Gas-phase Eliminations. Part XIV.† The Pyrolysis of 1-(1-Chloroethyl)-2-methylbenzene

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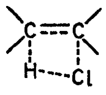
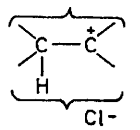
The gas-phase thermal decomposition of the title compound was studied in the temperature range 285—325° and with initial pressures between 25 and 105 mmHg. The only products detected were *o*-methylstyrene and hydrogen chloride. The reaction, which was homogeneous and unimolecular, followed the Arrhenius equation (i).

$$\log (k/\mathrm{s}^{-1}) = 13.55 - 44.83\,(2.303RT/\mathrm{kcal\ mol}^{-1})^{-1} \qquad \text{(i)}$$

The mechanism was identified as a four-centred type related to that of the aliphatic halides rather than the six-centred one proposed for 1-chloromethyl-2-methylbenzene.

THE gas-phase pyrolysis of alkyl halides has been widely studied.[1] The homolytic four-centred transition state[2] (I) originally proposed for the elimination of hydrogen halides has recently been replaced by an ion-pair[3] (II) or semi-ion-pair[4] (III) transition state. In addition, a six-centred transition state[5] (IV) was proposed to account for the pyrolysis of 1-chloromethyl-2-methylbenzene into benzocyclobutene and hydrogen chloride, and a pseudo-four-centred transition state (V)[6] for the decomposition of 1,2-bis(chloromethyl)benzene.


(I)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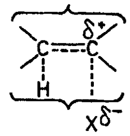
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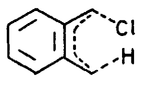
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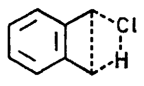
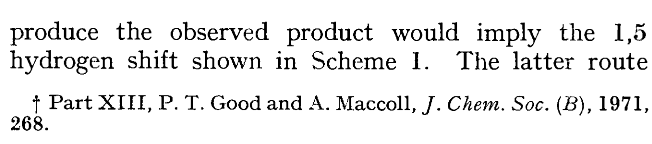

(V)

1-(1-Chloroethyl)-2-methylbenzene can in principle, react to yield methylbenzocyclobutene or *o*-methylstyrene and hydrogen chloride. The former route, to produce the observed product would imply the 1,5 hydrogen shift shown in Scheme 1. The latter route would appear to be preferred since the rate constant for α-phenylethyl chloride decomposition is some 60 times larger than that for 1-chloromethyl-2-methylbenzene. However, it was deemed desirable to verify the decomposition path.


SCHEME 1

EXPERIMENTAL

1-(1-Chloroethyl)-2-methylbenzene was prepared by bubbling dry hydrogen chloride into *o*-methylstyrene, cooled in an ice-bath, over 8 h. The product was fractionally distilled at 4 mmHg and the fraction boiling in the range 75—76° was collected. No impurities could be identified by either g.l.c. on several columns or by n.m.r. or mass spectrometry. Products were identified by mass spectrometry, g.l.c., and n.m.r. In each case, the product spectrum was compared with that of an authentic sample. Hydrogen chloride was determined by titration. The products were separated into three fractions by trap-to-trap distillation. Fraction (a) was hydrogen chloride, trapped at −196°, fraction (b) was substrate together with *o*-methylstyrene (−80°), and fraction (c) was an involatile substance, which remained mainly in the reaction vessel. The mass spectrum of (c) revealed it to be mainly the dimer, but with traces of the trimer and tetramer of *o*-methylstyrene.[6] In estimating the percentage decomposition by hydrogen chloride titration, the products were trapped in acetone at −196°. Hydrogen chloride was then titrated with a solution of sodium ethoxide, using Lacmoid indicator. G.l.c. analyses were done with a Perkin-Elmer chromatograph fitted with a flame ionisation detector. The columns used were 2 m 10% Apiezon L on Chromosorb P and 2 m 8% Anthorox on Chromosorb W AW-DMCS. Mass spectra were taken on an A.E.I. MS9 instrument.

The kinetic experiments were carried out in a conventional static system, the temperature of the vessel being maintained to better than ±0.2°. Pressures were measured either by an optical gauge or by a pressure transducer and chart recorder. The reaction vessel was seasoned with the products of allyl bromide decomposition. Because of the low vapour pressure of the substrate, it was

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† Part XIII, P. T. Good and A. Maccoll, *J. Chem. Soc.* (*B*), 1971, 268.

[1] A. Maccoll, *Chem. Rev.*, 1969, **69**, 33.

[2] A. Sherman, O. T. Quimby, and R. O. Sutherland, *J. Chem. Phys.*, 1936, **4**, 732.

[3] A. Maccoll and P. J. Thomas, *Nature*, 1955, **176**, 392.

[4] S. W. Benson and A. N. Bose, *J. Chem. Phys.*, 1963, **39**, 3463; S. W. Benson and G. R. Haugen, *J. Amer. Chem. Soc.*, 1965, **87**, 4036.

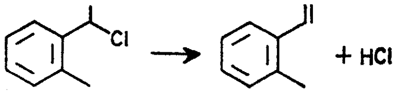
[5] A. G. Loudon, A. Maccoll, and S. K. Wong, *J. Amer. Chem. Soc.*, 1969, **91**, 7577.

[6] M. Umaña, Ph.D. Thesis, University of London, 1972.

injected directly into the reaction vessel with a syringe, through a silicone rubber septum, as described by Bridge.[7]

RESULTS

Analysis of the products showed the stoicheiometry (1). Prolonged experiments showed that $P_f < 2P_0$, P_f being the final pressure and P_0 the initial. The reversibility of the reaction was tested by leaving hydrogen chloride and *o*-methylstyrene in equimolar quantities overnight, under the normal reaction conditions. The total pressure decreased, although hydrogen chloride was not consumed; further in the prolonged experiments the hydrogen chloride produced was equal to the initial pressure of substrate. This, together with the observed polymers of *o*-methylstyrene in the products suggests that departures from the suggested stoicheiometry are due to polymerisation of the olefinic product. Up to 40% reaction, the percentage decomposition calculated from pressure measurements was in good agreement with that calculated from hydrogen chloride titration (Table 1) at 319°.



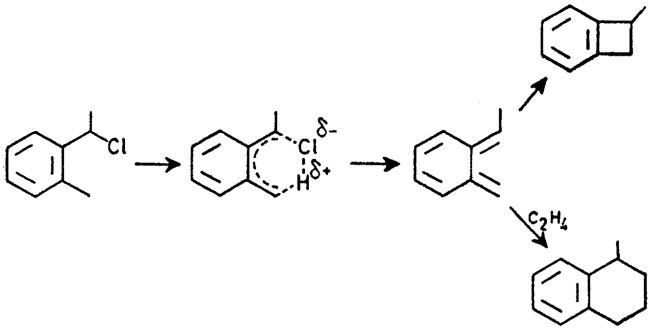
(1)

Table 1

Percentage reaction at 319° measured by (*a*) pressure increase, (*b*) HCl titration

(*a*)	7.5	14.8	21.0	36.7	43.0	54.3	60.8	63.6
(*b*)	9.2	15.4	21.1	37.0	45.5	59.5	71.0	80.4

A few runs were carried out in the presence of ethylene to see whether any 1,2,3,4-tetrahydro-1-methylnaphthalene was formed by Diels–Alder addition. These experiments were an attempt to trap *o*-quinodimethane intermediate that would participate in a six-centred transition state mechanism (Scheme 2). The results were negative and it was concluded that up to 40% reaction the stoicheiometry was in fact represented by reaction (1).



Scheme

The homogeneity of the reaction was tested by increasing the surface : volume ratio by a factor of five. Rates for the two $S : V$ ratios were equal within experimental error at three temperatures in the range studied. The reaction is clearly homogeneous. First-order rate coefficients calculated from $k_1 = (2.303/t)\log\{P_0/(2P_0 - P_t)\}$ were independent of pressure over the range 80—140 mmHg. Hence the reaction is first order. The temperature variation of the rate constants is shown in Table 2. The results in Table 2 led to the Arrhenius equation (2). Cyclohexene

$$\log(k/\text{s}^{-1}) = 13.55 \pm 0.22 - (44\,830 \pm 600)(2.303RT/\text{kcal mol}^{-1})^{-1} \quad (2)$$

has been widely used as an inhibitor of reaction chains. The results of runs in the presence of cyclohexene are shown in Table 3. The reaction is thus homogeneous, first order, and unimolecular.

Table 2

Temperature variation of the first order rate constants

No. of runs	6	7	9	9	11	8
T/°C	285.6	295.4	301.6	310.5	319.4	325.2
10^4k_1/s^{-1}	1.04	2.09	3.23	5.83	10.77	15.7

Table 3

Runs in the presence of cyclohexene

T/°C	P_0/mmHg	P_i/mmHg	10^4k/s^{-1}	10^4k/s^{-1} *
310.4	37.9	40.5	6.10	5.83
310.3	42.6	45.2	5.95	5.83
325.4	53.8	50.8	15.8	15.7
325.6	71.3	70.2	15.4	15.7
295.5	61.6	60.0	2.13 †	2.09

* Rate constant in absence of inhibitor, P_0 = substrate pressure, P_i = inhibitor pressure. † But-1-ene as inhibitor.

DISCUSSION

In principle 1-(1-chloroethyl)-2-methylbenzene can decompose *via* any of transition states (III)—(V). The various transition states will be analysed in the light of the experimental results obtained in this work. Table 4 shows the Arrhenius parameters of the substituted benzyl chlorides.

Table 4 shows that the experimental Arrhenius A factors agree better with those expected for a four-centred transition state than for a six-centred transition state mechanism. The lower limits for log A factors of four- and six-centred transition state mechanisms have been reported[8] to be 12.5 and 10.4 respectively. Moreover, using the method developed by Benson[9] we find a log A factor of 12.9 for the four-centred (III), 11.7 for the six-centred (IV), and 11.5 for the pseudo-four-centred (V) transition state mechanisms.

It has been known for some time[1] that α-methyl substitution increases the rate constant for reactions proceeding by the four-centred mechanism by a factor of *ca.* 150, while β- and γ-methylation have little or no effect upon the rate constant. The effect of

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[7] R. H. Boundy and R. F. Boyer, 'Styrene,' Reinhold, New York, 1952, pp. 215—288, 609—704.

[8] A. F. Trotman-Dickenson, 'Gas Kinetics,' Butterworth, London, 1955.

[9] S. W. Benson and H. O'Neal, *J. Phys. Chem.*, 1967, **71**, 2903.

methylation upon the six-centred mechanism is not definitely known. However, Harding *et al.*[13] have estimated a factor of *ca.* 70 for α-methylation from a consideration of *cis*-γ-methylallyl chloride and *cis*-α,γ-dimethylallyl chloride. Since 1-(1-chloroethyl)-2-methylbenzene is the α-methylated derivative of 1-chloromethyl-2-methylbenzene, the predicted rate (six-centred mechanism) is 3×10^{-4} s^{-1} (335°). For the four-centred mechanism the compound studied can be compared with 1-*p*-methylphenylethyl chloride, and so would be expected to decompose with about the same rate constant, that is 3×10^{-3} s^{-1} (300°). The experimental value is 2.5×10^{-3} s^{-1} (300°) and so it may reasonably be concluded that the four-centred mechanism is in fact involved.

TABLE 4

Arrhenius parameters

Compound	log (A/s^{-1})	E_a/ kcal mol^{-1}	Ref.
1-Phenylethyl chloride	12.6	44.9	10
1-*m*-Methylphenylethyl chloride	12.1	42.9	11
1-*p*-Methylphenylethyl chloride	14.1	47.6	12
1-(1-chloroethyl)-2-methylbenzene	13.5	44.8	This work
1-Chloromethyl-2-methylbenzene	11.5	46.9	5
1,2-Bis-chloromethylbenzene	11.1	45.7	6

The effect of methyl substitution at 335° on the 1-phenylethyl chloride system is shown in Table 5 where k_0 is the rate constant for HCl elimination from α-phenylethyl chloride and k_x that for the corresponding substituted derivative. Several detailed studies have been published on the *meta*- and *para*-substitution effect upon the gas-phase elimination of HCl, using some empirical relations.[9-11] These studies lead to the conclusion that gas-phase eliminations of this kind should involve a certain degree of charge separation as predicted by the quasi-heterolytic hypothesis. However, *o*-methyl-substituted derivatives are not suitable for such calculations since the relations employed are well known to be not valid for such derivatives.

TABLE 5

Effect of methyl substitution on elimination from 1-phenylethyl chloride at 335°

Substituent	10^4k/s^{-1}	k_x/k_0	Ref.
H	3.19	1.00	10
m-CH_3	4.67	1.46	11
p-CH_3	9.12	2.86	12
o-CH_3	25.70	8.05	This work

On the whole, it can be concluded that the reaction under study proceeds through the same mechanism as 1-phenylethyl chloride and its *m*- and *p*-methyl-substituted derivatives, that is to say a four-centred transition state mechanism with moderate charge separation.

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[13] C. J. Harding, A. Maccoll, and R. A. Ross, *J. Chem. Soc.* (*B*), 1969, 634.