54-7; 3,5-dichloronitrobenzene, 618-62-2; 3,4,5-trichloronitrobenzene, 20098-48-0; 2-chloronitrobenzene, 88-73-3; 2,3-dichloronitrobenzene, 3209-22-1; 2,4-dichloronitrobenzene, 611-06-3; 2,5-dichloronitrobenzene, 89-61-2; 2,3,4-trichloronitrobenzene, 17700-09-3; 2,3,5-trichloronitrobenzene, 34283-94-8; 2,4,5-trichloronitrobenzene, 89-69-0; 2,3,4,5-tetrachloronitrobenzene, 879-39-0; 2,6-dichloronitrobenzene, 601-88-7; 2,3,6-trichloronitrobenzene, 27864-13-7; 2,4,6-trichloronitrobenzene, 18708-70-8; 2,3,4,6-tetrachloronitrobenzene, 3714-62-3; 2,3,5,6-tetrachloronitrobenzene, 117-18-0; 2,3,4,5,6-pentachloronitrobenzene, 82-68-8.

Zinc Chloride Catalyzed Decomposition of 1,2-Dihydronaphthalene at 165 °C. A Coal-Related Model Compound Study

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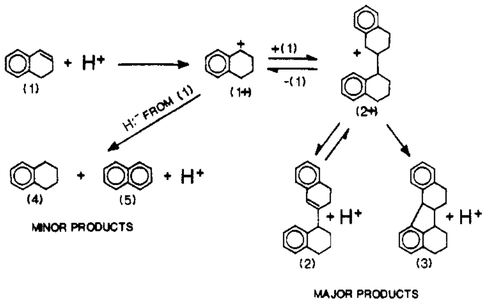
The zinc chloride catalyzed decomposition of 1,2-dihydronaphthalene (1) at 165 °C produces dimers of 1, tetralin, and naphthalene. Zinc chloride functions as a Friedel–Crafts type catalyst by coordinating with a hydroxyl from a water molecule and releasing a proton which initiates a carbonium ion reaction. The stoichiometric role of water has been established by measuring the activity of the zinc chloride–water complex as a function of the degree of hydration of the zinc chloride. The activity maximum occurs at a zinc chloride/water mole ratio of 1:1. Deuterium tracer experiments corroborate the role of water and also verify that the reaction occurs by a carbonium ion mechanism. The carbonium ion nature of the reaction is also inferred by the structures of the products. The 300-MHz ^{1}H NMR spectra of the dimer products are consitent with the previously reported structures of the compounds.

Zinc chloride is used as a catalyst for the hydrogenation of coal[1] and polycyclic aromatic hydrocarbons,[2] but the mechanism of its catalytic action has not been fully established.[3] Because of the importance of coal hydrogenation, a more complete understanding of the zinc chloride catalysis mechanism is also important. Most coal hydrogenations are carried out at thermolytic temperatures, and reactions other than hydrogenation occur concurrently, e.g., pyrolysis and reactions that can be catalytically initiated at subthermolytic temperatures. The latter reactions would proceed at accelerated rates at thermolytic temperatures. A knowledge of these concurrent reactions, some of which constitute the subject of this study, is a necessary background to the understanding of the hydrogenation chemistry.

Scheme I

$$H_2O + ZnCl_2 \rightleftharpoons H^+ + HOZnCl_2^-$$



In this paper the zinc chloride catalyzed subthermolytic decomposition of the coal-related model compound 1,2-dihydronaphthalene (1) is reported. Compound 1 was chosen as the model for the following reasons: (a) it is a hydro aromatic compound, and hydro aromatic structures are believed to be prevalent in coal;[4] (b) its decomposition is catalyzed by zinc chloride;[5] (c) it is the most thermodynamically stable of the possible dihydronaphthalenes, thus eliminating possible rearrangements from less stable to more stable isomers; (d) it contains an alkene-type double bond, which serves two useful purposes. The double bond renders the molecule suitable for future hy-

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(1) (a) Wood, R. E.; Wiser, W. H. *Ind. Eng. Chem. Process Des. Dev.* **1976**, *15*, 144. (b) Zielke, C. W.; Struck, R. T.; Evans, J. M.; Costanza, C. P.; Gorin, E. *Ibid.* **1966**, *5*, 158. Struck, R. T.; Clark, W. E.; Dudt, P. J.; Rosenhoover, W. A.; Zielke, C. W.; Gorin, E. *Ibid.* **1969**, *8*, 546. (c) Moulton, D. S.; Cowley, S. W.; Wiser, W. H. Technical Report for DOE Contract No. (49-18)-2006, Department of Energy Salt Lake City, UT.

(2) (a) Zielke, C. W.; Struck, R. T.; Evans, J. M.; Costanza, C. P.; Gorin, E. *Ind. Eng. Chem. Process Des. Dev.* **1966**, *5*, 151. (b) Reference 1c.

(3) Tanner, K. I.; Bell, A. T. *Fuel* **1981**, *60*, 52.

(4) (a) Deno, N. C.; Curry, K. W.; Greiger, B. A.; Jones, A. D.; Rakitsky, W. G.; Smith, K. A.; Wagner, K.; Minard, R. D. *Fuel* **1980**, *59*, 694. (b) Given, P. H. *Ibid.* **1960**, *39*, 147.

(5) Unpublished work of R.R.B. and L.L.A. has shown that (a) 1,2-dihydronaphthalene decomposes thermally in the absence of zinc chloride, (b) the rate of the thermolytic reaction is greatly accelerated in the presence of zinc chloride, and (c) in the presence of zinc chloride, reaction occurs at temperatures below where the uncatalyzed thermolytic reaction has ceased.

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drogenation studies, and it permits the zinc chloride catalysis mechanism suggested by Zielke et al.[2] to be tested. They have postulated that zinc chloride functions as a Friedel–Crafts-type catalyst by coordinating a hydroxyl ion from water and liberating a proton which attacks a double bond to initiate carbonium ion reactions.

Results and Discussion

This research indicates that in the zinc chloride catalyzed decomposition of 1 at 165 °C, zinc chloride does indeed function as a Friedel–Crafts catalyst and that the decomposition occurs by the carbonium ion mechanism shown in Scheme I.

Reactions. The reactions were run in small, evacuated, sealed Pyrex tubes which were agitated in a constant-temperature oil bath (165 ± 0.5 °C). Reaction mixtures were analyzed by GLC. Blank runs containing 1 but no zinc chloride or water showed no decomposition of the starting material. The products were isolated by preparative GLC and identified by their IR, NMR, and mass spectra. Compounds 2 [(±)-1,2,3,3′,4,4′-hexahydrobinaphthyl] and 3 [(±)-*cis,anti*-4,5,6,6a,6b,7,8,12b-octahydrobenzo[*j*]fluoranthene] are identical with the dimers of 1 reported by Dobbs et al.[6] Small amounts of two other compounds having GLC retention times close to those of 2 and 3 were also formed in the reaction. One of these, X eluted from the GLC immediately after 3 and was shown by its mass spectrum to have the same molecular weight as 2 and 3. Dobbs et al.[6] isolated a compound having very similar concentration (relative to 2 and 3) and GLC retention time properties and showed it to be a diasteriomer of 3. The nature of the other compound, Y, was not investigated, but it is tentatively assumed to be another dimer. Additional discussion concerning the structures of 2 and 3 to given later in the paper.

Mechanism. According to the mechanism shown in Scheme I, zinc chloride functions as a Lewis acid by coordinating with a water molecule. The zinc chloride–water complex (a Brønsted acid) donates a proton to the double bond of 1 to form the more stable benzylic carbonium ion 1^+. The products of the zinc chloride–water reaction have been arbitrarily written as $H^+ + HOZnCl_2^-$, but it has not been established whether the proton is free or loosely bound to the hydroxy–zinc chloride complex. Intermediate 1^+ reacts with an additional molecule of 1 by two different pathways. Via the major route, 1^+ attacks the double bond of 1 to form a new benzylic dimer intermediate (2^+) which eliminates a proton to produce 2. To a lesser extent, 2^+ cyclizes to give 3. This cyclization no doubt occurs by an intramolecular electrophilic aromatic substitution. Via the minor pathway, 1^+, by abstracting a hydride ion from 1, becomes 4, and the molecule of 1 that donated the hydride loses a proton to become 5.

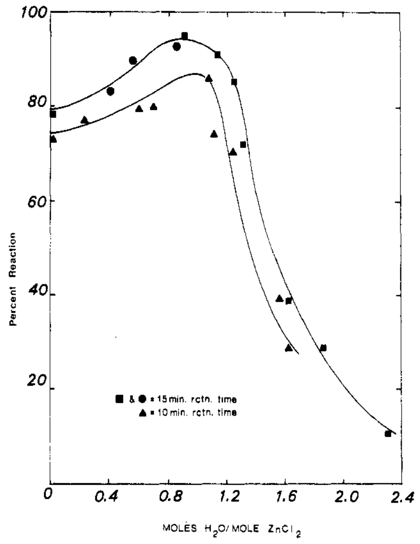
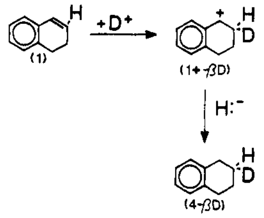


Figure 1. Catalytic activity of the zinc chloride–water complex for the decomposition of 1,2-dihydronaphthalene (165 °C) as a function of the degree of hydration of the zinc chloride.

Scheme II

$$D_2O + ZnCl_2 \rightleftharpoons D^+ + DOZnCl_2^-$$



The active form of the zinc chloride catalyst has been postulated to be $H^+ZnCl_2OH^-$[2] or $(H^+)_2ZnCl_2(OH)_2^{2-}$.[7] In this study, the stoichiometry of the zinc chloride–water complex has been quantitatively determined by a series of sealed-tube experiments in which the molar ratio of 1 to zinc chloride was held constant, while the molar ratio of water to zinc chloride was varied from 0.02 to 2.2. The results of these experiments are plotted in Figure 1. The maxima for the 15-min curve is approximately 0.93 mol of water/mol of zinc chloride while that of the 10-min curve lies near 0.97 mol of water/mol of zinc chloride. Obviously, the optimum water to zinc chloride molar ratio is one. Whether absolutely anhydrous zinc chloride catalyzes the reaction has not been established because the reaction has not been carried out in the presence of totally dry zinc chloride.[8] Moulton, Cowley, and Wiser[1c] have shown, however, that absolutely anhydrous zinc chloride (prepared from molten zinc and dry HCl in vacuo) does not abstract hydride or catalyze the protonation of double bonds.

The curves in Figure 1 show that the rate of reaction (percent reaction/time) drops rapidly as the water/zinc chloride molar ratio increases beyond 1. This is believed to happen because zinc, being electron deficient, coordinates with an unshared electron pair on the oxygen of a water molecule. The coordinated oxygen, by sharing an electron pair with zinc, acquires a positive charge and withdraws electron density from its O–H bonds, weakening them and allowing a proton to be released. It is postulated that when more than one water molecule coordinates to zinc, zinc's attraction for electron density begins to saturate, and the coordinated oxygens are more loosely bound. These oxygens acquire less positive charge and withdraw less electron density from their O–H bonds, causing protons to be less readily released than when only one water molecule is coordinated.

If the reaction occurs by the carbonium ion mechanism shown in Scheme I, then substitution of deuterium oxide for water would cause deuterium to be incorporated as

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(6) Dobbs, T. K.; Hertzler, D. V.; Keen, G. W.; Eisenbraum, E. J.; Fink, R.; Hassain, M. B.; van der Helm, D. *J. Org. Chem.* **1980**, *45*, 4769.

(7) Olah, G. A. "Friedel–Crafts and Related Reactions"; Wiley: New York, 1973; Vol. 1.

(8) The drybox environment in which the zinc chloride was transferred was not absolutely anhydrous, since zinc chloride in an open vessel in the drybox slowly gained weight (0.2-mg weight gain/g of $ZnCl_2$/min). Corrections were made by assuming the weight gain to be water. Thus tubes to which no water was intentionally added were calculated to contain ca. 0.02 mol of water/mol of zinc chloride.

Table I. Deuterium Content of Tetralin from Reaction of 1,2-Dihydronaphthalene with $ZnCl_2 \cdot D_2O$ at 165 °C

sample	reaction time, min	av no. of atoms/molecule			
		aromatic H			
		NMR	IR	α-H (NMR)	β-H (NMR)
undeuterated tetralin		4.03 ± 0.04		4.00 ± 0.08	4.09 ± 0.12
tetralin + $ZnCl_2 \cdot D_2O$	20	3.61 ± 0.04	3.24 ± 0.15	4.00 ± 0.06	4.16 ± 0.02
tetralin from rctn of	12	3.94 ± 0.05	3.88 ± 0.04	4.00 ± 0.03	3.63 ± 0.04
1,2-dihydronaphthalene	20	3.58 ± 0.01	3.67 ± 0.03	4.00 ± 0.04	3.65 ± 0.02
with $ZnCl_2 \cdot D_2O$	40	2.62 ± 0.08	2.66 ± 0.09	4.00 ± 0.23	3.08 ± 0.07

Table II. Deuterium Content of Unreacted 1,2-Dihydronaphthalene from the Reaction of 1,2-Dihydronaphthalene with $ZnCl_2 \cdot D_2O$ at 165 °C

sample	reaction time, min	av no. of H atoms/molecule		
		aromatic H	3-H	4-H
undeuterated 1,2-dihydronaphthalene		4.03 ± 0.04	1.03 ± 0.01	1.00 ± 0.02
unreacted 1,2-dihydronaphthalene	12	3.89 ± 0.02	0.98 ± 0.06	1.00 ± 0.02
from rctn of 1,2-dihydronaphthalene with $ZnCl_2 \cdot D_2O$	15	3.88 ± 0.03	1.00 ± 0.01	1.00 ± 0.01

Table III. Material Balance for the $ZnCl_2 \cdot H_2O$-Catalyzed Decomposition of 1,2-Dihydronaphthalene at 165 °C

time, min	concn, rel moles							matl balance (Σ rel moles)
	1	4	5	2 × 2[a]	2 × 3[a]	2 × X[a,b]	2 × Y[a,b]	
5.60	0.915	0.007	0.008	0.058	0.027	0.013	0.001	1.03
10.03	0.814	0.011	0.013	0.127	0.046	0.024	0.001	1.04
15.24	0.639	0.019	0.019	0.248	0.091	0.045	0.003	1.06
20.22	0.478	0.020	0.022	0.295	0.095	0.052	0.004	0.97
29.66	0.437	0.034	0.029	0.393	0.117	0.062	0.006	1.08
39.71	0.199	0.037	0.031	0.446	0.142	0.071	0.007	0.93
59.94	0.052	0.042	0.031	0.419	0.161	0.069	0.008	0.78
120.25	0.014	0.065	0.046	0.475	0.288	0.073	0.011	0.91

[a] Two times the relative dimer concentration is shown in order to express relative moles of dimer in terms of relative moles of 1,2-dihydronaphthalene. This allows the material balance to be obtained by simple addition of the relative concentrations. [b] See paragraph 4 of this paper.

shown in Scheme II; i.e., **I** should deuterate to produce **1**$^+$-***βd***, since the more stable benzylic ion forms preferentially. The deuterium would then be found in the β position of **4** (**4-*β-d***) and in the **3** position of unreacted **1** if the protonation of **1** to **1**$^+$ were reversible to any extent. (Compound **4** was used to trace the deuterium rather than **2** or **3** because of the considerable experimental difficulty associated with the isolation and purification of **2** and **3**.)

The deuterium tracer experiments were sealed-tube reactions in which **1** and $ZnCl_2 \cdot D_2O$ were agitated for a predetermined time at 165 °C, and the unreacted starting material and products were separated and isolated by preparative GLC. The position and quantitative extent of deuteration were determined by the loss in the integrated 60-MHz ^1H NMR peak area. Aliphatic deuteration was qualitatively verified by the appearance of the infrared C–D stretching band at 2170 cm^{-1}. It should be noted that this band does not distinguish α from β deuteration. Aromatic deuteration also occurred, as evidenced by the appearance of an infrared C–D stretching band at 2265 cm^{-1}. The aromatic deuteration was quantitatively measured both by NMR integration loss and by using Beer's law to calculate the loss of C–H bond concentration from the decrease in the infrared C–H stretching intensity of the aromatic band at 3020 cm^{-1}.

The results of the tetralin analysis are shown in Table I. The relatively good agreement between the IR and NMR values for aromatic deuteration serve as an independent verification of the validity of the NMR measurements.

The product from a blank run with undeuterated **4** and $ZnCl_2 \cdot D_2O$ as starting materials showed no deuteration at any of the aliphatic ring positions (no NMR integration loss, no C–D stretch at 2170 cm^{-1}) but did show aromatic deuteration. All three samples of **4** from the reaction of **1** with $ZnCl_2 \cdot D_2O$ (Table I) showed aliphatic deuteration in the β position only and also aromatic deuteration. The fact that the blank run showed no aliphatic deuteration indicates that deuterium appears in the aliphatic ring of tetralin only through deuteration of the double bond of **1**. The experimental results shown in Table I support the details of Scheme II, both with regard to the carbonium ion nature of the mechanism and also with regard to the fact that zinc chloride functions as an agent to transfer protons from water to the double bond of **1**.

The data in Table II indicate that there was a small amount of aromatic deuteration in the isolated, unreacted starting material, **1**, but within the errors of the measurements, no deuterium added to the 3-position of **1**; i.e., the protonation of **1** to form **1**$^+$ cannot be reversible to an extent greater than the magnitude of the errors in the measurements.

Concentration vs. time data for the disappearance of **1** and the appearance of products were obtained from a preliminary kinetic experiment.[9] From these data (Table III) it can be seen that after 1 h the concentration of **1** was decreasing, and the concentration of **3** was still increasing,

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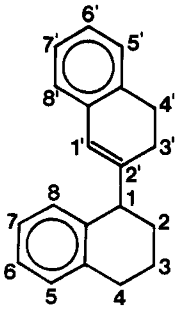
[9] Application of the steady-state approximation to intermediates I$^+$ and II$^+$ of Scheme I gives the expression $-d[1]/dt = k_{obsd}[H^+][1]$. Since the reaction is acid catalyzed, $[H^+]$ is constant, and the kinetics should be pseudo first order. (The concentration of the catalyst is also constant and is included as part of k_{obsd}.) The concentration vs. time data for the disappearance of 1 (Table III), when substituted into an integrated form of a first-order rate equation, gave what appeared to be a first-order plot. The data, however, were of insufficient accuracy to yield a certain conclusion with regard to the reaction order.

Table IV. 300-MHz ^1H NMR Spectrum of Compound 2



shift, δ	no. of protons	peak shape[a]	assignment
7.18	1	d	
7.09	6	m	aromatic
6.96	1	d	
6.19	1	s	1'
3.68	1	approx dd	1
2.76	4	m	4', 4
2.13	2	m	
1.92	2	m	2, 3, 3'
1.78	2	m	

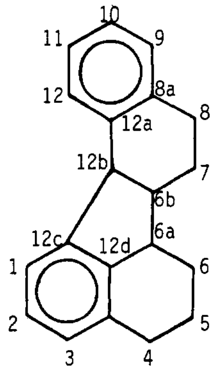
[a] s = singlet, d = doublet, m = complex multiplet.

but the concentration of 2 had become nearly constant. This suggested that the reaction $2^+ \rightleftharpoons 2 + H^+$ (Scheme I) was reversible. To test this hypothesis, we heated a mixture of dimers 2 and 3 (free of 1, 4, and 5) (165 °C) in the presence of zinc chloride monohydrate (tube reaction). GLC analysis of the reaction product showed a large decrease in the concentration of dimer 2 and a similar increase in the concentration of dimer 3. Smaller amounts of 1, 4, and 5 were also formed. In another tube reaction, pure 3 was heated (165 °C) in the presence of zinc chloride monohydrate. Some decomposition to 4 and 5 occurred, but no 2 or 1 was formed. In a control experiment, a mixture of dimers 2 and 3 (free of 1, 4, and 5) was heated (165 °C) in the absence of zinc chloride and water. In this case, no change in the concentrations of 2 or 3 occurred, and no 1, 4, or 5 was produced. It is evident that reactions $1^+ + 1 \rightleftharpoons 2^+$ and $2^+ \rightleftharpoons 2 + H^+$ (Scheme I) are reversible but that the reaction $2^+ \rightarrow 3 + H^+$ is not. These results corroborate those of Dobbs et al.,[6] who used an acidic ion-exchange resin rather than zinc chloride–water as the catalyst. No direct measurements have been made to support the proposed hydride transfer in eq 1. The hydride transfer has been inferred from the existence of 1^+ (see deuterium tracer work above) and the formation of products 4 and 5. Table III indicates that 4 and 5 were formed in equal amounts for almost 1 half-life, but thereafter, 5 was formed in lesser amounts than 4. These data are consistent with the proposed hydride transfer, since initially 1^+ could pick up hydride ion only from 1, and each 1 that donated a hydride ion would lose a proton to give a molecule of 5. Later in the reaction, 2 and/or 3 could also donate hydride ion to 1^+, and less 5 than 4 would be produced.

$$1^+ + 1 \xrightarrow[\text{trans}]{\text{H:}^-} 4 + 5 + H^+ \text{ (Scheme I)} \qquad (1)$$

It is possible that trimers or higher polymers are formed by reaction of 2^+ with 1 (see Scheme I). Trimers, if produced, would not be detected since they would not pass through the GLC columns used to analyze the reaction mixture. The material balance data shown in Table III indicate that the known products account for the entire reaction mixture for about 1 half-life. Trimer or higher polymer formation would explain the low material balance in the latter part of the reaction.

Table V. ^{13}C and 300-MHz ^1H Chemical Shifts[a] for Compound 3



$\delta(^{13}C)$	assignment	$\delta(^1H)$[b]
145.0	12c	*c*
144.3	12d	*c*
138.2	12a[d]	*c*
137.3	8a[d]	*c*
134.6	3a	*c*
128.8	3	7.02
128.7	12[e]	7.38
126.9	2	7.06
126.4	11[f,g]	7.03
126.2	9[e,g]	6.86
125.9	10[f]	7.02
122.9	1	7.29
47.7	6b	2.43
47.0	12b	4.06
43.0	6a	2.6
27.8	5	1.11, 2.07
26.9	8	2.87, 2.7
26.6	4	2.6 ± 0.1
23.8	7	1.84, 1.99
23.7	6	1.58, 1.95

[a] In parts per million from Me_4Si. ^{13}C chemical shifts were measured relative to internal dioxane and were converted to the Me_4Si using $\delta_{Me_4Si} - \delta_{dioxane} = 67.2$ ppm. Proton shifts are relative to internal Me_4Si. [b] ^1H chemical shift indicates center of observed multiplet and is not corrected for second-order effects. [c] These carbons do not, of course, have a large, one-bond coupling to any proton, but they do exhibit long-range splittings. The ^{13}C assignments have been made by comparison of the shifts to those of similar compounds and by observing the effects of decoupling the aromatic protons. Due to uncertainties in this procedure, these assignments must be considered tentative. [d-f] Having been determined by single-frequency decoupling, these assignments may be interchanged due to the lack of absolute characterization of the proton spectrum. [g] Single-frequency decoupling supports the assignment as given; however, the appearance of the multiplets in the coupled spectrum with concomitant proton irradiation in the aliphatic region indicates the assignment should be reserved.

Structures of Compounds 2 and 3. Compound 2, obtained by preparative GLC of the crude reaction mixture, was isolated as a viscous oil. Analytical GLC of the isolated 2 showed that it contained small amounts of 3 and some other unknown substances. The mass spectrum of the isolated 2 indicated its molecular weight to be 260, and its 60-MHz ^1H NMR spectrum was identical with that of an authentic sample of 2 prepared by the method of Dobbs et al.[6] The 300-MHz ^1H NMR spectrum of 2, tabulated in Table IV, is also consistent with its proposed structure.

Compound 3 was obtained as an oil by preparative GLC and was recyrstallized from methanol. Its mass spectrum showed it to have a molecular weight of 260, and its melting point (88–89 °C) indicates that it is the (±)-cis,anti isomer recently characterized by Dobbs et al.[6] Its 300-MHz ^{1}H and ^{13}C NMR spectra, tabulated in Table V, are consistent with the crystallographic data of Dobbs et al.[6] Integration indicates the presence of 20 protons, the signals for nine of which are isolated from other resonances, so that for many cases the patterns approach first order. In the aromatic region the three resolved doublets must result from protons having a single vicinal proton neighbor. Observation of the coupled ^{13}C spectrum (vide infra) together with single-frequency ^{1}H irradiation reveals that the partially resolved triplet at 7.06 ppm represents the signal of H-2. Homodecoupling of that proton collapses only one isolated resonance, that of the doublet at 7.29 ppm, indicating that the other two resolved doublets pertain to H-9 and H-12. The remaining aromatic protons are in the band at 7.0 ppm. In the aliphatic region ^{13}C–^{1}H and ^{1}H–^{1}H decoupling was used to make all assignments; for example the doublet at 4.06 ppm must result from H-12b, as it is adjacent to two aromatic rings; homodecoupling immediately locates H-6b at 2.93 ppm. Further utilization of the ^{1}H–^{1}H technique allows most assignments to be made; less definitive cases were verified by use of ^{13}C–^{1}H. The presence of large vicinal coupling constants indicates that a single conformation is probably dominant, but due to signal overlap of one of each geminal pair attached at C-5, C-6, C-7 and C-8 and near degeneracy of the protons of C-4, it is not possible to determine with complete certainty which are axial and which are equitorial. Generally speaking, the equitorial proton of an axial–equitorial pair is found downfield.

In the aromatic portion of the ^{13}C spectrum, five unprotonated and seven protonated carbons are observed. The coupled spectrum reveals that one protonated carbon is represented by a simple doublet. By consideration of the fingerprint criterion of Gunther et al.[10] for ortho-disubstituted benzenes, this can only be C-2. Some other resonances can be classified as resulting from α or β naphthelenic carbons by this means. Further assignments were made by single-frequency decoupling and comparison to the spectra of related compounds. Since the proton spectrum has not been totally characterized, some of the assignments are tentative.

The aliphatic portion of the ^{13}C spectrum arises from three methine and five methylene groups, as indicated by the coupled spectrum. Selective ^{13}C–^{1}H decoupling enables the carbons to be associated with individual protons, which in turn allows the assignments given in Table V to be made.

Experimental Section

Infrared spectra were recorded on a Beckman IR-33 spectrometer. NMR spectra were recorded on a Varian T-60 or a Varian SC-300 superconducting spectrometer. On the latter instrument, ^{1}H NMR spectra were obtained at 300.2 MHz, and ^{13}C spectra were obtained at 75.5 MHz, both in a Fourier transform mode. Mass spectra were taken on a Varian MAT-311 spectrometer interfaced with a Varian 620-I data system. GLC analyses and preparative separations were done on a Varian Aerograph 2800 preparative chromatograph. Integration of the GLC output was done with a Hewlett-Packard 3380A integrator. The following GLC columns and conditions were used: (A) $^1/_8$ in. × 3 m stainless steel, 10% Carbowax 20M on 80/100 Chromosorb W, He at 40 mL/min, 150 °C for 15 min and then 10 °C/min to 200 °C; (B) $^1/_8$ in. × 3 m stainless steel, 10% SP2100 on 80/100 Chromosorb W, He at 60 mL/min, 150 °C for 5 min, 10 °C/min for 10 min, and then 3 °C/min up to 300 °C; (C) $^3/_8$ in. × 23 ft aluminum, 20% Carbowax 20M on 45/60 Chromosorb A, He at 200 mL/min, 200 °C isothermal; (D) $^3/_8$ in. × 18 ft aluminum, 20% SP2100 on 45/60 Chromosorb A, He at 200 mL/min, 265 °C isothermal.

Anhydrous Zinc Chloride. Stock zinc chloride was placed in the bottom of a Pyrex tube (25 × 350 mm) and covered with thionyl chloride (24 h at room temperature). The thionyl chloride was removed under vacuum, and the zinc chloride was vacuum distilled (0.1–1 torr) by slowly (several hours) pushing the inclined tube into a tube furnace (450–500 °C).

1,2-Dihydronaphthalene (1). Compound 1 was prepared by the method of Yagi and Jerina,[11] i.e., reduction of tetralone to 1,2,3,4-tetrahydro-1-naphthol and dehydration of the naphthol in glacial acetic acid containing a catalytic quantity of concentrated hydrochloric acid.

Sealed-Tube Reactions. (a) Determination of the Optimum Water/Zinc Chloride Mole Ratio. In a drybox, 10–15 mg of anhydrous zinc chloride was weighed into open Pyrex tubes (5 × 50 mm) which were then stoppered with rubber caps. After removal of the tubes from the drybox, water (5–25 μL) was added through the rubber cap with a syringe (water/zinc chloride mole ratio 0.02–2.3), and the tubes were reweighed. A quantity of 1 was then added from a syringe with subsequent weighing to give a 1/zinc chloride mole ratio of 1.5:1. The tubes were degassed, sealed, agitated (10 or 15 min) in a constant-temperature oil bath (165 ± 0.5 °C), quenched in a water bath, and centrifuged. The tubes were opened, and a known quantity of 2-methylnaphthalene in benzene was added as an internal standard. After the mixtures were stirred, the tubes were again centrifuged, and the upper liquid phase was decanted. GLC column A was used to analyze for 1, 4, and 5.

(b) Deuterium Tracer Experiments. The procedure was the same as that outlined in part a except that deuterium oxide was used rather than water, and the quantities were scaled up by a factor of 10. When the tubes were opened, no internal standard was added. Compounds 1 and 4 were separated and collected by using preparative GLC column C. The NMR values reported in Tables I and II are the averages of five integrations of each sample. The averages of the integrations for the α-hydrogens in undeuterated and deuterated 4 (Table I) were normalized to 4.00, and all other integrations were scaled proportionately. Likewise, the average of the integrations for the hydrogen in the 4-position of compound 1 (Table II) was normalized to 1.00, and the other integrations were scaled proportionately. All IR measurements were made in a calibrated, variable path length cell.

(c) 1,2,3,3′,4,4′-Hexahydro-1,2′-binaphthyl (2) and 4,5,6,6a,6b,7,8,12b-Octahydrobenzo[*j*]fluoranthene (3). These tube reactions were identical (scale, procedure, and conditions) with those of part b, except that water was used rather than deuterium oxide. Compounds 2, 3, X, and Y (see paragraph 4) were separated and collected by using preparative GLC column D. Compound 2 was isolated as a viscous oil which could not be crystallized. Analytical GLC of the isolated 2 (column B) showed that it contained small amounts of 3 and some other unknown substances: IR (neat) 3075 (m), 3025 (m), 1606 (w), 1579 (w), 1493 (s), 1457 (s) (aromatic ring), 749 (s), 712 (w) (ortho-disubstituted aromatic ring), 3040 (m), 1648 (m) (double bond), 808 (m) (trisubstituted double bond) cm^{-1}; ^{1}H NMR (see Table IV); mass spectrum (70 eV), *m/e* (relative intensity) 260 (99.7, M^+), 229 (65), 215 (46), 156 (36), 130 (100), 115 (55), 108 (63), 95 (45).

Compound 3, as isolated, contained some 2 and was recrystallized three times from methanol: mp 88–89 °C (lit.[6] mp 92–93 °C); IR (KBr) 3075 (m), 3030 (m), 1603 (m), 1573 (w), 1491 (s), 1453 (s) (aromatic ring), 760 (s) (ortho-disubstituted aromatic ring) cm^{-1}; ^{13}C and ^{1}H NMR (see Table V); mass spectrum (70 eV), *m/e* (relative intensity) 260 (100, M^+), 232 (94), 217 (95), 202 (68), 169 (99.9), 130 (88), 115 (59), 108 (58), 91 (61); calcd mass for $C_{20}H_{20}$ *m/e* 260.1565, found *m/e* 260.1560 (M^+).

The nature of compound X was investigated only to the extent of obtaining its mass spectrum (70 eV): *m/e* (relative intensity) 260 (91, M^+), 232 (49), 169 (95), 141 (54), 129 (100), 115 (42), 104 (61).

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(d) Establishment of the $1^+ + 1 \rightleftharpoons 2^+ \rightleftharpoons 2 + H^+$ Equilibrium (Scheme I). These sealed-tube reactions were similar to those of part a in scale and procedure. Compound **3** or a mixture of **2** and **3** was used instead of **1**; the mole ratio of water to the zinc chloride was 1. The reaction time was 1–8 h at 165 °C. When the tubes were opened, no internal standard was added. GLC column A was used to analyze for **1**, **4**, and **5**, and GLC column B was used to analyze for the dimers.

Preliminary Kinetic Experiment (Table III). This reaction was run in a vessel consisting of two separate compartments in the configuration of an inverted Y. One compartment was loaded with zinc chloride monohydrate and the other with **1** (zinc chloride monohydrate/**1** molar ratio of 1:10). The apparatus was swept with nitrogen, equilibrated to 165 ± 0.5 °C in a constant-temperature oil bath, and then tilted to allow the reactants to mix. The two-phase reaction mixture was magnetically stirred, and samples of the upper hydrocarbon phase were withdrawn with a syringe at predetermined times. The samples were mixed with a known amount of internal standard (2-methylnaphthalene in benzene) and analyzed on GLC columns A (for **1**, **4**, and **5**) and B (for dimers).

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Occurrence of Even Telesubstitution in the Amination of Halogeno-2,6-naphthyridines[1-3]

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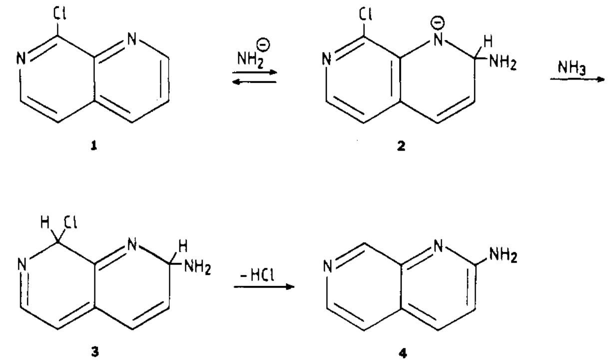
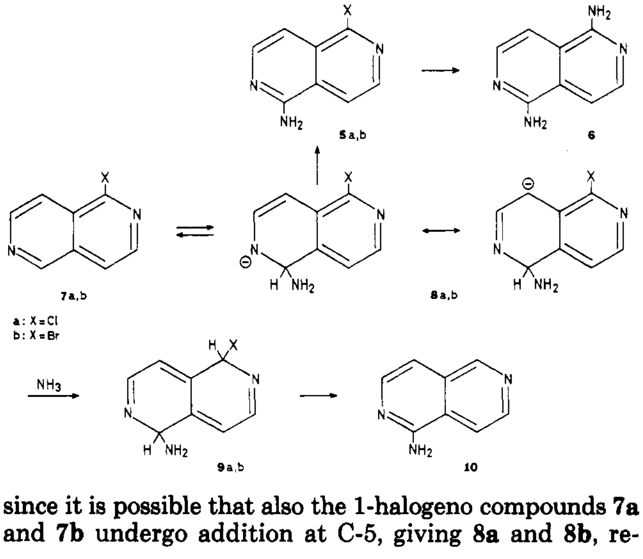
The conversion of 1-halogeno-2,6-naphthyridines into 1-amino-2,6-naphthyridine is shown to proceed via an even telesubstitution process [$S_N(AE)^{tele}$ process]. The amination of 2-bromo-1,5-naphthyridine into 2-amino-1,5-naphthyridine is shown to proceed via an $S_N(AE)^{ipso}$ substitution mechanism.

It has been reported[4,5] that 8-chloro-1,7-naphthyridine (**1**) when reacted with potassium amide in liquid ammonia (KNH_2/NH_3) undergoes a teleamination, leading to 2-amino-1,7-naphthyridine (**4**). As an even number of positions lies between the position of attack of the nucleophile and the position of departure of the leaving group, this reaction can be classified as an *even* telesubstitution. Odd telesubstitutions are also described, as exemplified by the amination of 7-chloro-2-deuterio-1,8-naphthyridine into 2-amino-1,8-naphthyridine.[4,5] The introductory step of the 1,4-teleamination of 8-chloro-1,7-naphthyridine (**1**) is the σ-adduct formation at position 2, yielding 2-amino-8-chloro-2,*X*-dihydro-1,7-naphthyridinide (**2**); its formation has been proved by NMR spectroscopy. Adduct **2** undergoes protonation at C-8 into **3** which by a base-catalyzed dehydrohalogenation gives product **4** ($S_N(AE)^{tele}$, Scheme I). This result induced us to study in more detail the generality of the phenomenon of even teleaminations in the naphthyridine series.

Scheme I



Scheme II



Recent investigations[3] have shown that 2,6-naphthyridine undergoes exclusively σ-adduct formation at C-1 (C-5) when dissolved in KNH_2/NH_3. This result induced our interest in the behavior of the 1-chloro(bromo)-2,6-naphthyridine (**7a,b**) toward potassium amide since it is possible that also the 1-halogeno compounds **7a** and **7b** undergo addition at C-5, giving **8a** and **8b**, re-

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