Mobile Keto Allyl Systems. XIV.[1] The Kinetics and Mechanism of the Thermal Decomposition of *trans*-2-Benzal-3-cyclohexylamino-4,4-dimethyl-1-tetralone

GEORGE GLAROS

Department of Chemistry, Russell Sage College, Troy, New York 12180

NORMAN H. CROMWELL*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508

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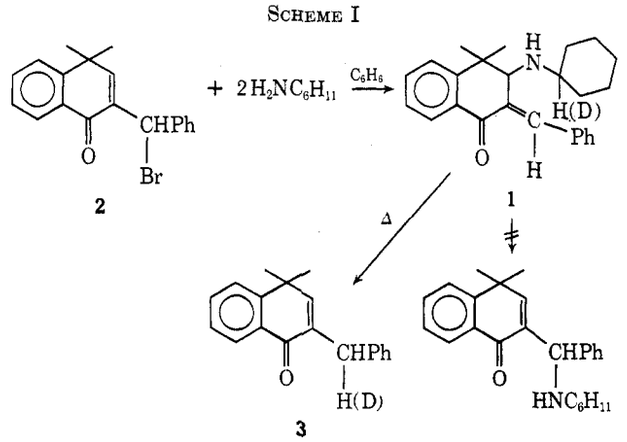
The thermal decomposition of the title compound was found to exhibit first-order kinetics: a large solvent effect, $k_{CHCl_3}/k_{isooctane} = 18$; as well as a primary isotope effect, $k_H/k_D = 2.2$. Possible mechanisms are discussed.

In an earlier paper in this series,[2] we described a thermal decomposition reaction of *trans*-2-*o*-methylbenzal-3-amino-4,4-dimethyl-1-tetralones as a retro-ene reaction involving the transfer of the hydrogen atom α to the nitrogen in the amino moiety to the benzylic position. It has also been shown[3] that this decomposition occurs in the corresponding unsubstituted benzal compounds. Four possible mechanisms were suggested[2] to account for the complete transfer of the α hydrogen, a proton transfer (path A), a hydride transfer (path B), a hydrogen atom transfer (path C), and a concerted cyclic transition state (path D). In this paper, we discuss the kinetics and mechanism of this thermal decomposition reaction.

Results and Discussion

The compound chosen for study was *trans*-2-benzal-3-cyclohexylamino-4,4-dimethyl-1-tetralone (**1**). Amino ketone **1** was prepared as previously described[3] from 2-(α-bromobenzyl)-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (**2**) and 2 equiv of cyclohexylamine. Although reasonably stable to rearrangement and decomposition at room temperature,[3] amino ketone **1** decomposes in high yield to the known[4] 2-benzyl-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene (**3**), Scheme I.

SCHEME I



Compounds **1** and **3** have significantly different uv spectra (Figure 1), which allowed the rate of the reaction to be followed by observing the decrease in absorbance due to **1** with time. The reaction was shown to follow first-order kinetics for 2 to 3 half-lives.

In Table I are listed the results of the kinetics in isooctane and chloroform, as well as several control experiments. Neither the presence of glass wool, radical initiators, or radical traps appreciably alters the rate of the reaction. Thus, this reaction does not appear to be a surface-catalyzed or a radical chain reaction.

TABLE I

[E_a(isooctane) = 25.4 kcal/mol; $\Delta S^{\ddagger} = -17$ eu at 135°; $k_H/k_D = 2.2$[g]]

Solvent	ϵ_{20}[a]	Temp, °C	[1]	k, sec^{-1}	k, sec^{-1}
Isooctane	1.9	120	0.00446	2.4×10^{-5}	
		120	0.00092	2.5×10^{-5}	
		120	0.00230	2.4×10^{-5}	2.4×10^{-5}
		135	0.00203	1.4×10^{-4}	
		135	0.00403	1.6×10^{-4}	
		135	0.000755	1.6×10^{-4}	1.5×10^{-4}
		135[b]	0.00205	1.6×10^{-4}	
		135[c]	0.00221	8.5×10^{-5}	
		150	0.00264	2.1×10^{-4}	
		150	0.00138	1.5×10^{-4}	
		150	0.00332	2.2×10^{-4}	1.9×10^{-4}
Chloroform	4.8	120	0.000464	5.0×10^{-4}	
		120	0.00115	4.7×10^{-4}	
		120	0.00217	4.0×10^{-4}	4.5×10^{-4}
		120[d]	0.00110	2.1×10^{-4}	
		120[d]	0.000456	2.3×10^{-4}	2.2×10^{-4}
		120[e]	0.000346	2.9×10^{-4}	
		120[f]	0.00140	1.9×10^{-4}	

[a] Dielectric constants taken from A. A. Maeyott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, Aug 10, 1951. [b] Sample tubes packed with glass wool. [c] Dibenzoyl peroxide added. [d] α-Deuterium compound. [e] Hydroquinone added. [f] Solution saturated with oxygen. [g] Corrected for isotopic purity, 98.3% atom/molecule as determined by mass spectral analysis.

The large solvent effect observed, $k_{CHCl_3}/k_{isooctane} = 18$, is indicative of a reaction in which charge is developed in the transition state.[5] Radical reactions are often characterized by their insensitivity to changes in solvent polarity.[6] Similarly, several examples[7] of a symmetry-allowed concerted 1,5-hydrogen shift[8] show little variation in rate with a large variation in solvent

(1) (a) For paper XIII in this series, see G. Glaros and N. H. Cromwell, *J. Org. Chem.*, **37**, 867 (1972). (b) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972.

(2) G. Glaros and N. H. Cromwell, *J. Org. Chem.*, **36**, 3033 (1971).

(3) G. Glaros and N. H. Cromwell, *J. Org. Chem.*, **37**, 862 (1972).

(4) A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, **80**, 893 (1958).

(5) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 379.

(6) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 13.

(7) A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741, 1189 (1963).

(8) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

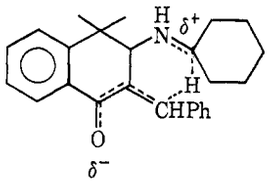
polarity. Thus, neither the hydrogen atom transfer (path C) nor the concerted 1,5-hydrogen shift (path D) seems to be involved in this reaction. The mechanisms which best explain the large solvent effect are the ionic pathways A and B.

When the reaction was carried out in ethanol, the decomposition was essentially complete in the 15 min usually allowed for temperature equilibration. Since the ethanol could act as a polar solvent or as an external source of hydrogen atoms or protons, the rate enhancement could be attributed to either property. When the decomposition was carried out in methanol-d_1, the product contained no deuterium. Thus, the rate enhancement is probably due to the increased polarity of the solvent. The primary isotope effect k_H/k_D = 2.2 is also considerably smaller than the maximum value of around 12 for highly concerted 1,5 shifts in which the hydrogen atom is equally bonded to both carbon atoms in the transition state.[9]

As a control experiment, the α-deuterio amino ketone **1** was decomposed with an equal molar amount of *trans*-2-*o*-methylbenzal-3-cyclohexylamino-4,4-dimethyl-1-tetralone.[2] The crude reaction mixture was analyzed by mass spectrometry and the 2-*o*-methylbenzyl-1,4-dihydro-4,4-dimethyl-1-ketonaphthalene obtained was shown to contain no deuterium.

Pathways C and D, which do not involve a large degree of charge separation, may be ruled out because of the large solvent effect. Path A, the proton transfer, may be ruled out, since the intermediate involves an unfavorable disposition of charges, and the most acidic hydrogen (the one on nitrogen or the methanol-d_1) is not transferred.[2] All the data are consistent with a hydride transfer to give a dipolar intermediate, which is resonance stabilized. Attempts to trap this intermediate with dimethyl acetylenedicarboxylate were unsuccessful. This may be due to the steric hindrance of the addition or the short life of the intermediate.

In this decomposition, the resonance effect in the ground state of the molecule makes the benzal position susceptible to nucleophilic attack by the hydride ion, and the main driving force of the reaction is probably the conversion of the thermodynamically less stable exocyclic unsaturated ketone to the endocyclic unsaturated ketone.[10] Thus, these results are best explained by a concerted reaction passing through a dipolar transition state such as that shown below, *via* path B, the hydride transfer.



Experimental Section[11]

Preparation of Materials.—Spectrograde isooctane was dried over sodium prior to use. Reagent grade chloroform was passed through a column of alumina (Woelm activity I) to remove water and ethanol and was used immediately after purification.

Amino ketone **1** was prepared as previously described[2] and had mp 94–95° (lit.[3] mp 94–95°). The amino ketone was recrystallized from 95% ethanol, powdered, dried under vacuum, and stored in a desiccator. The deuterated amino ketone was prepared by the method previously described.[2]

Kinetic Method.—Aliquots of a stock solution of **1** were placed in test tubes; the tubes were sealed and placed in a constant-temperature bath. At appropriate intervals, tubes were removed from the bath and the reaction was quenched in Dry Ice–acetone. The tube was then opened and the contents were diluted to an appropriate volume. The concentration of **1** was determined spectrophotometrically at four wavelengths, λ 310, 312, 314, and 316 mμ.

The rate constants were obtained by plotting the log of the concentration of **1** *vs.* time. Activation parameters were calculated by standard methods[12] using the following expressions: $k_1 = A \exp(-E_a/RT)$, $E_a = \Delta H^{\ddagger} + RT$, $k_1 = kT/h \exp(-\Delta F^{\ddagger}/RT)$, and $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

Reaction of 1 in Methanol-d_1.—A 0.238-g (0.66 mmol) sample of amino ketone **1** was dissolved in 1 ml of methanol-d_1 and heated at 135° for 45 min in a sealed tube. The tube was opened and the contents were passed through a column of Florisil. The resulting oil crystallized upon trituration and was recrystallized from 95% ethanol to yield 0.091 g (53%) of white crystals, mp 112–113° (lit.[4] mp 113–113.5°). The nmr spectrum follows: δ 1.4 (s, 6 H), 3.77 (d, 2 H, J = 0.6 Hz), 6.56 (t, 1 H, J = 0.6 Hz), 7.1–7.7 (m, 8 H), and 8.23 (1 H).

Reaction of 1 with Dimethyl Acetylenedicarboxylate.—A 0.359-g (1 mmol) sample of amino ketone **1**, 0.287 g (2 mmol) of dimethyl acetylenedicarboxylate, and 2 ml of isooctane were heated in a sealed tube at 135° for 4–5 hr. The tube was cooled and opened, and the contents were triturated with 95% ethanol to yield 0.102 g (39%) of a white solid, mp 109–110°. The nmr spectrum showed it to be **3**.

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Registry No.—**1**, 33240-02-7; **3**, 42262-37-3.

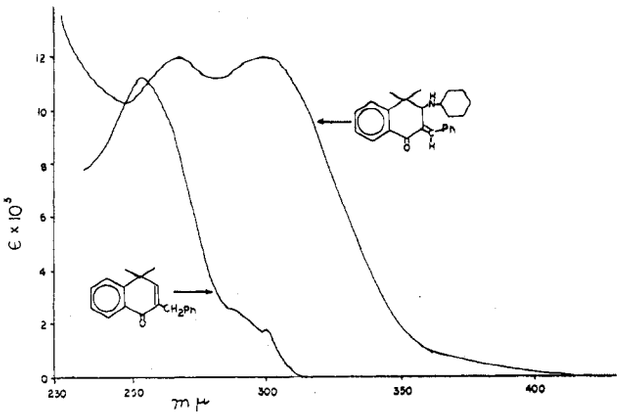

Figure 1.—Ultraviolet absorption spectra of amino ketone **1** and unsaturated ketone **3**, measured in isooctane.

(9) (a) H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969); (b) W. R. Roth, *Chimia*, **20**, 229 (1966).

(10) N. H. Cromwell, R. P. Ayer, and P. W. Foster, *J. Amer. Chem. Soc.*, **82**, 130 (1960).

(11) Melting points were taken by the capillary method in a Mel-Temp melting point apparatus and are uncorrected. Ultraviolet spectra were taken on a Cary Model 14 recording spectrophotometer. For kinetics, a Beckman DB-G grating spectrophotometer was used. Proton magnetic resonance spectra were obtained on a Varian A-60D spectrometer employing $CDCl_3$ solutions and are reported in parts per million (δ) relative to internal TMS (0.0). Mass spectra were obtained with a Hitachi Model RMU-6D spectrometer. Rate constants were calculated by the least-squares method on an IBM-360 computer.

(12) W. J. Moore, "Physical Chemistry," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1955, pp 546 and 568.