Unusual Thermal Behaviour of Tricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (Tropovalene)

Yoshikazu Sugihara,*a Takashi Sugimura,b Naoki Saito,c and Ichiro Murata*a

^a Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

^b Basic Research Laboratory, Himeji Institute of Technology, 2167 Shosha, Himeji 671–22, Japan

° Ashigara Research Laboratories, Fuji Photo Film Co. Ltd., 210 Nakanuma, Minamiashigara, Kanagawa 250–01, Japan

Thermolysis of tricyclo[4.1.0.0^{2,7}]hept-4-en-3-one constitutes an unusual bond reorganisation reaction in which the alkenic carbon atoms are responsible for the construction of the cyclobutene ring in the product, bicyclo[3.2.0]hepta-3,6-dien-2-one.

Thermal rearrangements of bicyclobutane incorporated into a cyclic framework at the C(2) and C(4) positions such as (1) are of experimental and theoretical interest and have been extensively examined for many years.¹ In the well studied cases,² the rearrangements are generally interpreted to proceed *via* biradical (2), which collapses to either the cyclobutene (3) or the 1,3-butadiene (4) moiety, resulting from C(1)–C(2) bond fission of a bicyclobutane ring. The observed activation enthalpies for these processes are compat-

ible with those expected from theoretical considerations and the activation entropies are found to lie close to $zero \pm 5$ cal K^{-1} mol (cal = 4.184 J).

A notable exception is the thermal rearrangement of benzvalene which converts to benzene with substantially low activation enthalpy (25.9 kcal/mol).³ As for the activation entropy (1.6 cal K^{-1} mol⁻¹),³ the rearrangement falls within the above category. On the basis of molecular orbital considerations⁴ the thermal conversion is regarded as the



allowed process. On the other hand, thermal conversion of tricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (tropovalene) (5) into bicyclo[3.2.0]hepta-3,6-dien-2-one (6) was first reported by Prinzbach.⁵ Later we have found⁶ that, unlike a deuteriated tricyclo $[4.1.0.0^{2,7}]$ hepta-4-ene (homobenzvalene) (7)^{2a} which is known to give 6,7-dideuteriobicyclo[3.2.0]hept-3,6-diene (8) on thermolysis, 4-acetoxytricyclo[4.1.0.0^{2,7}]hept-4-en-3one (acetoxytropovalene) (9) underwent thermal rearrangement to 1-acetoxybicyclo[3.2.0]hepta-3,6-dien-2-one (10). In order to eliminate the effect of the acetoxy group we reinvestigated the thermolysis of the parent compound $(5)^{5,7}$ with deuterium labelling. 5-Deuteriotropovalene (5-D) and 3-deuteriobicyclo[3.2.0]hepta-3,6-dien-2-one (6-Da) were prepared starting from 4,4-dideuteriobicyclo[3.2.0]hept-6-en-2-one⁶ and the corresponding undeuteriated ketone,⁶ respectively, according to the procedures shown in Scheme 2.⁺ When (5-D) was heated in benzene containing a small amount of N, N, N', N'-tetramethylethylenediamine at 140 °C in a sealed tube, a mixture of the labelled bicycloheptadienones was produced quantitatively (Scheme 3). The same result was obtained by thermolysis at 170 °C. In each case the ¹H n.m.r. spectrum of the product mixture revealed that the integrated areas of signals attributable to H-4 (δ 7.70) and H-7 (δ 6.38) were found to be equal and halves as compared with those of other alkenic proton signals. Thus, it can be concluded that the site of deuterium incorporation into the bicyclo[3.2.0]heptadienone skeleton must be at the 4-(6-Db) and 7-positions (6-Dc), respectively, and the ratio of (6-Db) and (6-Dc) should be 1:1. Since (6-Da) prepared independently (Scheme 2) is stable and no detectable [3,3]sigmatropic shift could be observed under the same thermal conditions, (5-D) isomerises directly to (6-Db) and (6-Dc). These facts imply that the alkenic carbon atoms in (5) are also responsible for the construction of the cyclobutene ring in (6). Another feature of (5) is its marked thermal stability as compared with related compounds.^{2a-c,5,8} That is, the calculated rate for the thermal

† Satisfactory spectroscopic data were obtained for all the new compounds reported in this paper.



Scheme 2. Reagents and conditions: i, 450 W high pressure Hg lamp, acetone, ice cooling, 4 h; ii, lithium di-isopropylamide (1.5 equiv.), tetrahydrofuran (THF) -78 °C, 30 min 0 °C, 20 min, then PhSSPh, THF/hexamethylphosphoramide (1:1.2 v/v), 0 °C, 2 h; iii, 3-chloroperoxybenzoic acid (*m*-CPBA) (1.3 equiv.), CH₂Cl₂, -78 °C, 30 min; iv, CCl₄, reflux, 2 h; v, K₂CO₃ (cat.), MeOD, room temp., 2 h.



rearrangement of $(5)^5$ is approximately 100 times slower than that of (7).^{2a}

In order to gain further insight into the rearrangement, kinetic experiments for the thermolysis of (5) in [²H₆]benzene were carried out by ¹H n.m.r. spectroscopy monitoring within the temperature range 150—176 °C. Carefully purified (5) underwent quantitative isomerisation to (6) with first order kinetics.‡ An Arrhenius plot ($\gamma = 0.9973$) of the data afforded the activation parameters: $\Delta H^{\ddagger} = 30.3 \pm 1.6$ kcal/mol, $\Delta S^{\ddagger} = -10.7 \pm 2.0$ cal K⁻¹ mol⁻¹, $E_a = 31.2 \pm 1.6$ kcal/mol, and log

[‡] First-order rate constants for the thermolysis of (5) are $k^{423} = 8.50 \times 10^{-6}$, $k^{434} = 2.28 \times 10^{-5}$, $k^{443} = 4.74 \times 10^{-5}$, $k^{449} = 6.59 \times 10^{-5}$ s⁻¹.



 $A = 11.0 \pm 0.6$. The relatively negative entropy causes the thermal stability of (5).§

The equal distribution of (6-Db) and (6-Dc) in thermolyses at two divergent temperatures was reasonably rationalised by assuming the existence of a symmetrical transition state or an intermediate which collapses to the products. Although the observed activation enthalpy is relatively small, the value is consistent with those for thermolyses¶ which have been interpreted in terms of a biradical mechanism rather than a concerted one with a symmetrical transition state. Thus, both the product distribution and the kinetic data are in line with a biradical pathway shown in Scheme 4. Only a hypothetical intermediate, cis,trans,cis-tropone⁹ (A), is fitted with the observed product ratio.¹⁰

Received, 11th November 1988; Com. 8/04498H

§ A referee has suggested that the replacement of methylene in homobenzvalene by carbonyl stabilises both ground state and transition state but apparently the larger stabilisation is of the ground state. This seems to be a reasonable idea since stabilising interactions between the Walsh-type orbital of the bicyclobutane (M. Pomerantz and E. W. Abrahamson, J. Am. Chem. Soc., 1966, **88**, 3970) and the enone moiety in tropovalene have been supported by spectroscopic data.^{6,7} However, there is no clear evidence of stabilisation in transition state.

¶ The activation enthalpies reported for the thermolyses of azulvalene,^{2c} naphtho[1,8]tricyclo[$4.1.0.0^{2.7}$]heptene,^{2b} and homobenz-valene^{2a} are 27.5, 32.1, and 31.5 kcal/mol, respectively.

References

- For theoretical studies, see: M. J. S. Dewar, Angew. Chem., 1971, 83, 859; M. J. S. Dewar and S. Kirschner, J. Am. Chem. Soc., 1975, 97, 2931; M. J. S. Dewar, *ibid.*, 1984, 106, 209. For experimental studies, see: K. B. Wiberg and J. M. Lavanish, J. Am. Chem. Soc., 1966, 88, 5272; K. B. Wiberg, Tetrahedron, 1968, 24, 1083; G. L. Closs and P. E. Pfeffer, J. Am. Chem. Soc., 1968, 90, 2452.
- 2 (a) M. Christl, V. Heinemann, and W. Kristof, J. Am. Chem. Soc., 1975, 97, 2299; (b) N. J. Turro, V. Ramamurthy, R. M. Pagni, and J. A. Butcher, Jr., J. Org. Chem., 1977, 42, 92; (c) Y. Sugihara, T. Sugimura, and I. Murata, J. Am. Chem. Soc., 1984, 106, 7268; (d) D. P. Kjell and R. S. Sheridan, Tetrahedron Lett., 1985, 26, 5731; (e) M. J. S. Dewar and K. M. Merz, Jr., J. Am. Chem. Soc., 1986, 108, 5146.
- 3 N. J. Turro, C. A. Renner, T. J. Katz, K. B. Wiberg, and H. A. Cannon, *Tetrahedron Lett.*, 1976, 4133.
- 4 M. J. S. Dewar and S. Kirschner, J. Am. Chem. Soc., 1975, 97, 2932.
- 5 H. Prinzbach, H. Babsch, and H. Fritz, *Tetrahedron Lett.*, 1976, 2129.
- 6 Y. Sugihara, A. Yamato, and I. Murata, *Tetrahedron Lett.*, 1981, **22**, 3257.
- 7 Y. Sugihara, N. Morokoshi, and I. Murata, *Tetrahedron Lett.*, 1977, 3887.
- 8 H. Babsch, H. Fritz, and H. Prinzbach, *Tetrahedron Lett.*, 1975, 4677.
- 9 J. E. Baldwin and M. S. Kaplan, J. Am. Chem. Soc., 1972, 94, 668.
- 10 For related study, see: E. W. Otterbacher and J. J. Gajewski, J. Am. Chem. Soc., 1981, 103, 5862.