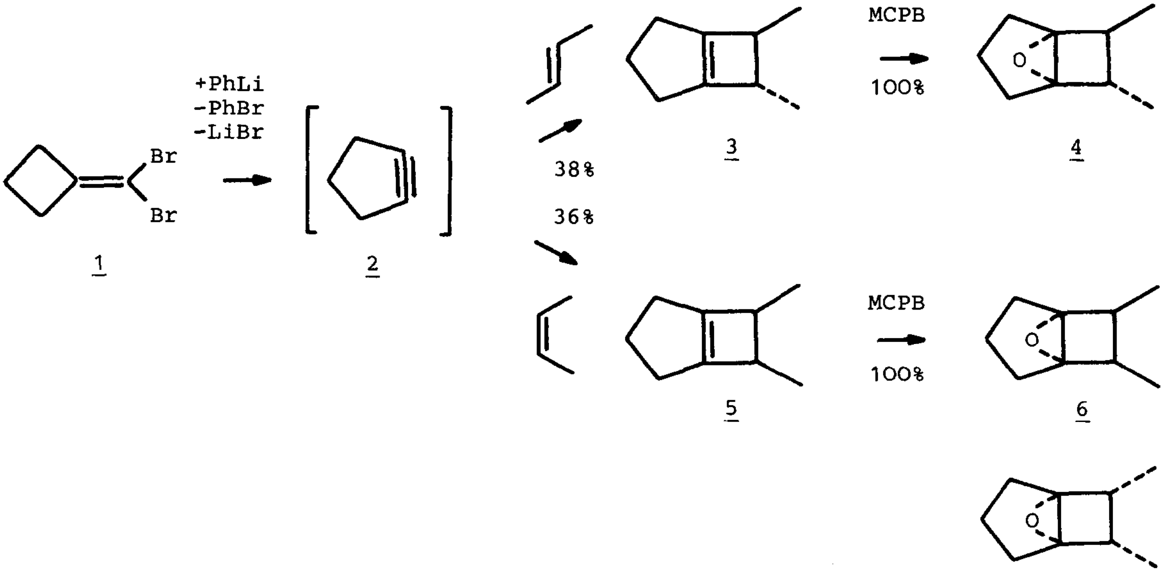
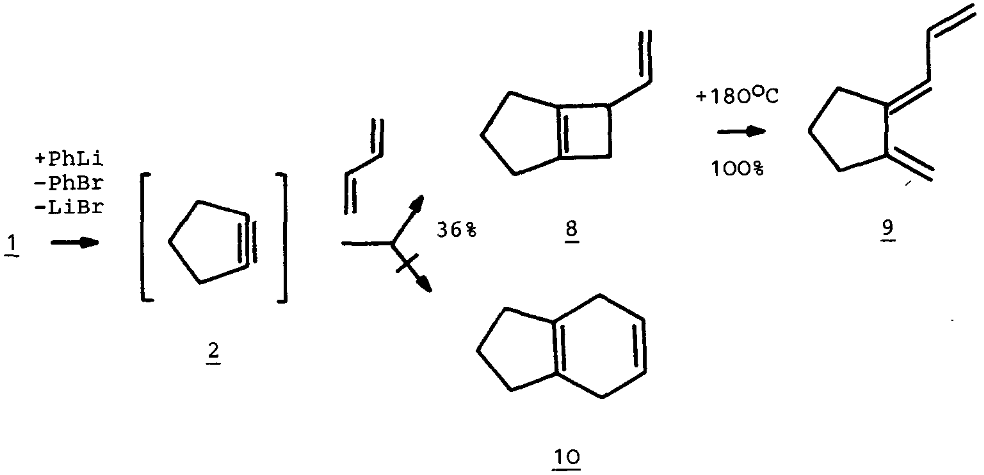
Summary: Cyclopentyne 2, as generated from dibromomethylenecyclobutane 1, adds stereospecifically cis to both cis- and trans-2-butene and prefers 1,2- to 1,4-addition with 1,3-butadiene. This points to an antisymmetrical singlet ground state of the cyclopentyne diradical.

We have recently found[1)] that cyclopentyne 2, as generated from dibromomethylenecyclobutane 1, undergoes [2+2]-cycloadditions with a variety of olefins, yielding bicyclo[3.2.0]hept-1(5)-ene derivatives. We have now investigated the stereochemistry of this unusual process and report here on our findings with cis-2-butene, trans-2-butene and 1,3-butadiene and consequences therefrom concerning the spin state and symmetry of the cyclopentyne diradical.

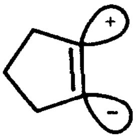


When dibromomethylenecyclobutane 1[1] (4.0 mmol) was reacted with phenyllithium [2.0 ml (4.0 mmol) of a 2.0 m solution in benzene/ether (75/25)] in *cis*-2-butene (40 mmol, 99% pure) and *trans*-2-butene (40 mmol, 99% pure) respectively for 15 min at -40°C and 45 min at 0°C, single cycloadducts (36% from *cis*-2-butene and 38% from *trans*-2-butene)[2] arose in both cases. The stereochemical differentiation proved difficult on the basis of the pure hydrocarbons but could readily be achieved upon epoxidation[3]. The cycloadduct of *trans*-2-butene yielded a single epoxide 4[4], which had lost the symmetry of its olefinic precursor and thus proved to be derived from 3[4]. The cycloadduct from *cis*-2-butene yielded a 1.3:1 mixture of two stereoisomeric epoxides 6[4,5] and 7[4,5], which had retained the symmetry of their olefinic precursor and thus proved to be derived from 5[4]. It was hence obvious that cyclopentyne 2, as generated from dibromomethylenecyclobutane 1, had added stereospecifically *cis* to both *cis*- and *trans*-2-butene.



To verify the now highly probable preference of cyclopentyne 2 for 1,2- rather than 1,4-addition with conjugated dienes, we reacted dibromomethylenecyclobutane 1[1] (2.0 mmol) with phenyllithium [1.0 ml (2.0 mmol) of a 2.0 m solution in benzene/ether (75/25)] in 1,3-butadiene (20 mmol, 99% pure) as well. Indeed, within 15 min at -40°C and 45 min at -10°C the [2+2]-cycloadduct 8[4] was formed in 36% yield[2], no [2+4]-cycloadduct 10 being detectable[6]. Pure 8 was found to be highly prone to polymerisation but could be readily transformed to the stable *trans*-1,3,5-hexatriene 9[4,7] via a thermally allowed conrotatory outward cycloreversion. This process was complete within 2 min at +180°C.

We feel that the observed stereospecific *cis*-addition of cyclopentyne 2 to *cis*- and *trans*-2-butene and its preference for 1,2- rather than 1,4-addition with 1,3-butadiene may best be explained in terms of orbital symmetry control assuming an *antisymmetrical* singlet ground state 11 of the cyclopentyne diradical. This is in sharp contrast to what is known[8,9] for the structurally related 1,2-dehydrobenzene, where a *symmetrical* singlet ground state 12[8] causes nonstereospecific 1,2-additions and a strong preference for stereospecific 1,4-additions[9]. Nevertheless, the behaviour of cyclopentyne 2 is not without precedence: 1,8-dehydronaphthaline adds stereospecifically *cis* to both *cis*- and *trans*-2-butene[10] and here in fact an *antisymmetrical* singlet ground state 13 has been shown[8] to be involved.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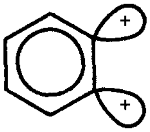
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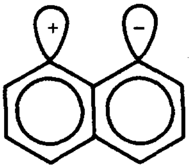
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In summary, the stereospecific *cis*-addition of cyclopentyne 2 to both *cis*- and *trans*-2-butene and the selective 1,2-addition to 1,3-butadiene provide evidence for an *antisymmetrical* singlet ground state of the cyclopentyne diradical. As no calculations on the spin state and symmetry of cyclopentyne itself exist, a thourough theoretical study is clearly warranted.

Acknowledgement: This work has been supported by the Fonds der Chemischen Industrie.

References and notes

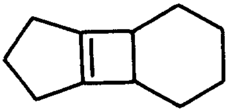
1) Cycloalkynes, 2. Part 1: L.Fitjer, U.Kliebisch, D.Wehle and S.Modaressi, *Tetrahedron Lett*. *1982*, 1661.

2) The yields of 3, 5 and 8 were determined by glpc (3m x 1/4" all-glass system, 15% SE 30 on chromosorb W AW/DMCS, 60/80 mesh, 50-180°C) with n-octane as internal standard. 3 and 5 were cross-checked and found to be detectable in concentrations of less than 1%. 3, 5 and 8 were prepurified by flash chromatography over silica gel in n-pentane (partial isomerisation of 8 to 9 occurred) and then subjected to preparative glpc.

3) The cycloadduct in question (1.0 mmol) was dissolved in methylene chloride (20 ml), buffered with potassium bicarbonate (5.0 mmol) and then treated with m-chloroperoxybenzoic acid (2.0 mmol) for 1 hr at rt. Preparative glpc yielded the pure epoxides. The epoxidation of the parent bicyclo-[3.2.0]hept-1(5)-ene has been described: K.B.Wiberg, J.E.Hiatt and G.Burgmaier, *Tetrahedron Lett*. *1968*, 5855.

4) All new compounds gave correct elemental analyses or high resolution mass spectral data. IR, Raman (3,5), ^{1}H NMR, ^{13}C NMR and mass spectral data are in accord with the structures given. ^{13}C NMR data ($CDCl_3$) are as follows: 3: 17.63, 26.19, 29.74, 44.62, 152.70; 4: 14.22, 17.01, 25.79, 26.13, 30.68, 39.29, 43.85, 61.68, 62.14; 5: 14.11, 26.31, 29.77, 38.66, 153.86; 6: 10.67, 27.07, 28.89, 35.19, 62.31; 7: 10.91, 25.14, 26.38, 35.30, 64.48; 8: 26.28, 30.74, 31.05, 35.62, 44.62, 113.51, 141.24, 148.91, 152.29; 9: 23.94, 30.53, 34.27, 102.91, 116.70, 119.80, 134.56, 142.88, 149.49; 15: 18.46, 19.41, 25.70, 26.81, 37.24, 64.69.

5) The configurational assignment of 6 and 7 is based on a ^{13}C NMR chemical shift correlation with a single epoxide 15$^{4)}$ obtained from 14$^{1)}$ according to ref. $^{3)}$ and thought to be formed by an exclusive attack of the reagent from the less hindered *exo*-side.



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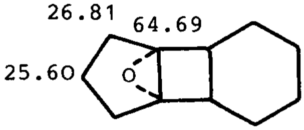

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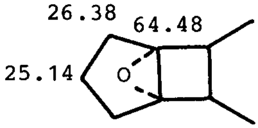

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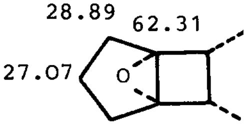

7

6) Glpc analysis of the original reaction mixture and of a sample with added 10 (purchased from Ega-Chemie, D-7924 Steinheim, West Germany, and purified by glpc) revealed that no 10 had been formed.

7) The thermal isomerisation of 3-vinylcyclobutene has been reported to yield *trans*-1,3,5-hexatriene exclusively: J.Meinwald and P.H.Mazzocchi, J. Amer. Chem. Soc. 88, 2850 (1966).

8) R.Hoffmann, A.Imamura and W.J.Hehre, J. Amer. Chem. Soc. 90, 1499 (1968).

9) M.Jones Jr. and R.H.Levin, J. Amer. Chem. Soc. 91, 6411 (1969).

10) C.W.Rees and R.C.Storr, J. Chem. Soc. Chem. Commun. 1965, 193; J. Chem. Soc. (C) 1969, 765.

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