

The Gas-phase Thermal Reactions of 1-Methylbicyclo[3.2.0]hept-2-en-7-one

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The kinetics of the thermal reactions of 1-methylbicyclo[3.2.0]hept-2-en-7-one have been studied in the gas phase over the temperature range 489–565 K. The primary reaction appears to occur *via* two parallel first-order homogeneous isomerizations to yield 5-methylbicyclo[2.2.1]hept-5-en-2-one and 2-methylhepta-1,3,6-trien-1-one. Under the experimental conditions employed, 2-methylhepta-1,3,6-trien-1-one undergoes rapid secondary reactions which have heterogeneous components. First-order rate constants for the disappearance of reactant, obtained by an internal standard technique, fit the Arrhenius relationship $\log k/s^{-1} = 14.50 \pm 0.28 - (183.8 \pm 2.8 \text{ kJ mol}^{-1})/2.303RT$. The mode of reaction and Arrhenius parameters are different from those found for compounds with the bicyclo[3.2.0]hept-2-en-6-one structure and can be rationalized by a diradical mechanism.

THE sole observable pathway in the pyrolyses of bicyclo[3.2.0]hept-2-en-6-one¹ and 7,7-dimethylbicyclo[3.2.0]hept-2-en-6-one² is the formation of cyclopentadiene *via* a keten elimination reaction. Preliminary studies of the thermal reactions of 6,6-dimethylbicyclo[3.2.0]hept-2-en-7-one³ revealed, however, that cyclopentadiene formation was not an important reaction path, and this has also been found for bicyclo[3.2.0]hept-2-en-7-one.⁴ The present kinetic investigation of the thermal reactions of 1-methylbicyclo[3.2.0]hept-2-en-7-one was undertaken to obtain quantitative information concerning the differences in behaviour between the 6- and 7-oxo-derivatives of bicyclo[3.2.0]hept-2-ene.

The pyrolysis of the title compound in a flow reactor packed with glass beads has been studied by Schiess and Fünfschilling^{5,6} and the identification of the products in the present work was facilitated by the co-operation of these authors.

EXPERIMENTAL

Materials.—A sample of 1-methylbicyclo[3.2.0]hept-2-en-7-one (170 mg) was supplied by Mr. P. Fünfschilling of Basel University. This material was diluted about tenfold with nonane (Fluka puriss), and *p*-ethyltoluene (83 mg) (Aldrich) was added as an internal standard. The resulting solution was used as starting material for all the kinetic experiments.

Apparatus and Procedures.—The conventional static

reaction system used in this study was essentially the same as that described previously.⁷ A Teflon-coated stainless-steel reaction vessel (805 ml) and a Pyrex vessel (2 l) were employed. For heterogeneity tests, a Pyrex vessel (2 l) packed with thin-walled glass tubes giving a surface : volume ratio of 32 times that of the unpacked vessel was used.

For runs in the Teflon vessel, the starting material was injected directly into the vessel through a Teflon-coated silicone rubber septum. For runs in the glass vessel, the starting material was introduced into a heated injection volume directly above the reaction vessel, and the material remaining in this dead space was removed after isolating the reaction vessel by means of a Teflon valve. A kinetic run was terminated by condensing the contents of the reaction vessel into a trap cooled in liquid nitrogen. Any non-condensable gas (normally negligible) was pumped off by means of an automated Toepler pump, and the remaining material was transferred to a small volume sampling vial and stored under nitrogen at 0 °C. The contents of the vial were analysed by g.l.c. using liquid injections. A Carlo Erba Fractovap model G1 instrument, fitted with a flame ionization detector was employed. A 9 m × 4 mm stainless steel column, packed with 15% Carbowax 20 M on 80–100 Celite and operated at 162 °C gave good separation of the components. Peak areas were measured by an 'Infotronics' model CRS 208 electronic integrator.

RESULTS

The gas-phase pyrolysis of 1-methylbicyclo[3.2.0]hept-2-en-7-one in the temperature range 489–565 K yields

⁴ P. W. Schiess and M. Wisson, *Tetrahedron Letters*, 1971, 2389.

⁵ P. Schiess and P. Fünfschilling, *Tetrahedron Letters*, 1972, 5191.

⁶ P. Schiess and P. Fünfschilling, *Tetrahedron Letters*, 1972, 5195.

⁷ K. W. Egger, *J. Amer. Chem. Soc.*, 1969, **91**, 2867.

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¹ K. W. Egger and A. T. Cocks, *J.C.S. Perkin II*, 1972, 211.

² K. W. Egger, *Internat. J. Chem. Kinetics*, 1973, **5**, in the press.

³ A. T. Cocks and K. W. Egger, unpublished experiments.

toluene, 5-methylbicyclo[2.2.1]hept-5-en-2-one (I), 3-methylbicyclo[3.2.0]hept-2-en-7-one (II), 1-formyl-5-methylcyclohexa-1,3-diene (III), and *m*-methylbenzaldehyde as major observable products. These materials were identified by comparison of their g.l.c. retention times on the analytical Carbowax column and on a Castorwax capillary column with those of authentic samples kindly provided by Mr. P. Fünfschilling. These compounds, together with 1-formyl-3-methylcyclohexa-1,3-diene and 1-formyl-5-methylcyclohexa-1,4-diene have also been observed in the flow pyrolysis of 1-methylbicyclo[3.2.0]hept-2-en-7-one at 619–723 K.^{5,6}

The rate of depletion of 1-methylbicyclo[3.2.0]hept-2-en-7-one was monitored using *p*-ethyltoluene as an internal standard and first-order rate constants *k* are shown in Table 1, together with relevant experimental details. The

TABLE 1

First-order rate constants for the depletion of 1-methylbicyclo[3.2.0]hept-2-en-7-one

<i>T</i> /K	<i>P</i> ₀ /Torr ^a	<i>t</i> /min	Conversion (%)	10 ⁴ <i>k</i> /s ⁻¹
489.1	4.7	390	13.7	0.0630
489.7	2.7	240	9.8	0.0713
489.9	4.2	1020	37.5	0.0768
495.0	7.0	930	45.8	0.103
501.6	4.0	180	21.4	0.223
502.7	3.9	960	78.4	0.266
504.0	4.8	360	40.0	0.236
513.4 ^b	20.0	120	41.8	0.752
517.1 ^b	13.8	60	31.0	1.03
517.2 ^b	13.5	240	75.2	0.968
517.6 ^b	18.1	30	17.7	1.08
518.0 ^b	12.3	120	54.0	1.08
518.8 ^c		60	38.8	1.36
541.8	5.3	30	59.5	5.00
542.6	4.7	20	48.8	5.57
543.0	5.0	5	17.8	6.51
544.5	5.0	10	32.7	6.60
548.2 ^b		20	72.2	10.7
563.6	5.0	3	36.2	24.9
564.0	5.0	10	78.6	25.7
564.4	5.0	5	56.5	27.8
564.7	5.0	2	32.0	32.2

^a Total initial pressure of reaction mixture. ^b Teflonized reactor. ^c Packed vessel, not included in least squares analysis.

extent of reaction was also calculated using the solvent nonane as an internal standard, and these results were normally within 2% of those obtained using *p*-ethyltoluene.

The rate constants show no systematic deviation with initial pressure or extent of conversion. A least-squares analysis yields the Arrhenius relationship (1) where the quoted errors are standard deviations.

$$\log k/s^{-1} = 14.50 \pm 0.28 - (183.8 \pm 2.8 \text{ kJ mol}^{-1})/2.303RT \quad (1)$$

The standard deviations of the rate constants within a temperature bloc range from ± 3 to $\pm 9\%$, and these uncertainties are due to errors introduced in the handling procedures which are accentuated by the small amounts of material involved. Based on these deviations, the maxi-

mum likely error in the activation energy is calculated⁸ to be $\pm 4 \text{ kJ mol}^{-1}$.

The rate constants obtained in the Teflon vessel appear to be a little faster than those observed using the Pyrex vessel. This is probably partly due to systematic errors arising from the different methods of introduction of the starting material and partly due to a small heterogeneous component in the Teflon reactor. The lack of an appreciable heterogeneous component in the primary reaction in the Pyrex reactor is demonstrated by the fact that the rate constant found using the packed Pyrex vessel, with a surface: volume ratio 32 times that of the unpacked vessel, was within 35% of that calculated from the Arrhenius equation (1), obtained using unpacked vessels.

Assuming the response factors for all g.l.c. peaks to be unity, the major products [(I)–(III), toluene, *m*-methylbenzaldehyde] accounted for 70–80% of the extent of decomposition calculated by the internal standard technique in both Pyrex and Teflon reactors. Other observable products normally totalled 3–10% and the discrepancy between total g.l.c. products and conversion based on the internal standard was typically 15–20%. Some of this discrepancy is probably due to calibration factor errors, but it is likely that some undetected polymeric material was also formed.

In both glass and Teflon vessels, the amount of (I), expressed as a fraction of the total major products was independent of extent of conversion within experimental error at all temperatures (5–7%). In the glass vessel, the corresponding fraction for (II) was also constant (20–23%) but decreased with conversion in the Teflon vessel (34–24%). Compound (III) formed an increasing proportion with conversion in the glass vessel (16–41%) but was approximately a constant and much smaller fraction in the Teflon vessel (6%). The proportion of (III) was also decreased in the packed vessel. In the Pyrex vessel, the fraction of *m*-methylbenzaldehyde decreased with conversion (56–31%) but an increase with conversion (55–65%) was observed in the Teflon vessel. Toluene, as a proportion of the major products, tended to decrease with increasing conversion (6–3%) in both vessels.

DISCUSSION

From the product-time behaviour, it would appear that compound (I) is formed in an independent primary step *via* the well documented^{9,10} bicyclo[3.2.0]hept-2-ene \rightarrow bicyclo[2.2.1]hept-2-ene rearrangement.

It has been suggested⁴⁻⁶ that the formation of the monocyclic products occurs *via* initial ring opening to form the linear keten, 2-methylhepta-1,3,6-trien-1-one (IV). A 1,5 hydrogen transfer followed by cyclization would yield 5-methyl-5-formylcyclohexa-1,3-diene (V),^{5,6} a precursor of the observed monocyclic materials.

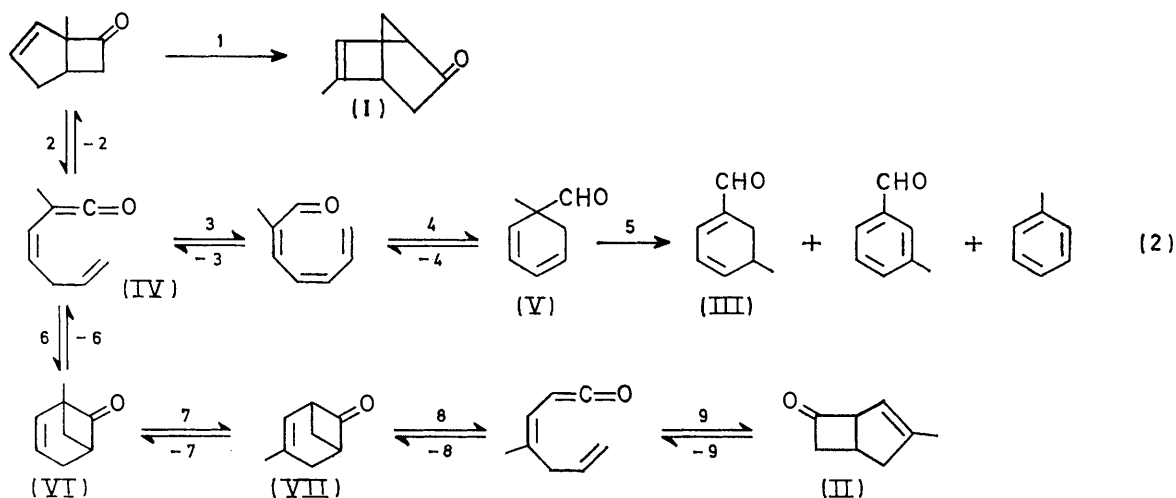
The formation of (II) is more difficult to rationalize. A possible route involves the 'abnormal' ring closure of (IV) to 1-methylbicyclo[3.1.1]hept-2-en-6-one (VI).¹¹ Rearrangement of (VI) to 3-methylbicyclo[3.1.1]hept-2-en-6-one (VII), followed by ring opening and 'normal'

⁸ S. W. Benson, 'The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 91.

⁹ J. A. Berson, *Accounts Chem. Res.*, 1968, **1**, 152.

¹⁰ A. T. Cocks and H. M. Frey, *J. Chem. Soc. (A)*, 1971, 2564.

¹¹ W. F. Erman, R. S. Treptow, P. Bakuzis, and E. Wenkert, *J. Amer. Chem. Soc.*, 1971, **93**, 657.



internal keten addition would yield (II). Such a pathway would explain the interdependence of (II) and the C_6 monocyclic products, but would indicate a complex kinetic scheme involving the equilibria shown in the reactions (2).

To account for the observed kinetic behaviour with respect to the depletion of starting material, routes 3 and 6 must be much faster than route -2, which is not unreasonable. However, evaluation of this scheme in terms of the likely magnitudes of the rate constants for comparison with the observed product distributions, is not possible due to the heterogeneous components.

The thermal reactions of 1-methylbicyclo[3.2.0]hept-2-en-7-one are different from those observed for bicyclo[3.2.0]hept-2-en-6-one¹ and 7,7-dimethylbicyclo[3.2.0]hept-2-en-6-one² in which a keten elimination to form cyclopentadiene is the only important reaction path. In the present study, no evidence for appreciable amounts of methylcyclopentadiene was obtained. The Arrhenius parameters for the depletion of reactant in the case of 1-methylbicyclo[3.2.0]hept-2-en-7-one are also substantially different from those for the bicyclo[3.2.0]hept-2-en-6-ones. These parameters, together with those for other cyclobutanones studied to date, are summarized in Table 2. In the temperature range of the present study, 1-methylbicyclo[3.2.0]hept-2-en-7-one reacts at only about 0.05–0.1 the rate of the 2-en-6-one compounds.

The parameters for the elimination reactions of cyclobutanones have been rationalized on the basis of polar transition states possessing a quasi-zwitterionic structure¹² in which positive charge is developed at the carbon centre diagonally opposite the carbonyl group in the four-membered ring, and the corresponding negative charge resides on the oxygen. On this model, the parameters for the decomposition of 1-methylbicyclo[3.2.0]hept-2-en-7-one would be predicted to be similar to those for bicyclo[3.2.0]heptan-6-one which in fact reacts at a much slower rate. This would explain the absence

of keten elimination in the present study and would indicate that the reactions of the 7-one compound occur

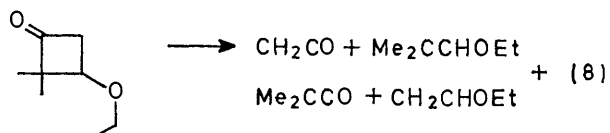
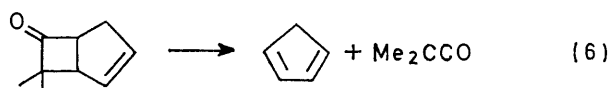
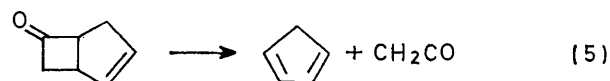
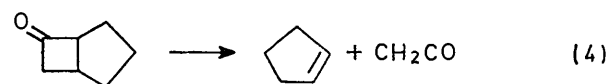
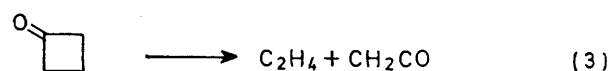


TABLE 2
Arrhenius parameters for the thermal reactions of cyclobutanone derivatives

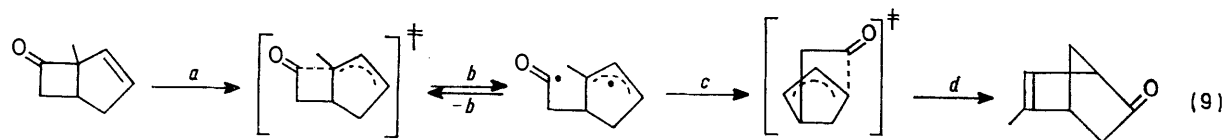
Reaction	$\log (A/s^{-1})$	$E_a/kJ\ mol^{-1}$	Ref.
(3)	14.6	218	a
(3)	14.55	217	b
(4)	14.21	203	c
(5)	13.16	157	1
(6)	12.90	158	2
(7)	14.50	184	This work
(8)	13.61	169	12

^a M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *J. Amer. Chem. Soc.*, 1954, **76**, 6271. ^b T. H. McGee and A. Schleifer, *J. Phys. Chem.*, 1972, **76**, 963. ^c A. T. Cocks and K. W. Egger, *J.C.S. Perkin II*, 1972, 2014.

¹² K. W. Egger, *J. Amer. Chem. Soc.*, 1973, **95**, in the press.

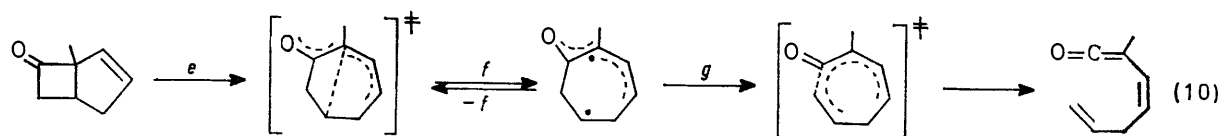
via a mechanism different from that for the other cyclobutanone derivatives.

A plausible alternative mechanism involves diradical intermediates, and the diradical scheme for the formation of 5-methylbicyclo[2.2.1]hept-5-en-2-one is shown in reaction (9).



The enthalpy change (in kJ mol^{-1}) in forming the diradical is estimated to be 248.5 (bond dissociation energy) -93.3 (ring strain)¹³ = 155.2 . The activation energies for ring closure in steps $-b$ and c should both be *ca.* 29 kJ mol^{-1} ¹⁴ resulting in an estimated activation energy of *ca.* 184 kJ mol^{-1} . The A factor should not differ greatly from that estimated for the analogous reaction of bicyclo[3.2.0]hept-2-ene ($10^{14.3}$).¹⁰ Using this A factor and the observation that the pathway to 5-methylbicyclo[2.2.1]hept-5-en-2-one constitutes *ca.* 6% of the total reaction, an activation energy of *ca.* 192 kJ mol^{-1} is obtained. The diradical analysis thus predicts a slightly faster rate than that observed, but this is within the likely error limits of the analysis. The failure to observe methylcyclopentadienes as reaction products would imply that the decomposition of the diradical requires an activation energy in excess of 45 kJ mol^{-1} .

The biradical scheme for the formation of 2-methylhepta-1,3,6-trien-1-one is depicted in (10). The ring



strain change in forming the diradical is likely to be close to the ring strain in cyclobutanone and hence, the total enthalpy change (in kJ mol^{-1}) is given by 258 (bond dissociation energy) $-93 - X = 165 - X$, where X is the stabilization energy of the alkylacetyl radical

¹³ G. Wolf, *Helv. Chim. Acta*, 1972, **55**, 1446.

¹⁴ S. W. Benson and H. E. O'Neal, 'Kinetic Data on Gas Phase Unimolecular Reactions', NSRDS-NBS 21, National Bureau of Standards, Washington, 1970.

¹⁵ A. T. Cocks and K. W. Egger, *J.C.S. Perkin II*, 1973, 199.

the value of which is still in dispute.¹⁵ This energy is lost in step g , and hence, this step is likely to be rate determining. The enthalpy change in step g due to ring strain release is difficult to estimate but is unlikely to be far from 1/2 the strain energy in cyclohepta-1,3-diene (28 kJ mol^{-1}).¹⁴ The activation energy for decom-

position of the diradical is therefore estimated to be $X - 14 \text{ kJ mol}^{-1}$, and the resulting total activation energy is *ca.* 180 kJ mol^{-1} . The total entropy of activation is also difficult to estimate but limits of $5 - 21 \text{ J K}^{-1} \text{ mol}^{-1}$ appear reasonable. The A factor required to fit the observed rates with an activation energy of 180 kJ mol^{-1} is $10^{14.1}$ which corresponds to an entropy of activation of $13 \text{ J K}^{-1} \text{ mol}^{-1}$.

Thus, the diradical models can account for the reaction rates observed for both pathways in the pyrolysis of 1-methylbicyclo[3.2.0]hept-2-en-7-one, and predict Arrhenius parameters for the total reaction close to those found. A diradical analysis of the thermal decomposition of the bicyclo[3.2.0]hept-2-en-6-one compounds, however, using the latest value for the strain energy in cyclobutanone,¹³ predicts reaction rates of only 10^{-3} times those observed. Although a 'concerted' process cannot be completely ruled out in the pyrolysis of 1-methylbicyclo[3.2.0]hept-2-en-7-one, there is strong evidence that a change in position of the carbonyl group

from the 6- to the 7-position in the bicyclo[3.2.0]hept-2-ene series brings about a change in mechanism from 'polar-concerted' to diradical.

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