Kinetic Studies of the Decomposition of Norbornan-2-one and Norborn-5-en-2-one Tosylhydrazone Sodium Salts

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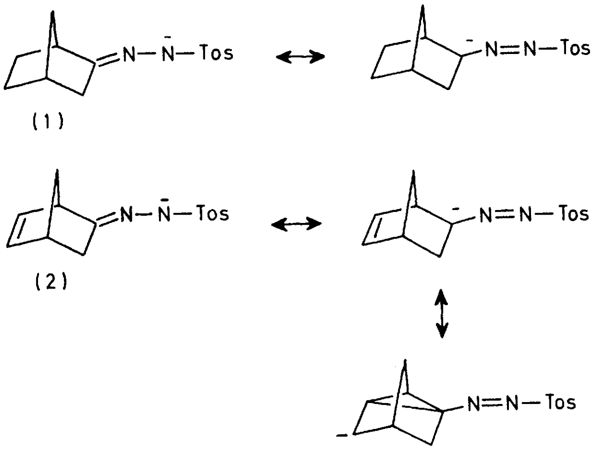
The thermal decomposition of norbornan-2-one and norborn-5-en-2-one tosylhydrazone sodium salts [(1) and (2)] has been studied over the temperature range 100—150 °C in 2,5,8-trioxanonane, dimethyl sulphoxide, and hexamethylphosphoramide as in solvents. First-order kinetics were observed in all cases. The results are interpreted in terms of a solvent effect and of homoallylic stabilization in the latter case (2).

TOSYLHYDRAZONE sodium salts have been used extensively as precursors of diazo-compounds,[1] which decompose thermally to yield carbenes and nitrogen

$$>C{=}N{-}\bar{N}Ts \xrightarrow{k_a} >C{=}N_2 + Ts^- \qquad (a)$$

$$>C{=}N_2 \xrightarrow{k_b} >C: + N_2 \qquad (b)$$

according to equations (a) and (b). However, it is not known which of these steps is rate determining. We have investigated the kinetics of the decomposition of norbornan-2-one and norborn-5-en-2-one tosylhydrazone sodium salts [(1) and (2), respectively] in an attempt to clarify this point and to determine the effects of the presence of the 5,6-double bond.



SCHEME

EXPERIMENTAL

G.l.c. analyses were carried out with a Perkin-Elmer F-11 instrument equipped with a flame ionization detector; peak areas were measured with a ball and disc integrator. All solvents were purified by standard procedures.

(a) *Preparation of Tosylhydrazone Sodium Salts.*—Norbornan-2-one tosylhydrazone, was prepared according to the procedure of Cristol;[2] m.p. 201—202 °C (decomp.) [lit.,[3] 201.5—202.5 °C (decomp.)]. Norborn-5-en-2-one tosylhydrazone was prepared by Freeman's procedure;[4] m.p. 183—184 °C (decomp.) [lit.,[4] 185—188 °C (decomp.)]. The tosylhydrazones were converted into their sodium salts by neutralization with sodium methoxide in absolute methanol.[2] The solutions were evaporated and the resulting white solids were stored in a freezer under nitrogen.

(b) *Kinetic Procedure.*—The tosylhydrazone sodium salt (0.5 g) was mixed with thermoequilibrated solvent (10 ml) in a vessel which was immersed in an oil-bath (temperature controlled to within ±0.1 °C) and connected to a gas burette. The first-order rate coefficients were determined by a least-squares fitting procedure from a plot of $\log(V_\infty - V_t)$, against time where V_∞ is the volume of nitrogen collected at infinite time (at least ten half-lives) and V_t the volume at time t.

(c) *Product Analysis.*—The tosylhydrazone sodium salt (1 g) in solvent (20 ml) was heated at 130—140 °C until

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[1] M. Jones, jun., and R. A. Moss, 'Carbene,' vol. 1, Wiley-Interscience, New York, 1973.

[2] S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, 1963, **28**, 1413.

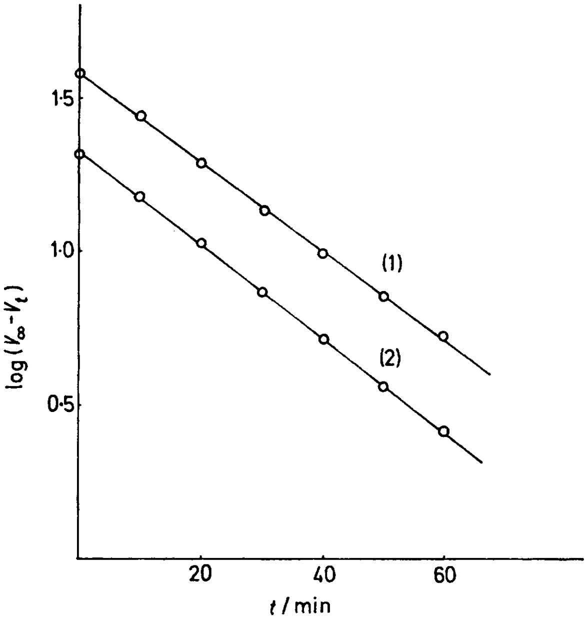
[3] P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, 1964, **29**, 1682.

[4] P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, 1963, **28**, 3234.

nitrogen evolution ceased. The mixture was then diluted with water (200 ml) and extracted with light petroleum (b.p. 30—60 °C; 2 × 20 ml). The combined extracts were washed with water (2 × 40 ml), dried ($MgSO_4$), and carefully concentrated at atmospheric pressure to *ca.* 5 ml. This solution was then analysed by g.l.c. (stainless steel 11 ft × 1/8 in o.d. column packed with 20% Carbowax 20M on 80—100 mesh Chromosorb W, operated at 100 °C; carrier gas flow rate 30 ml min^{-1}). Products were identified by comparison of their retention times with those of authentic samples.

RESULTS

The thermal decompositions obeyed first-order kinetics to at least 75% reaction (the first-order rate constants were determined by least-squares analysis from a minimum of six V_t *vs.* t points for each experiment). The Figure shows typical first-order plots. Table 1 lists typical rate constants for the decompositions in dimethyl sulphoxide (errors quoted are standard deviations) and Table 2 summarizes the kinetic parameters.



First-order plots for the thermal decomposition of the tosylhydrazone salts (1) and (2) at 117.5 °C in dimethyl sulphoxide

TABLE 1

Rate constants for decomposition of the salts (1) (k_1) and (2) (k_2) in dimethyl sulphoxide

t/°C	$10^4k_1/s^{-1}$	$10^4k_2/s^{-1}$
100.4	0.85 ± 0.02	0.80 ± 0.01
110.2	2.56 ± 0.05	2.45 ± 0.02
117.5	5.54 ± 0.12	5.93 ± 0.09
125.0	11.72 ± 0.29	12.94 ± 0.08
134.0	29.84 ± 0.64	32.21 ± 0.32

Decomposition of the salt (1) in the various solvents afforded nortricyclene (3) and norbornene (4) in the yields given in Table 3. These results agree with previous work on this system [3] and suggest that the propensity for rearrangement of the norbornan-2-ylidene [5] system is unaffected by the nature of the solvent.

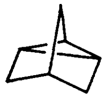
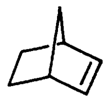
TABLE 2

Kinetic parameters for thermal decomposition of tosylhydrazone sodium salts (1) and (2)

	(1)	
Solvent	E_a/kJ mol^{-1}	log A
$(MeO{\cdot}CH_2{\cdot}CH_2)_2O$	157.4 ± 3.5	16.95 ± 0.44
Me_2SO	132.0 ± 1.9	14.39 ± 0.25
$PO(NMe_2)_3$	128.5 ± 2.3	14.27 ± 0.30
	(2)	
Solvent	E_a/kJ mol^{-1}	log A
$(MeO{\cdot}CH_2{\cdot}CH_2)_2O$	157.9 ± 8.4	16.92 ± 0.87
Me_2SO	145.5 ± 3.6	16.20 ± 0.48
$PO(NMe_2)_3$	142.6 ± 4.1	16.11 ± 0.54

TABLE 3

Yields of products (%) from the tosylhydrazone salt (1)

Solvent	 (3)	 (4)
$(MeO{\cdot}CH_2{\cdot}CH_2)_2O$	94.1	5.9
Me_2SO	99.8	0.2
$PO(NMe_2)_3$	99.6	0.4

The sole product observed from decomposition of the salt (2) in the solvents studied was norbornadiene, identified by comparison of g.l.c. retention time and i.r. spectrum with an authentic sample. This also agrees with literature reports.[4]

DISCUSSION

Whereas the diazo-compounds resulting from the decomposition of the salts (1) and (2) are unstable under our conditions, diazodiphenylmethane is stable under the same conditions.[6] At 85 °C, the first-order rate constant for the decomposition of diazodiphenylmethane [6] is *ca.* 10^{-4} s^{-1}; however our observed first-order rate constants are much smaller (*i.e. ca.* 10^{-6} s^{-1}). This indicates that k_{obs} is not k_b, but is more likely to be k_a. The energies of activation and A factors reported in Table 2 are too high in comparison with literature parameters [6,7] for the decomposition of diazo-compounds, but do agree with parameters reported for the decomposition of salt-like molecules.[8] If step (b) were rate determining, the first-order plot obtained from nitrogen measurements

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[5] W. M. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971.

[6] D. Bethell, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 1965, 2466.

[7] M. T. H. Liu, P. Banjoko, Y. Yamamoto, and I. Moritani, *Tetrahedron*, 1975, **31**, 1645.

[8] E. A. Moelwyn-Hughes, 'The Chemical Statics and Kinetics of Solutions,' Academic Press, New York, 1971.

would be curved, owing to the build-up of the diazo-intermediate.[9] The fact that no curvature is observed (Figure) supports our view that step (a) is rate-determining. In the decomposition of diphenyldiazomethane, the rate is not dependent on solvent polarity, but in the present system, the nature of the solvent does change the decomposition rate. Table 2 reveals that in 2,5,8-trioxanonane the activation energy of the saturated salt (1) is the same as that of the unsaturated salt (2). This suggests that the participation of the double bond in (2) has similar effects (*e.g.* homoallylic interactions or bond angle strain) on both initial and penultimate states. In the other two more-polar solvents the activation energies are both lower, probably owing to poor solvation of the ground state anion. The extent of this lowering is less pronounced for compound (2), possibly owing to homoallylic stabilization in the ground state of this molecule. The activated states for both (1) and (2) must have charge localized in the tosylate group; thus delocalization effects are not possible for the activated complex. We may visualize the ground states for (1) and (2) as shown in the Scheme.

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[9] B. M. Jennings and M. T. H. Liu, *J. Amer. Chem. Soc.*, 1976, **98**, 6416.