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6-BROMO-6-(TRIMETHYLSTANNYL)BICYCLO[3.1.0]HEXANE AS A THERMAL PRECURSOR OF 1,2-CYCLOHEXADIENE

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Summary.- Flash vacuum pyrolysis and matrix-isolation studies of 6-bromo-6-(trimethylstannyl)bicyclo[3.1.0]hexane (**1**) gave evidence for the formation of 1,2-cyclohexadiene (**2**) from this precursor. At high temperatures (>600°C) **2** is not stable and fragmentates to 1-butene-3-yne (**4**) and ethylene.

The chemistry of strained, cyclic allenes is of considerable interest both for preparative[1)] and theoretical[2)] organic chemistry. The most strained allene which has been generated and trapped in solution is **2**[3)]. Recently Wentrup et al.[4)] reported on the matrix-isolation and IR spectroscopic characterization (sharp absorption at 1886 cm^{-1}) of **2**, generated by flash vacuum pyrolysis (800°C, 10^{-4} Torr)) of bicyclo[3.1.0]hexane-6-carbonylchloride.

Our interest in the mechanism of the thermal cleavage of carbenoids prompted us to investigate the thermochemistry of the bromo(trimethylstannyl) compound **1**. Earlier investigations of the solution thermochemistry of **1** by Seyferth et al.[5)] did not conclusively show products derived from **2**. We therefore used the flash vacuum pyrolysis technique in a preparative scale (P-FVP)[6)] or in combination with matrix-isolation in Ar at 10 K (M-FVP)[7)] to investigate the mechanism of the fragmentation of **1**. Products of the P-FVP were identified by NMR, GC-MS and GC-FT-IR, while M-FVP allowed us to observe reactive intermediates by IR spectroscopy.

The thermal fragmentation of **1** started at pyrolysis temperatures of 400°C; 50% conversion was found at 550°C and complete conversion at 700°C (Tab.1). The main products were $Sn(CH_3)_3Br$, 1-butene-3-yne (**4**) and ethylene (Scheme I). The most reasonable explanation for the formation of **4** and C_2H_4 is the retro Diels-Alder fragmentation of allene **2**. Other hydrocarbons found both in P-FVP and M-FVP experiments were 1,3-cyclohexadiene (**6**), benzene and trans-1,3,5-hexatriene, the latter two being known products of the pyrolysis of **6**[8)] (Tab.1).

The formation of **6** from **2** requires a formal [1,3]H shift. Another route to **6** is the abstraction of HBr from **8** or $Sn(CH_3)_3H$ from **9**. Compounds **7**, **8**, **9** and **10**, found in low yields in the P-FVP experiments, are derived from radical

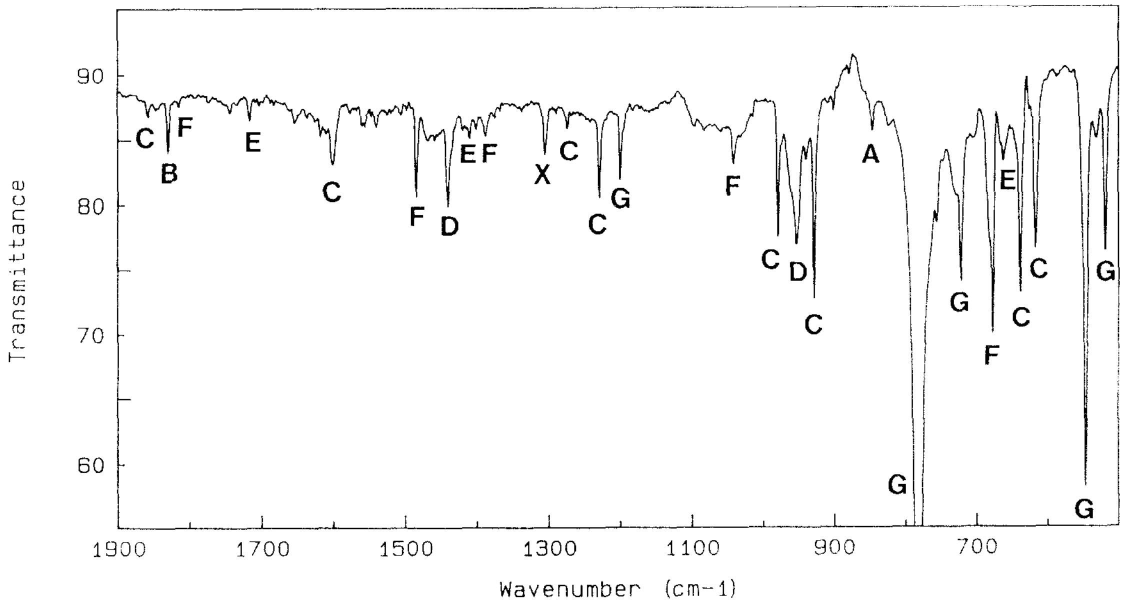
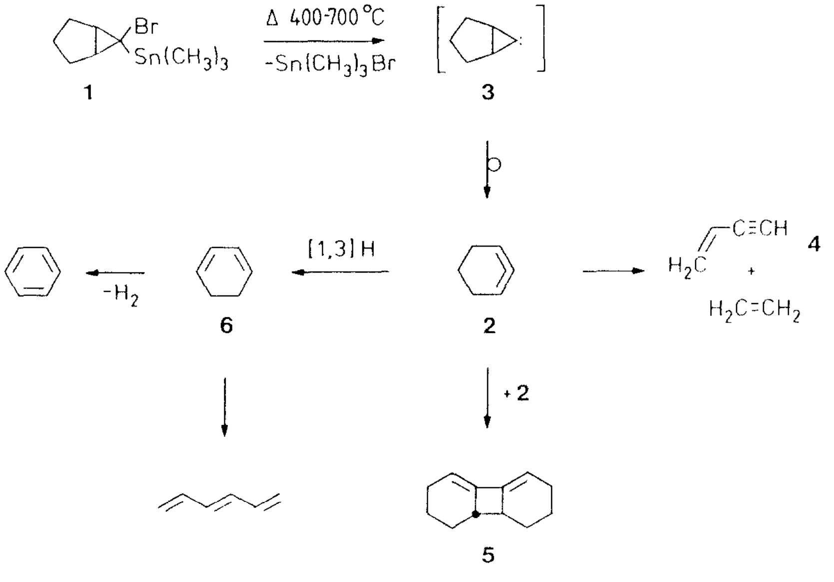
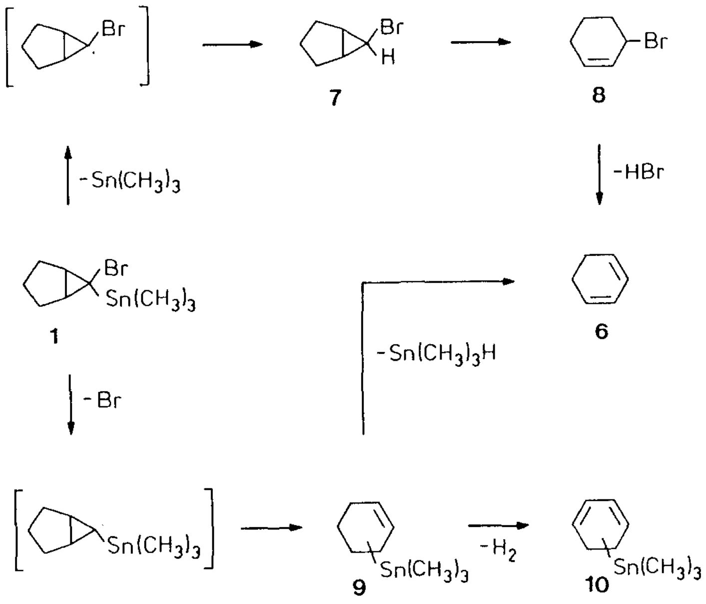


Fig.1 IR-spectrum of the pyrolysis products of **1** isolated in Ar at 10 K. Pyrolysis temperature 600°C. A: **1**; B: tentatively assigned to **2**; C: **4**; D: ethylene; E: **6**; F: benzene; G: $Sn(CH_3)_3Br$.

Scheme I



Scheme II



pathways in the thermal decomposition of **1** (Scheme II); **9** and **10** might also be formed by secondary reactions between $Sn(CH_3)_3$ radicals and **6** during warming the trapped pyrolysis products from 77 K to room temperature.

Additional evidence for the formation of **2** comes from the observation (P-FVP) of small amounts of dimer **5** (Scheme I, Tab.1). The maximum yield of **5** was found at 575°C pyrolysis temperature. At higher temperatures the yield of **4** increased sharply and at lower temperatures the decomposition of **1** was incomplete. Under similar conditions (600°C pyrolysis temperature) a weak to medium

T [°C]	**1**	**4**	**5**	**6**	a)	b)	**7**+**8**	c)	**10**
425	94.0	-	-	5.0	-	-	-	1.0	-
500	70.4	1.1	0.6	-	1.1	-	2.7	5.5	5.7
575	38.7	1.0	1.6	2.9	2.9	1.0	4.6	23.8	8.7
650	7.9	19.2	0.4	5.5	13.1	1.3	7.3	29.5	5.0
725	0.5	30.5	0.3	4.8	18.6	0.0	0.6	37.1	0.6
800	0.2	31.6	0.04	1.0	32.0	0.6	0.4	26.6	0.4

Tab.1 Relative GC peak intensities[10] (in %, normalized to 100%) of some of the P-FVP products of **1**. a) benzene; b) cyclohexatriene; c) $Sn(CH_3)_3Br$.

intensity band at 1829 cm^{-1} appeared in the M-FVP experiments which was tentatively assigned to **2** (Fig.1). Assignment of other bands to **2** was precluded by the complexity of the observed spectrum. Although the frequency of this band comes close to the frequency expected for strained allenes (cycloheptatetraene: 1816, 1824 cm^{-1} 9)), isotopic labeling experiments might enable a definitive assignment. The IR band at 1886 cm^{-1}, assigned to **2** by Wentrup et al.4), did not appear under any conditions used in our experiments. If **4** is indeed produced by the fragmentation of **2**, and not by a less likely path from other possible precursors (Scheme I,II), we do not expect **2** to survive thermolysis temperatures higher than 700°C in substantial amounts. This discrepancy with the earlier report4) is the subject of additional work currently done in our laboratory.

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6) In a high vacuum system **1** was slowly (20 mg/h) sublimed through a quartz tube (10 cm length) heated to 400-800°C. The products were trapped at 77 K. After 1-5 hrs the products were directly sublimed from the trap into a NMR tube. Less volatile products were washed down with $CDCl_3$ or n-undecane after purging the system with N_2. For description of the general technique and a similar apparatus see: R.F.C.Brown in H.H.Wasserman , "Organic Chemistry Vol.41: Pyrolytic Methods in Organic Chemistry, Academic Press, New York 1980.
7) An Air products closed cycle He refrigerator was used for generating the low temperatures. The distance of the pyrolysis oven (quartz tube, 5 cm pyrolysis zone) to the cold window was 3-4 cm. For description of a similar apparatus see: R.J.McMahon, O.L.Chapman, R.A.Hayes, T.C.Hess, H.-P. Krimmer, J.Am.Chem.Soc. **107**, 7597 (1985).
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10) GC column OV101; a temperature program from 40-200°C with a gradient of 5°C/min was used in all experiments.

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