Dehydroamination Reaction of 9-Amino-9,10-dihydrophenanthrene and Related Compounds by Thermolysis

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(Received November 6, 1992)

Dehydroamination of 9-alkylamino-9,10-dihydrophenanthrene occurred at 190—250 °C under non-basic conditions to give phenanthrene exclusively. The thermal reaction of *cis*-9-*t*-butylamino-10-methoxy-9,10-dihydrophenanthrene gave both 9-methoxyphenanthrene and 9-*t*-butylaminophenanthrene, while 9-aminophenanthrene was obtained from the thermal reaction of 9-amino-10-methoxy-9,10-dihydrophenanthrene. The thermal reaction of 9-amino-9,10-dihydroanthracene gave both anthracene and 9-aminoanthracene. Analysis of activation energies and frequency factors showed that the dehydroamination proceeds via an intramolecular proton transfer from C-10 to the amino group and subsequent C–N bond cleavage.

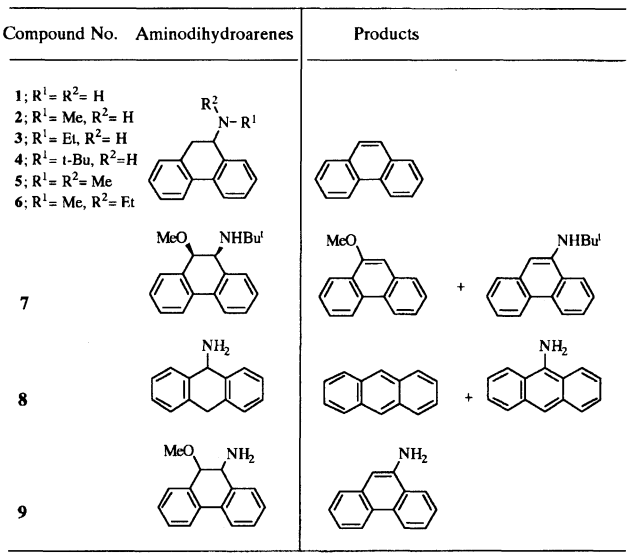
Elimination reactions such as dehydroacetoxylation,[1] dehydroamination,[2] dehydrocyanation,[3] and dehydromethoxylation[4] have been extensively studied from mechanistic and synthetic points of view. Recently, Boyd et al.[5] reported that the dehydration reaction of dihydronaphthols to naphthalene by an acid-catalyzed reaction proceeds much faster compared with that of acyclic analogs. They proposed an aromatic stabilization as a factor to enhance the reactivities of dihydronaphthols. However, analogous dehydroamination of aminodihydroarenes to arenes is still unknown. Therefore, we are interested in dehydroaminations of 9-amino-9,10-dihydrophenanthrene and related compounds, since we have already found a convenient method to prepare the aminodihydroarenes by a photoreaction.[6]

Results and Discussion

Dehydroamination. Thermal reactions of aminodihydroarenes were performed by heating a degassed diphenyl ether or dibutyl ether solution (0.05 mol dm^{-3}) at 190—250 °C (Scheme 1). The thermal reaction of 9-alkylamino-9,10-dihydrophenanthrenes (**1**—**6**) gave phenanthrene as an exclusive product. In the case of *cis*-9-*t*-butylamino-10-methoxy-9,10-dihydrophenanthrene (**7**), both 9-methoxyphenanthrene and 9-*t*-butylaminophenanthrene were formed in a ratio of 1 : 0.23—0.25. The thermal reaction of 9-amino-9,10-dihydroanthracene (**8**) gave both anthracene and 9-aminoanthracene in a ratio of 1 : 0.11—0.39. The thermal reaction of a mixture of *cis*- and *trans*-9-amino-10-methoxy-9,10-dihydrophenanthrenes (**9**) underwent dehydromethoxylation to give 9-aminophenanthrene exclusively. These aminodihydroarenes, **1**—**8**, are highly reactive molecules, compared with an acyclic analog, 1-amino-1,2-diphenylethane, which did not give stilbene even at temperatures higher than 250 °C. Interestingly, the present dehydroaminations occurred under non-basic conditions, although usual dehydroaminations such as Hofmann elimination[7] and other cases[2] proceed by a base-catalyzed reaction.

The total rate constants (k_t) for the thermal reactions at various temperatures were determined from linear plots of ln (C/C_0) vs. the reaction time in seconds; C_0 and C represent the molar concentrations of each aminodihydroarene before thermolysis and at a given reaction time, respectively. C_0 equals the summation of C and the molar concentration of the product(s), since the products were exclusively the corresponding arenes. Bimolecular mechanisms can be safely ruled out, since the reaction did not follow second-order kinetics. In the cases of **1**—**6**, the k_t values equal the rate constants (k_a) for the dehydroaminations. In the cases of **7** and **8**, the k_a and the rate constant (k_b) for the dehydromethoxylation or the dehydrogenetion were obtained from k_t multiplied by the molar proportion of the relevant product. Table 1 summarizes the calculated rate constants (k_t, k_a, and k_b) at various temperatures. Figures 1 and 2 show Arrhenius plots from which the activation energies (E_a) and the frequency factors (A) were obtained, as listed in Table 2. Moreover an endothermic peak of 82.1 kJ mol^{-1} corresponding to the dehydroamination was observed from a DSC measurement of **4**, as shown in Fig. 3.

Mechanism. A Hammett plot of E_a for the de-



Scheme 1.

Table 1. Rate Constants for the Thermal Reactions of **1**—**8**[a)]

1	T/K	498	503	508	513	518
	k_a/s^{-1}	1.7×10^{-6}	2.3×10^{-6}	3.1×10^{-6}	4.5×10^{-6}	1.1×10^{-5}
2	T/K	503	508	513	518	523
	k_a/s^{-1}	2.6×10^{-5}	3.4×10^{-5}	4.5×10^{-5}	4.6×10^{-5}	7.0×10^{-5}
3	T/K	498	503	508	513	518
	k_a/s^{-1}	9.7×10^{-6}	1.4×10^{-5}	1.6×10^{-5}	2.1×10^{-5}	2.6×10^{-5}
4	T/K	498	503	508	513	518
	k_a/s^{-1}	2.1×10^{-5}	2.4×10^{-5}	3.0×10^{-5}	3.3×10^{-5}	3.7×10^{-5}
5	T/K	483	488	493	498	503
	k_a/s^{-1}	2.5×10^{-5}	3.6×10^{-5}	5.3×10^{-5}	6.9×10^{-5}	9.9×10^{-5}
6	T/K	493	498	503	508	513
	k_a/s^{-1}	1.5×10^{-5}	2.2×10^{-5}	2.8×10^{-5}	4.4×10^{-5}	5.5×10^{-5}
7	T/K	493	498	503	508	513
	k_t/s^{-1}	3.9×10^{-5}	6.5×10^{-5}	8.4×10^{-5}	8.9×10^{-5}	1.3×10^{-4}
	k_a/s^{-1}	7.8×10^{-6}	1.3×10^{-5}	1.6×10^{-5}	1.7×10^{-5}	2.4×10^{-5}
	k_b/s^{-1}	3.1×10^{-5}	5.2×10^{-5}	6.8×10^{-5}	7.2×10^{-5}	1.1×10^{-4}
8	T/K	423	433	443	453	463
	k_t/s^{-1}	1.9×10^{-6}	4.5×10^{-6}	1.0×10^{-5}	1.9×10^{-5}	3.9×10^{-5}
	k_a/s^{-1}	1.4×10^{-6}	3.6×10^{-6}	8.1×10^{-6}	1.6×10^{-5}	3.5×10^{-5}
	k_b/s^{-1}	5.3×10^{-7}	9.3×10^{-7}	1.9×10^{-6}	2.8×10^{-6}	3.9×10^{-6}

a) k_t; rate constant for the consumption of **7** and **8**, k_a; rate constant for the dehydroamination of **1**—**8**, k_b; rate constant for the dehydromethoxylation of **7** and the dehydrogenation of **8**.

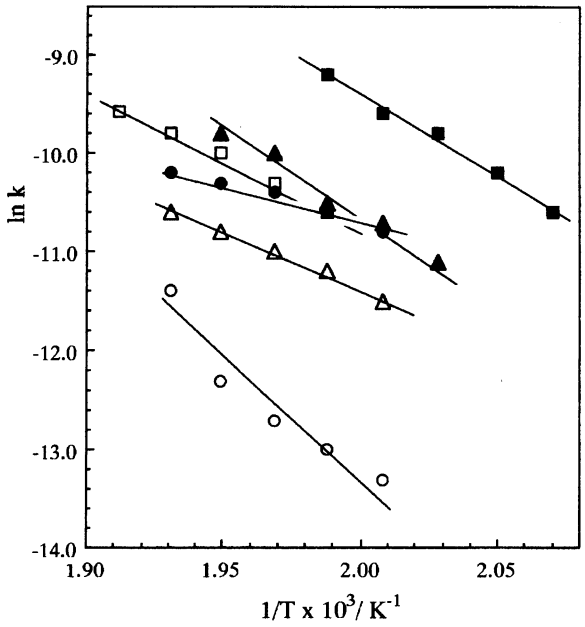


Fig. 1. Arrhenius plots for the dehydroaminations of **1** (○), **2** (□), **3** (△), **4** (●), **5** (■), and **6** (▲).

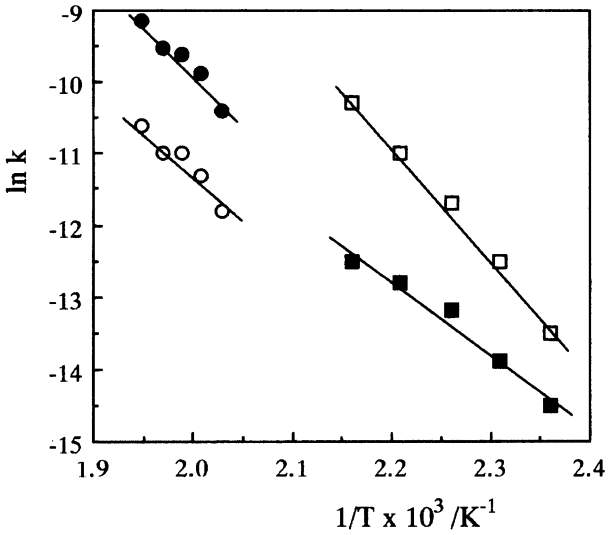


Fig. 2. Arrhenius plots for the dehydroaminations of **7** (○) and **8** (□), the dehydromethoxylation of **7** (●), and the dehydrogenation of **8** (■).

hydroaminations of **1**—**4** vs. a substituent parameter of Taft σ^* for the alkyl groups (R^1 and R^2) on the nitrogen atom gave a good linear correlation with a positive slope, as shown in Fig. 4. The E_a decreased with an increase in electron-donating ability of the alkyl groups on the amino group. Therefore, a substantial positive charge should develop over the nitrogen atom in the transition state. Hofmann elimination is a typical deamination reaction which requires a moderately strong base and positively charged nitrogen center for the elimination of the amino group and an adjacent hydrogen atom.[7)] In accord with the mechanism of Hofmann elimination, an intramolecular proton transfer from a benzylic carbon (C-10) to the amino group and subsequent C–N bond cleavage were proposed as key steps for the dehydroamination of aminodihydroarenes (Scheme 2). The above Hammett plot shows that the rate determining step for the dehydroamination of **1**—**4** lies in the proton-transfer step to give a zwitter-ion intermediate (**10**). On the other hand, the plots of the E_a values of **5** and **6** vs. Taft σ^* deviated from the linear correlation of Fig. 4. Since the ammonium ion of the

Table 2. Thermochemical Parameters for the Thermal Reactions of Dihydroaminoarenes (**1**—**8**)

Dihydroaminoarene	E_a/kJ mol^{-1} [a]	log A [b]
1	193	14.4
2	112	7.1
3	95	5.0
4	64	2.1
5	137	10
6	139	9.9
7	114	7.0
	118[c]	8.1[c]
8	130	10
	84[d]	4[d]

a) Activation energy. b) Frequency factor. c) For dehydromethoxylation. d) For dehydrogenation.

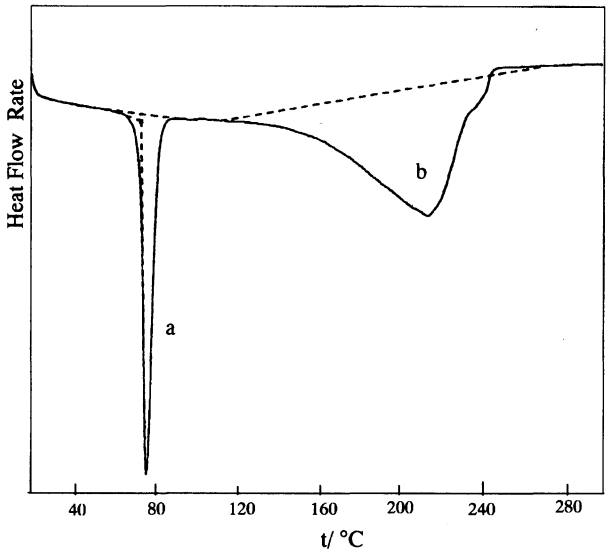


Fig. 3. DSC thermogram obtained for **4** at an increasing temperature rate of 10 °C min^{-1}. The endothermic peaks *a* and *b* correspond to the melting point and the dehydroamination reaction of **4**, respectively.

tertiary amines are, in general, more stable than those of the primary or the secondary amines, the zwitterion intermediates formed from **5** and **6** are more stable than those from **1**—**4**. Therefore, the proton transfer in **5** and **6** proceeds relatively fast, resulting in the rate-determining step being shifted to the C–N bond cleavage step.

Also, the dehydroamination of 9-*t*-butylamino-10-methoxy-9,10-dihydrophenanthrene (**7**) proceeds presumably by a mechanism similar to the case of **4**. The E_a value for **7**, however, was much greater than that for **4**. This is attributed to the destabilization of the zwitter-ion by the methoxyl group on C-10. No dehydroamination of **9** occurred but dehydromethoxylation of **9** occurred to give 9-aminophenanthrene, since the basicity of the amino group is too weak to abstract hydrogen from the methoxy-substituted C-10. The 1,4-dehydroamination of **8** occurs via an intramolecular proton-transfer, while the dehydrogenation of **8** may proceed via a concerted mechanism involving six electrons because of a small log A value.

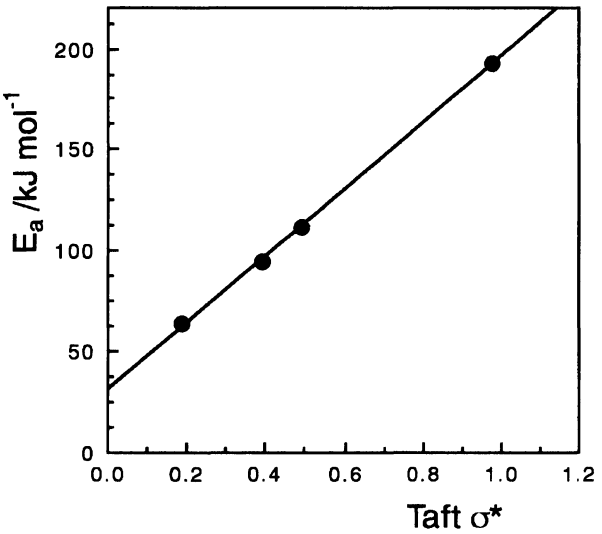
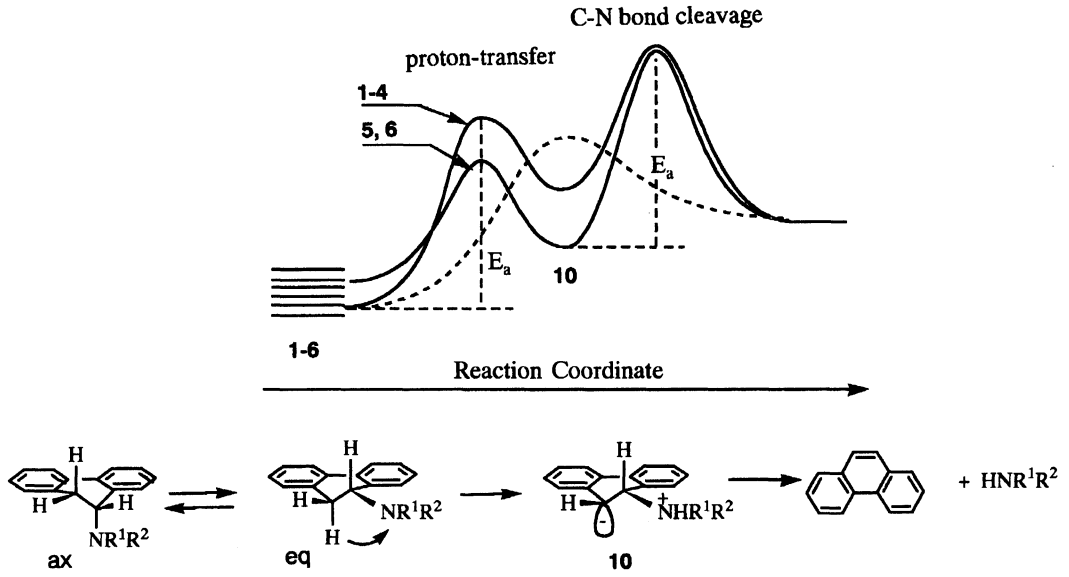


Fig. 4. A Hammett plot of E_a vs. Taft σ^*.

Although an exothermic process was reported for the dehydration of dihydronaphthol to naphthalene,[5] the dehydroamination reaction of **4** was an endothermic process as determined by the DSC experiment of **4**. The dehydroaminations of other aminodihydroarenes are suggested to proceed endothermically. Therefore, it is apparent that aromatic stabilization is not an important factor for the present dehydroamination. We propose that the stereochemically-rigid conformation of the aminodihydroarenes operates favorably for the proton transfer compared with the acyclic analogs. When the electron pair of **10** exists in an axial position, maximum orbital overlap of the electron pair with the π-orbital on the aromatic ring can be achieved. Therefore, deprotonation may occur preferably from an axial position rather than from an equatorial position. 9-Alkylamino-9,10-dihydrophenanthrene can take two conformations where the amino group occupies either the axial or the equatorial positions, as shown in Scheme 2. The amino group in the equatorial form can locate closely to the axial proton on C-10 compared to the axial form. It is concluded that 9-alkylamino-9,10-dihydrophenanthrene takes an equatorial form preferably for the effective intramolecular proton transfer from C-10 to the amino group. Although the stereochemistry of the dehydroamination could not be confirmed from product analysis, the above discussion suggests that the dehydroamination may proceed by *cis*-elimination.

MM2 calculations of the steric energy of the equatorial and axial forms showed that an axial form is more stable for **1** but that the steric energy of an axial form is very close to that of an equatorial form for **4**: steric energy/kJ mol^{-1}; 0.38 for ax-**1**; 5.0 for eq-**1**; 30.8 for ax-**4**; 30.7 for eq-**4**. Therefore, the dehydroamination of



Scheme 2.

1 occurs with a relatively large steric change from the axial form to the equatorial transition state, while the dehydroamination of **4** occurs with a very small steric change from the equatorial form. This is in accord with the small log *A* value for the case of **4** compared with that of **1**. Owing to the very small log *A* value of **4**, however, an alternative pathway via a concerted reaction represented as a dashed line in Scheme 2 could not be ruled out for the dehydroamination of **4**.

Experimental

^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions on a Bruker AC 250P spectrometer. The MS spectra were recorded on a Hitachi M-2000A spectrometer. DSC measurements were performed on a Seiko Instruments DSC-200 at an increasing temperature rate of 10 °C min^{-1}. Diphenyl ether and dibutyl ether were used after vacuum distillation. The aminodihydroarenes (**1**—**9**) were prepared by the photoamination reported in the literature.[6,8] Into an acetonitrile–water (9 : 1) solution containing an arene and *m*-dicyanobenzene was bubbled gaseous ammonia. The solution was irradiated by a high-pressure mercury lamp at room temperature. After evaporation of the solvent, the photolysates were dissolved in benzene and extracted with dilute HCl. The acidic aqueous layer was basified with saturated $NaHCO_3$ followed by extraction with diethyl ether. Evaporation of the ether left the crude aminated product. The oily aminodihydroarenes were decomposed by distillation under reduced pressure. The aminodihydroarenes were used for the thermal reaction without further purification except for **4** which was recrystallized from methanol. The purities of the aminodihydroarenes were determined to be >90% by ^1H NMR spectra. For DSC measurements, crystalline **4** was used. The spectral data of **1**—**5**, **8**, and **9** have been described in previous papers.[6,8] The spectral data of **6** and **7** are as follows:

***N*-Ethyl-*N*-methyl-9-amino-9,10-dihydrophenanthrene (6).** ^1H NMR δ=1.06 (3H, t, J=7.1 Hz), 2.20 (3H, s), 2.35—2.68 (2H, m), 2.91 (2H, q, J=7.1 Hz), 3.86 (1H, t, J=5.9 Hz), 7.18—7.38 (6H, m), and 7.51—7.53 (2H, m). ^{13}C NMR δ=13.14, 28.44, 37.63, 47.43, 60.81, 123.44, 123.60, 126.46, 126.87, 127.03, 127.34, 127.48, 127.61, 133.88, 134.61, 135.88, and 137.34. Exact mass: Calcd for $C_{17}H_{19}N$: M, 237.1516. Found: *m/z* 237.1762.

***cis*-9-*t*-Butylamino-10-methoxy-9,10-dihydrophenanthrene (7).** ^1H NMR δ=1.20 (9H, s), 1.67 (1H, brs), 3.20 (3H, s), 4.06 (1H, d, J=3.2 Hz), 4.11 (1H, d, J=3.2 Hz), 7.20—7.44 (6H, m), and 7.68—7.97 (2H, m). ^{13}C NMR (at 50 °C) δ=30.38, 50.76, 53.82, 56.38, 82.04, 123.32, 124.27, 126.82, 126.91, 127.86, 128.05, 129.37, 129.60, 133.06, 133.90, 134.35, and 139.51. Exact mass: Calcd for $C_{19}H_{23}NO$: M, 281.1778. Found: *m/z* 281.1791.

Thermal Reaction. Aliquot portions (2 cm^3) of diphenyl ether solutions of **1**—**7** and **9** (0.05 mol dm^{-3}) were introduced into Pyrex tubes (8 mm i.d.), thoroughly degassed by four freeze-pump-thaw cycles under reduced pressure, and then heated in an electric furnace that had been preheated at a given temperature. The products analyses of the thermal reactions of **1**—**7** and **9** were performed by GLC on a Shimadzu GC-14A using a capillary column (CBP1-M25-025). Since **8** decomposed under GLC analysis conditions, an analysis of the thermal reaction of **8** in dibutyl ether was performed by HPLC on a Waters 510 and 484-UV detector using μ-Bondapak C_{18} (Waters Co., Ltd.); monitor: 375 nm, eluent: MeOH–H_2O (9 : 1).

The reaction products, phenanthrene, 9-aminophenanthrene,[9] 9-methoxyphenanthrene, anthracene, and 9-aminoanthracene, were identified by direct comparison with authentic samples on GLC or HPLC. The preparation of 9-*t*-butylaminophenanthrene was performed by the reaction of **7** (0.2 g) with Pd/C (0.1 g) in *p*-xylene (10 ml) at 140 °C.

9-*t*-Butylaminophenanthrene. ^1H NMR δ=1.52 (9H, s), 2.12 (1H, br s), 6.98 (1H, s), 7.24—7.91 (6H, m), and 8.52—8.68 (2H, m). ^{13}C NMR δ=28.78, 50.50, 107.54, 121.36, 122.53, 123.46, 125.24, 126.34, 126.66, 126.93, 127.43, and 128.89. MS *m/z* 249 (M^+). The preparation

of 9-aminoanthracene[10] was performed by the reduction of 9-nitroanthracene with $SnCl_2$ in ethanol.

We are grateful to Professor Y. Inoue of Himeji Institute of Technology for analyzing the optimized conformation using the MM2 molecular mechanics program and to Mr. Ryugo Maeda, Dainippon Ink and Chemicals Inc. for the DSC measurements.

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