Tetrahedron Letters No. 46, pp 4569 - 4572.
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0040-4039/78/1108-4569$02.00/0

PREPARATION OF BENZOCYCLOBUTENES BY FLASH VACUUM PYROLYSIS

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Flash pyrolysis is an old and useful method in organic chemistry [1] which has seen a revival in recent years [2]. Investigating preparative applications of pyrolytic HCl-eliminations [3] we have found recently that flash vacuum pyrolysis of tris-chloromethylmesitylene 1 leads to the benzocyclobutenes 2 and 3 and to hexaradialene 4 through the loss of one, two and three moles of HCl respectively [4], [5].

Scheme 1

We now wish to report that we have prepared a variety of benzocyclobutenes through flash pyrolysis of appropriate o-methyl-benzylchlorides. Previous examples of similar transformations have been reported by Hart [6] and by Maccoll [7] and very recently by Boekelheide [8]. With this communication we wish to demonstrate the simplicity of the pyrolytic access to benzocyclobutenes [9], a class of increasingly important synthetic intermediates [10], and at the same time indicate some of the limitations of the pyrolytic method.

Nine mono- and bis-chloromethyl compounds which are all either commercially available or easily prepared from substituted benzenes have been subjected to flash pyrolyis on a 1 - 30 g scale (contact time: 0.01 - 0.1 s). Condensation of the gaseous reaction products at -78° and workup as usual led to the expected benzocyclobutenes (see table). The simplicity of the operations involved may be exemplified by the following procedure for obtaining the parent compound from α-chloro-o-xylene:

<u>Benzocyclobutene:</u> α-Chloro-o-xylene (24.4 g) was distilled within 4 hours at 0.5

Torr trough a quartz tube (30 x 1 cm) filled with quartz chips and heated to 720°. The pyrolysate was condensed immediately at the exit of the pyrolysis tube on a cold finger at -78°. It was dissolved in pentane (80 ml), washed with bicarbonate solution and dried with Na_2SO_4. Evaporation of the solvent and distillation of the residue through a 25 cm spinning band column gave 9,5 g benzocyclobutene as a colourless oil of bp. 87-88,5°/100 Torr, containing 3 % of styrene. In addition 7,9 g starting material, b.p. 105-109°/48 Torr could be recovered.

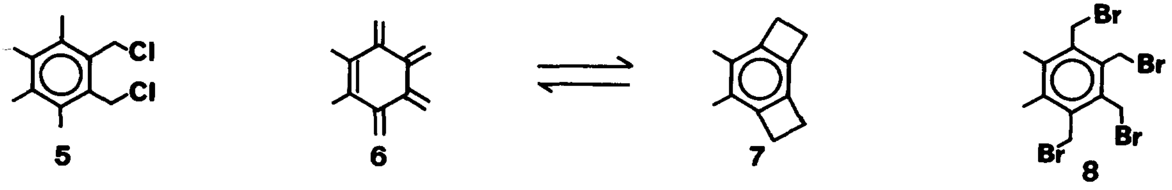
Some of the limitations of the pyrolytic method for preparing benzocyclobutenes shall be mentioned briefly:

1. Ring cleavage products such as styrene (3 % in reaction 1) or o-chlorostyrene and phenylacetylene (5 % each in reaction 5) are formed. The amount of these products can be kept within limits however, by avoiding unnecessary high reaction temperatures and thus keeping conversion well below 100 %.

2. Dimerization occurs if the reaction pressure is raised. 1,2-5,6-dibenzocyclooctadiene and anthracene (5-20 % each) were isolated in reaction 1 and 1,2-5,6-dibenzoanthracene (15 %) in reaction 6 if pyrolysis was carried out at 14 instead of 0.1 Torr.

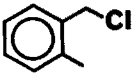
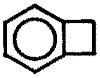
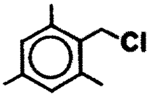
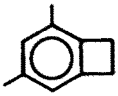
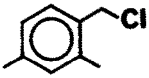
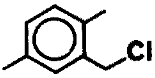
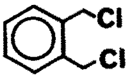
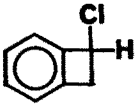
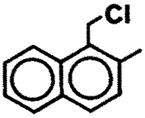
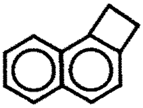
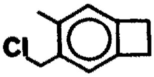
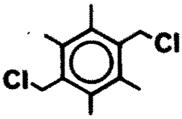
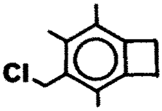
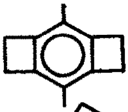
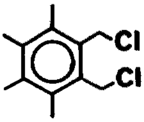
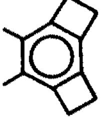
3. Polymeric material, insoluble in most organic solvents is formed to a considerable extent in reactions 6 to 9. In reaction 9 the reactive, monomeric precursor of this polymer was shown to be 6, a valence isomer of the expected biscyclobuteno-o-xylene 7. In addition to the ^{1}NMR-signals of 7 (2.04 ppm, s, 6H; 3.04 ppm, s, 8H) the following signals of 6 were present in the 690°-pyrolysate of 5 trapped at -78° in $CDCl_3$: 2.00 ppm (s, 6H); 5.08 and 5.40 ppm (broad s, 2H each); 5.15 and 5.25 ppm (d, 1.5 cps, 2H each). The signals of 6 rapidly disappeared upon warmup of the solution to room temperature. Integration showed the two isomers 6 and 7 to be formed in a 4 : 1 ratio. Chemical proof of structure 6 was obtained by the isolation of 8 (40 %, mp. 197-199°) upon addition of bromine to the cold pyrolysate in $CHCl_3$. The formation of 6 in preference to its tricyclic valence isomer 7 is not unexpected considering the ΔH_f^o-values for these two compounds as calculated from additive group increments [17] (scheme 2).

Scheme 2



ΔH_f^o = 52 kcal/mol ΔH_f^o = 53 kcal/mol [17]

T A B L E Benzocyclobutenes through flash pyrolysis of benzylchlorides

	reactant	temp./pressure (conversion)	product	ref.	yield	bp./Torr (mp.)
1.		720°/0.5 Torr (68%)		[11]	77%[a]	87-89°/100
2.		580°/12 Torr (77%)		[12]	69%[a]	75-76°/12
3.		720°/0.1 Torr (82 %)		[13]	55%[a]	63-64°/15
4.		770°/0.1 Torr (88%)			61%[a]	
5.		660°/0.2 Torr (74%)		[14]	53%[a]	90-92°/27
6.		675°/0.01 Torr (89%)		[15]	20%[b]	135-140°/11
7.		705°/0.05 Torr (60%)			35%[c]	(51-52°)
		750°/0.15 Torr (90%)		[16]	24%[b]	(101-102°)
8.		600°/0.03 Torr (45%)			20%[c]	(66-70°)
		630°/0.03 Torr (69%)		[8]	24%[b]	(120-121°)
9.		690°/0.03 Torr (98%)			8%[b]	(115-116°)

a) Isolated product in preparative 20-30 g run; corrected for the amount of reactant recovered.

b) Isolated product in 1-3 g run.

c) Determined by vpc; isolated by fractional sublimation and crystallisation.

In reaction 9 the main product, bis-cyclobuteno-p-xylene of mp. 120-121° (24 %) is accompanied by 6 % of its angular isomer 7. We therefore conclude that 6, the reactive valence isomer of 7, also in reaction 8 must be a major precursor of the polymeric material isolated upon room temperature workup.

Our results show that flash vacuum pyrolysis of o-methyl-benzylchlorides constitutes a simple and efficient method for the preparation of either benzocyclobutenes or of their reactive o-xylylene valence isomers depending on their mutual thermodynamic stability. Ring cleavage and dimerization are sidereactions which can be kept within limits by control of reaction temperature and pressure.

We wish to thank the Swiss National Science Foundation (project Nr. 2.943-0.77) and Ciba-Geigy Co. for their support.

Notes and References

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(Received in UK 14 September 1978)