Tetrahedron Letters,Vol.23,No.36,pp 3665-3668,1982 0040-4039/82/363665-04$03.00/0
Printed in Great Britain

A KINETIC STUDY OF PYROLYTIC PATHWAYS TO BENZOCYCLOBUTENE

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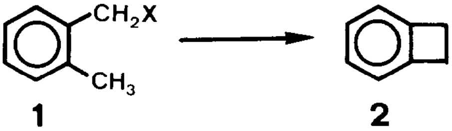
Summary: A simple gas flow reactor simulating flash vacuum pyrolysis conditions is described which yields approximate rate values for monomolecular gas phase reactions and which has been used for a comparison and optimisation of pyrolytic elimination reactions leading to benzocyclobutene.

Flash vacuum pyrolysis in recent years has gained importance as a preparative method in organic chemistry [1]. A representative example is the formation of benzocyclobutene 2 through 1,4-elimination of HCl from 2-methyl-benzylchloride 1 (X=Cl). This reaction, first reported by Maccoll in 1968 [2], has recently been used by us [3] and by others [4] for the preparation of a variety of substituted benzocyclobutenes [5].



One problem in carrying out and in describing flash vacuum pyrolytic experiments is that reaction conditions are often ill defined. While pyrolysis temperatures may be known more or less accurately, frequently there is little information as to the actual residence time of the molecules in the hot reaction zone. In this communication we wish to describe a simple gas flow reactor which simulates flash vacuum pyrolysis conditions, i.e. high reaction temperature, low reactant partial pressure and short residence time. This reactor has yielded approximate rate values for many monomolecular gas phase reactions. It thus has allowed to quantitatively compare different pyrolytic processes leading to 2 and has been used to optimise reaction conditions for the transformation 1 → 2.

The reactor shown schematically in figure 1 has an injection port sealed to a quartz pyrolysis tube (1.5 x 250 mm) and is directly coupled to a gas chromatography column. Experiments are carried out by injecting dilute reactant solutions through the septum and measuring conversion to products as a function of pyrolysis temperature. The temperature is determined at which 50% conversion of reactant is observed. At this temperature, $T_{50\%}$, the residence time of the molecules in the hot reaction zone equals their half life in the thermally induced primary process. Keeping carrier gas flow rate constant throughout all experiments, $T_{50\%}$-values are directly proportional to the free activation energies $\Delta G^{\ddagger}$ of the processes under investigation. A calibration curve for the reactor (figure 2) was obtained by measuring $T_{50\%}$-values of four test reactions for which reliable gas phase kinetic data are available. It shows that the linear relationship between $T_{50\%}$ and $\Delta G^{\ddagger}$ holds over a wide range of temperatures.

Figure 1

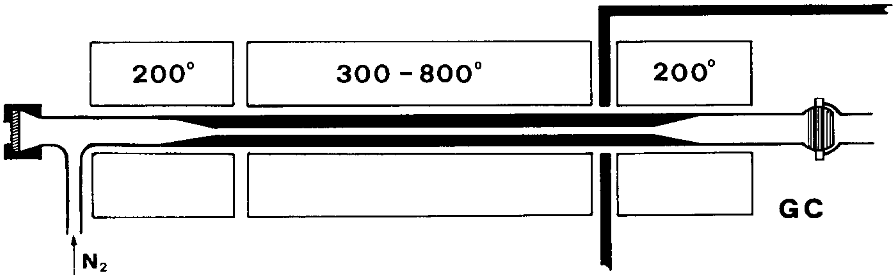
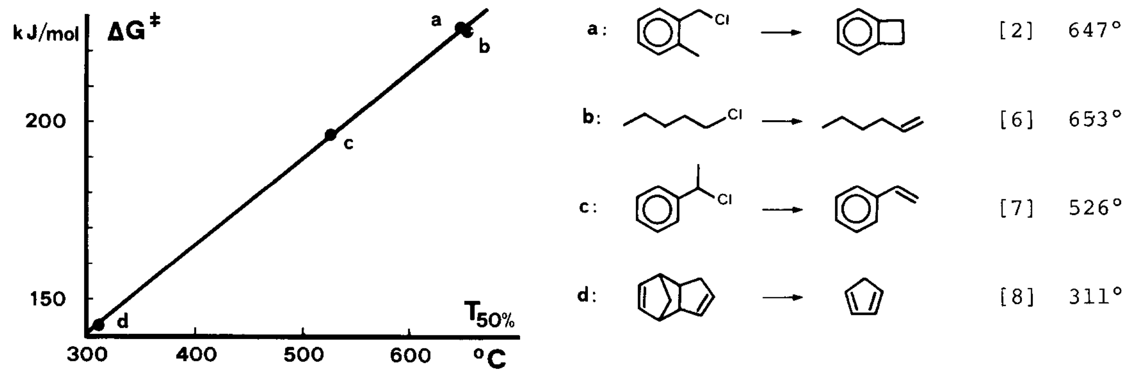


Figure 2 Calibration curve for the gas flow reactor



The high temperature required for the elimination of HCl from 1a limits the usefulness of this process if less stable, substituted derivatives of 2 should be prepared. We therefore have sought to find a pyrolytically more reactive leaving group X in 1 than chloride. Some results of this search are reported in Table 1. The bromide 1b, the most reactive of the compounds tested, gave a lower yield of 2 and more styrene than 1a. From this we conclude that in 1b homolytic cleavage of the CX-bond competes to a larger extent with concerted 1,4-elimination than in 1a, the formation of styrene being accounted for by radical induced isomerisation of 2. The best result was obtained with trifluoroacetate 1e which had a $T_{50\%}$-value 44° lower than 1a and gave 2 in high yield without other products.

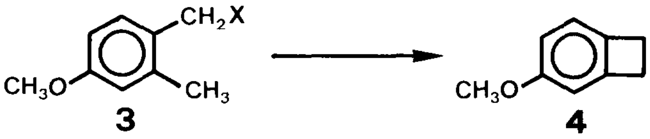
Table 1 1,4-Elimination of HX from 1 upon pyrolysis in flow reactor.

	X	$T_{50\%}$	products a)		
			2	styrene	others
a:	Cl	647°	80%	2%	-
b:	Br	549°	64%	10%	-
c:	F	770° b)	30%	41%	-
d:	$OCOCH_3$	691°	28%	1%	2-ethyltoluene 25%
e:	$OCOCF_3$	603°	82%	-	-

a) Formed at 50% conversion, determined by vpc.

b) Lower limit; conversion in flow reactor depends on amount of sample injected due to surface catalysis.

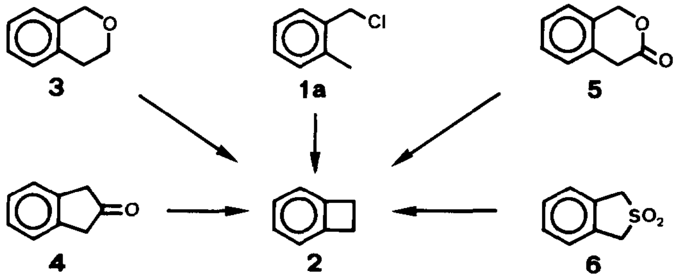
The trifluoroacetate group has been used in the preparation of 4-methoxy-benzocyclobutene (4). Upon flash vacuum pyrolysis of the chloride 3a (650°/0.1 mbar) 4 was formed in 19% yield only. In addition, much polymeric material was obtained, presumably through thermally induced cleavage of the ether function [9]. The trifluoroacetate 3b, however, being more reactive than 3a, required a lower pyrolysis temperature for conversion (580°/0.1 mbar) and gave 4 in a yield of 78% [10].



	X	$T_{50\%}$
3a:	Cl	570°
3b:	$OCOCF_3$	480°

With our reactor we have compared the reactivity of several precursors known to yield 2 upon flash vacuum pyrolysis (Scheme 1). Elimination of SO_2 from bicyclic sulfone 6 [11] is the reaction with the lowest $T_{50\%}$-value of those tested by far.

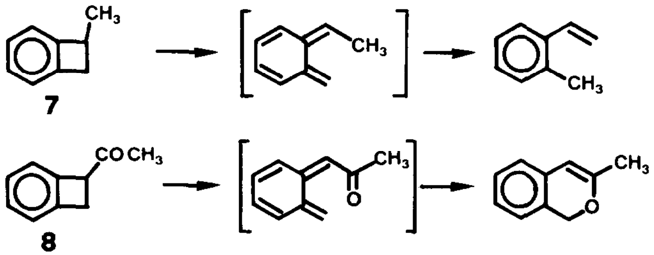
Scheme 1



	$T_{50\%}$
3	685°
4	667°
1a	647°
5	570°
6	362°

Many substituted benzocyclobutenes, especially those carrying a substituent in the four-membered ring, are thermolabile. The pathway of isomerisation for two typical examples is shown in scheme 2 together with $T_{50\%}$-values determined in our reactor.

Scheme 2



$T_{50\%}$

417°

[12] 333°

A comparison of $T_{50\%}$-values in scheme 1 and 2 shows that appropriately substituted sulfones of type _6_ are reactive enough to serve as precursors of α-alkyl-benzocyclobutenes like _7_ [13]. Less stable derivatives of benzocyclobutene like _8_, however, cannot be prepared by any of the pyrolytic processes shown in scheme 1. For these other pathways of synthesis have to be considered [14].

We wish to thank the Swiss National Science Foundation (project Nr. 2.887-0.80) and CIBA-GEIGY Co. for their generous support.

Notes and References

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(Received in Germany 7 June 1982)