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ON THE INTERMEDIACY OF BICYCLO[3.2.0]HEPT-6-YNE, A CYCLOBUTYNE DERIVATIVE

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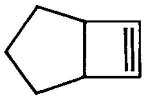
Summary: Treatment of 6-chloro-, 6-bromo- and 6-iodobicyclo[3.2.0]hept-6-ene, respectively, with LDA in the presence of LiSPh led to identical mixtures of thioethers 3e and 4a. The results are rationalized by the assumption that cyclobutyne 2 and carbene 7 are formed as intermediates.

Although the results of nonempirical MO calculations leave no doubt that cyclobutyne (1) is a local minimum on the C_4H_4 potential energy hypersurface $^{1)}$, the existence of 1 or of a system with a cyclobutyne structural subunit has not been experimentally established $^{2,3)}$. We now wish to report preliminary experimental evidence for the formation of bicyclo[3.2.0]hept-6-yne (2) as a fleeting intermediate in the reaction of 6-halobicyclo[3.2.0]hept-6-ene (3a-c) with strong bases.

1



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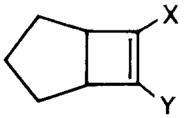
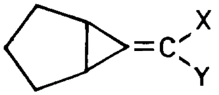


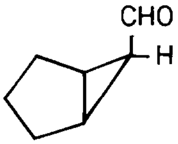
3

3	**a**	**b**	**c**	**d**	**e**	**f**
X	Cl	Br	I	Br	SPh	Li
Y	H	H	H	$SiMe_3$	H	H



4

4	X	Y
a	SPh	H
b	Ph	H
c	Ph	D
d	Ph	Li



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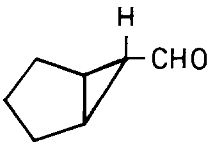
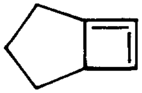


5b

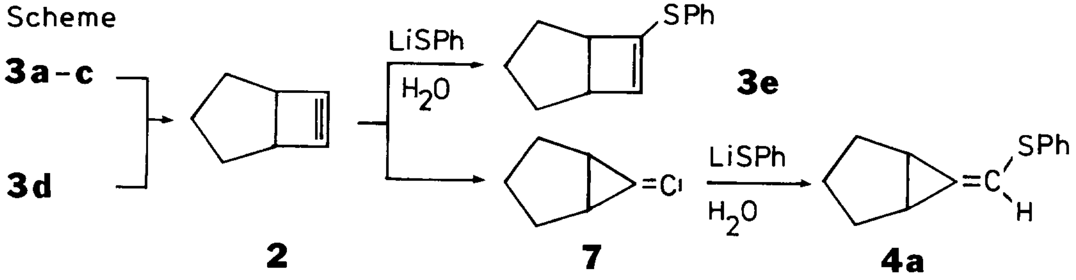


6

When 1.0 mmol bromide 3b [4] reacted with 3.0 mmol lithium diisopropylamide (LDA) in the presence of 10.0 mmol lithium thiophenolate (LiSPh) in 15 ml tetrahydrofuran (THF) for 30 min at 0°C, aqueous work-up resulted in a 0.14:1.0 mixture of the thioethers 3e and 4a in 67% total yield. In the absence of LDA, 3b and LiSPh failed to react. Starting with the chloride 3a or the iodide 3c, under otherwise identical reaction conditions, product ratios 3e:4a of 0.14 (total yield 63%) and, respectively, 0.15 (35%) were obtained. The structure of 3e was confirmed by independent synthesis via lithium-bromine exchange with the complex of *n*-butyllithium and tetramethylethylenediamine at -78°C, followed by functionalization of 3f with diphenyl disulfide yielding 56% 3e. The hydrolysis of 4a with aqueous mercuric acetate led to a 8:1 mixture of the known aldehydes 5a and 5b [5].

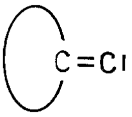
As LDA is able to initiate single electron processes [6], the base was changed and the starting material was modified. The reaction of 3b, potassium *tert*-butoxide (KO-t-Bu) and KSPh (ratio 1:20:20) in dimethyl sulfoxide at 25°C afforded a 40:60 mixture of 3e and 4a (total yield 74%). More significantly, 6-bromo-7-trimethylsilylbicyclo[3.2.0]hept-6-ene (3d) [7] was isolated unchanged after treatment with LDA and LiSPh in THF. However, the same reaction with KO-t-Bu instead of LDA (2.0 mmol 3d, 50 mmol KO-t-Bu, 50 mmol KSPh, 50 ml THF) furnished a 0.1:1.0 mixture of 3e and 4a [8] (total yield 28%). These observations seem to exclude single electron transfer reactions as well as the cycloallene derivative 6 as an intermediate. On the other hand, the mechanism depicted in the Scheme is consistent with our findings.

Scheme



The essential point of this mechanism is certainly the formation of the cyclobutyne derivative 2. This highly strained molecule is only in part trapped by the nucleophile, in part it rearranges to the carbene 7, which also reacts with LiSPh to give 4a. It is interesting to note that the reverse reaction, the ring enlargement of carbenes of type 8, represents a documented route to cycloalkynes 9 9). Obviously, the high strain energy of 2 is responsible for the reversal of the rearrangement.

The mechanism in the Scheme requires that raising the concentration of LiSPh should increase the product ratio 3e:4a. This was confirmed experimentally. When 3b reacted with 3.0 equiv. of LDA in 15 ml THF at 0°C in the presence of 10, 20 and 30 equiv. of LiSPh, respectively, 3e:4a ratios of 0.14, 0.21 and 0.35 were determined (total yields 67%, 72%, 61%). Not unexpectedly, the product composition depended considerably on the reaction temperature. 3b, LDA (3.0 equiv.) and LiSPh (10.0 equiv.) at -40°C and -78°C, respectively, afforded mixtures of 3e:4a of 0.53:1.0 and 1.03:1.0 (total yields 50% and 73%).



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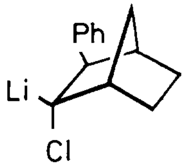

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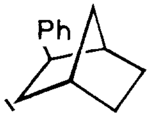

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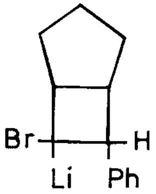

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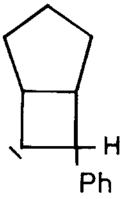

13

The reaction of bromide 3b with phenyllithium (PhLi) (13.3 equiv.) and LDA (5.0 equiv.) in THF at 0°C after 90 min yielded 65% 6-benzylidenebicyclo[3.1.0]hexane (4b) as the only product. This result is reminiscent of the reaction of PhLi with 2-chloronorbornene, which gave 5-benzylidenebicyclo[2.1.1]hexane via adduct 10 and carbene 11 10). For the reaction of 3b with PhLi this mechanism predicts the intermediacy of 12 and 13. Deuterium oxide trapping experiments, however, indicate that the reaction of these components does not follow that course. When a 1:5 mixture of 3b and PhLi was stirred for 15 h at 25°C in THF and then treated with deuterium oxide, fully deuterated 4c was isolated in 55% yield. Obviously, 4d is an intermediate, which is probably formed via 2 and 7. In a control experiment it was ascertained that the hydrocarbon 4b was not metalated by PhLi to give 4d under the reaction conditions.

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Tab. 1. Selected NMR Data of 3b, 3e and 4a in $CDCl_3$

3b: ^{1}H NMR: δ = 0.96-1.91 (m; 6 H), 3.08-3.56 (m; 2 H), 5.92 (s; 1 H). - ^{13}C NMR: δ = 22.6, 24.6, 26.4 (3 t), 47.1, 55.5 (2 d), 118.3 (s), 136.5 (d).

3e: ^{1}H NMR: δ = 0.70-1.91 (m; 6 H), 3.00-3.35 (m; 2 H), 5.64 (s; 1 H), 7.05-7.60 (m; 5 H). - ^{13}C NMR: δ = 23.0, 25.3, 27.0 (3 t), 45.6, 50.2 (2 d).

4a: ^{1}H NMR: δ = 0.88-2.03 (m; 8 H), 6.45 (s; 1 H), 7.11-7.52 (m; 5 H). - ^{13}C NMR: δ = 21.4, 22.7, 23.8 (3 t), 29.2, 30.1 (2 d), 112.0, 126.0, 128.8, 129.0 (4 d), 136.5, 136.8 (2 s).

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4) 3a, 3b and 3c were obtained by addition of chlorine, bromine or of iodine chloride to bicyclo[3.2.0]hept-6-ene, followed by hydrogen halide elimination with KO-t-Bu in THF.

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7) 3d was prepared by thermal rearrangement of 1-bromo-7-trimethylsilyltricyclo[4.1.0.0^{2,7}]-heptane (i) (H.-G. Zoch, G. Szeimies, R. Römer, G. Germain and J.-P. Declercq, Chem. Ber. 116, 2285 (1983)) at 450°C/0.001 mm in a flow system. We have recently discovered that the treatment of i with KO-t-Bu generates also the bridgehead olefin tricyclo[4.1.0.0^{2,7}]hept-1(7)-ene.

8) In this reaction, KSPh was only partly dissolved, which is the probable cause for the low product ratio 3e:4a.

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