curvature should be obtained for reactions run in water. A plot of k_{obsd} vs. a_H for reactions of **5** in 0.1–1.0 M HCl was linear, and differences in partitioning ratios in the two solvents would have to be much larger than sensible to account for curvature. It is unlikely that the values of K_{SH} and K_{SD}, the dissociation constants for protonated and deuterated **1–6**, are in the acidity range of this study. However, if they were, then K_{SH} would have a predicted value 2–5 times greater than that of K_{SD}, and should be kinetically detectable in the acidity range of the study. Regarding this point, the pK_a of 2,6-dimethyl-γ-pyrone, a stable model for **1–6**, is only ~0.15 pK_a unit larger in D_2O than in H_2O and a similar pK_a difference between SH^+ and SD^+ would require that K_{SH} be kinetically detectable if K_{SD} is.

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Base-Catalyzed Carbon-to-Oxygen Acyl Rearrangement via an Aromatic Transition State[1]

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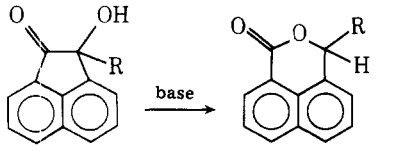
Homologues of 2-hydroxyacenaphthenone undergo a facile base-catalyzed carbon-to-oxygen acyl rearrangement to peri ring-expanded naphthalides. The several examples studied include rearrangement of the cyanohydrin of acenaphthenequinone. The rearrangement is catalyzed by nonnucleophilic bases such as the bicyclic tertiary amidine DBU, and the naphthalide product can be crystallized directly from the reaction mixture under hydroxide catalysis. Consequently, the reaction does not appear to proceed via nucleophile-induced peri ring cleavage to an intermediate hydroxynaphthoic acid followed by lactonization. An alternative mechanism is proposed that involves base-catalyzed formation of an intermediate α-oxanol followed by bridgehead carbon–carbon bond cleavage to an aromatic carbanion isoelectronic with the 14 π-electron phenalenyl carbanion.

Cyclic, unsaturated ketol homologues of 2-hydroxyacenaphthenone undergo a facile, frequently quantitative carbon-to-oxygen acyl rearrangement[3] to peri ring-expanded naphthalides. In earlier reports of the overall reaction,[4,5] the rearrangement was interpreted as first involving nucleophile (hydroxide)-induced cleavage of the peri carbon–carbon bond, giving an open-chain hydroxynaphthoic acid, followed by lactonization to the naphthalide. The purpose of the present paper is threefold: to report several new examples of the rearrangement, to present evidence that the reaction does not proceed via the open-chain hydroxy acid intermediate, and to propose alternatively that this facile rearrangement proceeds via a cyclic, aromatic transition state.

Results and Discussion

The new examples of the reaction are shown in Chart I. Cyanohydrin **1**, precursor of acenaphthenones **2** and **3**, is prepared by addition of HCN to acenaphthenequinone (ACQ) at pH 5.0. The compound is thermodynamically unstable and at neutral pH is decomposed by water and methanol (and presumably basic solvents in general); at higher pH, the ketol rearranges to naphthalide **8**. However, the compound is kinetically stable at low pH and may be recrystallized from acetic acid–water. Acenaphthenones **4–7** are prepared by appropriate Grignard addition to ACQ; the mesityl and tipyl (2,4,6-triisopropylphenyl) homologues have previously been reported.[6] Unlike acenaphthenones **1–7**, naphthalides **8–14** exhibit intense blue fluorescence under UV light, and this allows convenient monitoring of the rearrangement by TLC.

Chart I. Base-Catalyzed Carbon-to-Oxygen Acyl Rearrangement



1, R = CN	**8**, R = CN
2, R = $CONH_2$	**9**, R = $CONH_2$
3, R = CO_2Et	**10**, R = CO_2Et
4, R = Ph	**11**, R = Ph
5, R = Mes	**12**, R = Mes
6, R = Tip	**13**, R = Tip
7, R = CH_3	**14**, R = CH_3

Carbon-to-oxygen acyl rearrangement of **1–7** occurs under generally mild base catalysis and in high yield. That the reaction is not observably acid catalyzed is demonstrated by the failure of ketol **3** to rearrange under the acidic conditions of its synthesis. In contrast, base-catalyzed rearrangement occurs readily at low temperature with nonnucleophilic bases such as DBU (1,5-diazabicyclo[5.4.0]undec-5-ene)[7] in DMF solution and KH suspended in benzene. Under homogeneous hydroxide catalysis, the naphthalide product can be crystallized directly from the strongly basic reaction mixture. (The solvent or substrate must provide a proton, and hence the Grignard adducts giving **4–7** do not rearrange.) Rearrangement of the deuterioxy-labeled ketol **5** by *tert*-butoxide in benzene solution can be used to label the naphthalide with deuterium in the 3 position.[8] The rate of acyl rearrangement decreases as a function of substituent R in the order $CO_2Et > CONH_2 \gg Ar \gg CH_3$ and decreases as a function of solvent under *tert*-butoxide catalysis in the order $Me_2SO >$ benzene > *tert*-butyl alcohol.

A reaction mechanism involving nucelophile-induced carbon–carbon bond cleavage to an open-chain hydroxy acid intermediate is unlikely under the above conditions. The bicyclic tertiary amidine DBU, chosen as a base because of its nonnucleophilicity, is probably not sufficiently nucleophilic to cleave the peri ring of acenaphthenones[9] at room temperature. Likewise, rearrangement of overcrowded ketol **5** by KH suspended in benzene would require that the nucleophile be the conjugate base of the substrate, an unlikely event since the hydroxyl and outside methyl groups of that compound in-

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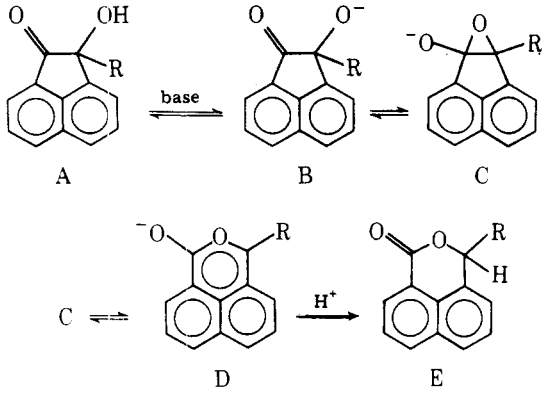
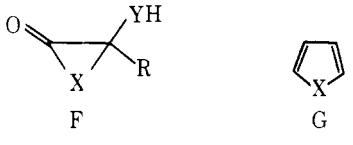
Chart II. Proposed Aromatic Mechanism



teract with a ground-state strain of about 10 kcal/mol.[10] Crystallization of the hydroxide-catalyzed naphthalide product directly from the strongly basic reaction mixture appears to exclude the nucleophilic mechanism since the open-chain hydroxy acid intermediate would be trapped under these conditions as the hydroxy carboxylate salt,[11] which could lactonize only very slowly.

A more probable mechanism is shown as sequence A–E in Chart II. The essential features of the mechanism are that the peri ring is cleaved only after formation of tetracyclic intermediate C and cleavage then gives aromatic carbanion D. The second step of the mechanism, equilibrium formation of intermediate α-oxanol C, is well precedented as a general process[12] and has been proposed in another acenaphthenone system.[13] The observed solvent effect probably reflects the effect of solvent on *tert*-butoxide basicity, which in turn affects the equilibrium concentration of α-oxanol C. Aromatic carbanion D is isoelectronic with the 14 π-electron phenalenyl carbanion, whose conjugate acid has a pK_a of only 19.[14] Accordingly, the naphthalides are appreciably acidic, readily evolving hydrogen and generating deep colors when treated with NaH in DMF. The large observed substituent effect on the reaction would follow from carbanion D being the rate-limiting intermediate. According to the Hammond postulate and its generalizations,[15] the transition state for that step is "product"-like and hence has aromatic character.

The aromatic mechanism should be generalizable to other classes of cyclic ketones that have the correct number of π electrons and to α-heteroatoms other than oxygen. That is, the mechanism would be expected for ketones of the form F, where X is a π-electron system such that structure G is aromatic and group Y contains a heteroatom. In the present case, X is the naphthalene nucleus and G is pleiadiene. A simpler case would have X as merely a double bond.



Experimental Section

General. Melting points were determined on a capillary apparatus at 1–2 °C/min and are corrected. The IR spectra, generally as Nujol mulls, were recorded on Perkin-Elmer 137 and 237 B spectrophotometers. TLC employed Eastman Chromogram Sheet 6060 silica gel examined with a UV Mineralight. Further details may be found in the earlier report.[16]

Hydrocyanic Acid (In Situ). A new and convenient method was developed. Below the surface of a stirred solution of 100.9 g (0.80 mol) of oxalic acid dihydrate in 900 mL of water was rapidly added a solution of 39.2 g (0.80 mol) of NaCN in 100 mL of water. The resulting white mixture was stirred for 15 min and then allowed to stand in ice for 2 h. The ice-cold hydrocyanic acid solution was (cautiously) decanted from the insoluble sodium hydrogen oxalate (0.62 mol) through glass wool.

2-Hydroxy-2-cyano-1-acenaphthenone (1). To a stirred solution of 0.8 mol of 0.67 M hydrocyanic acid at pH 5.0 (adjusted with 10% NaOH), as prepared above, was added in one portion 25.8 g (80 mmol) of acenaphthenequinone–sodium bisulfite addition product (ACQ·HSO_3). A solution immediately formed, followed by slow precipitation of a white solid. The mixture was stirred for 2 h at room temperature and 4 h at 0 °C. The resulting white viscous mixture was adjusted to pH 2 and filtered by suction. The solid was dissolved in 250 mL of ether and worked up to give 8.1 g (49%) of white cyanohydrin **1**, which may be recrystallized from toluene to give highly crystalline material: mp 155 °C dec; IR 3450, 2290 (weak), 1720 cm^{-1}; mass spectrum (10 eV), *m/e* (rel intensity) 209 (100), 182 (48), 154 (31). Anal. Calcd for $C_{13}H_7NO_2$: C, 74.63; H, 3.37; N, 6.70. Found: C, 74.72; H, 3.33; N, 6.77.

2-Hydroxy-2-carbamoyl-1-acenaphthenone (2). The crude cyanohydrin **1** prepared from 70 mmol of ACQ·HSO_3 as above was dissolved in 200 mL of glacial acetic acid, to which was then added 200 mL of concentrated HCl dropwise over 15 min. After the mixture was allowed to stand for 45 min, the solvent was removed in vacuo and the solid was washed with acetone (80 mL) and dried to give 7.5 g (est. 95%) of white product. Recrystallization from glacial acetic acid gave pure amide **2**: mp 240–242 °C; IR 3425 (sharp), 3270 (broad), 3205 (shoulder), 1730, 1725 (shoulder), 1670 (strongest band) cm^{-1}; mass spectrum (10 eV), *m/e* (rel intensity) 227 (100), 210 (8), 184 (33), 183 (21), 182 (17), 154 (3). Anal. Calcd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16. Found: C, 68.71; H, 4.08; N, 6.11.

2-Hydroxy-2-carbethoxy-1-acenaphthenone (3). Anhydrous HCl (14.1 g) was added to an ice-cold solution of 4.2 g (20 mmol) of crude dry cyanohydrin **1** in 50 mL of absolute ethanol containing a trace of HCl, and the solution was allowed to stand at 0 °C for 1 h. Water was added, the solution was partially neutralized, and the product was allowed to crystallize to give 3.2 g of white solid. Recrystallization from ethanol–water gave pure ester **3**: mp 105–106 °C; IR 3400, 1730, 1710 (strongest band) cm^{-1}; mass spectrum (10 eV), *m/e* (rel intensity) 256 (100), 210 (53), 183 (72). 182 (36). Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.07; H, 4.65.

A mixture of 0.1 g of pure ester **3** (mp 105–106 °C) and 10 g of 10% aqueous Na_2CO_3 was refluxed for 20 min, at which time it consisted of a water-white homogeneous solution. The mixture was cooled and acidified to give a white solid, mp 210–211 °C (lit.[17] 210–212 °C). The IR spectrum was as expected for naphthalide-3-carboxylic acid and was identical with that of the carbonate saponification product of naphthalide **10**.

2-Hydroxy-2-phenyl-1-acenaphthenone (4). To a stirred solution of 5.5 g (30 mmol) of acenaphthenequinone (ACQ) in 600 mL of dry diglyme (at 35–40 °C to prevent crystallization of the solute) was rapidly added 11 mL (32 mmol) of 2.9 M phenylmagnesium bromide in ethyl ether. After being allowed to stand for 25 min at ambient temperature, the mixture was poured into a mixture of dilute acid and benzene and worked up to give an oil that soon solidified. A sample was washed with 10% aqueous $NaHSO_3$, treated with carbon, and recrystallized from acetic acid–water to give white hydroxy ketone **4**: mp 146–147 °C; IR 3470, 1710, 1680 (shoulder) cm^{-1}; mass spectrum (10 eV), *m/e* (rel intensity) 260 (100), 252 (45), 231 (12). Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.02; H, 4.56.

2-Hydroxy-2-methyl-1-acenaphthenone (7). The compound was prepared analogously to ketol **4** by Grignard addition of methylmagnesium bromide to ACQ in diglyme solution. Recrystallization from ethanol–water gave ketol **7**: mp 121–122 °C; IR 3350, 1700 cm^{-1}.

3-Cyanonaphthalide (8). Method A. To a stirred solution of 9.0 g of NaCN in 300 mL of water was added 9.0 g (30 mmol) of ACQ·HSO_3. The resulting solution was stirred for 15 min, and 150 mL of 33% aqueous $NaHSO_3$ was rapidly added. Stirring was continued for 30 min, and the milky white suspension was collected, washed, and dried to give 5.3 g (91%) of solid. Recrystallization from methanol gave pure naphthalide **8**: mp 165–166 °C; IR 1740 cm^{-1} (no visible CN absorption); NMR ($CDCl_3$ solvent) δ 6.0 (s, 1 H), 6.9–7.8 (aromatic ring protons, total area 6 H); mass spectrum (10 eV), *m/e* (rel intensity) 209 (100), 155 (73). Anal. Calcd for $C_{13}H_7NO_2$: C, 74.63; H, 3.37; N, 6.70. Found: C, 74.54; H, 3.39; N, 6.97.

Method B. To 3 g of 33% aqueous NaCN was added in one portion 0.1 g of powdered, recrystallized cyanohydrin **1**. The rapidly formed solution was acidified with 10% HCl to precipitate a voluminous white solid. TLC demonstrated, by comparison with authentic **8**, virtually quantiative conversion to 3-cyanonaphthalide.

3-Carbamoylnaphthalide (9). To a solution of 0.5 g of pure amide **2** in 1.0 mL of dry DMF was added 0.5 g of DBU (1,5-

diazabicyclo[5.4.0]undec-5-ene). After 30 min at room temperature, 2 mL of glacial acetic acid was added to the deep purple solution; this dispelled the color and crystallization began. The highly crystalline, pure-white material was collected and washed with benzene to give 0.43 g of product. Recrystallization from glacial acetic acid gave large transparent needles of pure naphthalide **9**: mp (sealed tube, under argon) 290 °C dec; IR 3450, 3400, 3350, 3290, 1730, 1680 cm^{-1}; mass spectrum (10 eV), *m/e* (rel intensity) 227 (21), 184 (48), 183 (100), 155 (12). Anal. Calcd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16. Found: C, 68.79; H, 3.81; N, 6.38.

A mixture of 0.1 g of amide **9** (mp 290 °C dec) and 5 mL of 10% NaOH was heated on the steam bath for 30 min. The colorless solution was cooled, acidified with 10% HCl, filtered, and washed to give a white powder: mp 200–204 °C (lit.[17] 210–212 °C); the IR spectrum indicated that it was naphthalide-3-carboxylic acid as prepared from both esters **3** and **10**.

3-Carbethoxynaphthalide (10). Method A. To a stirred solution of 513 mg (2.0 mmol) of ester **3** in 20 mL of anhydrous *tert*-butyl alcohol (freshly distilled from sodium) was rapidly added 1.0 mL (0.1 mmol) of 0.1 M sodium *tert*-butoxide in *tert*-butyl alcohol. The resulting purple color faded in a few seconds, and TLC after 1 min showed quantitative conversion. Water (60 mL) was added, and crystallization began. The solid was collected and washed with water to give 425 mg (83%) of snow-white needles. Recrystallization from petroleum ether gave an analytical sample of naphthalide ester **10**: mp 82–83 °C; IR 1730 cm^{-1}; mass spectrum (10 eV), *m/e* (rel intensity) 256 (46), 183 (100). Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.24; H, 4.70.

Hydrolysis with 10% $NaCO_3$, as for hydroxyacenaphthenone **3**, gave naphthalide-3-carboxylic acid, mp 211–213 °C (lit.[17] 210–212 °C).

Method B. To a solution of 0.1 g of ester **3** in 0.2 mL of dry DMF was added 2 drops of DBU. The mixture immediately turned deep blue. After 20 min, TLC showed clean, nearly quantitative rearrangement to **10**; addition of acetic acid dispelled the color.

Method C. A mixture of 0.1 g of ester **3** and 0.1 g of tri-*n*-butylamine was heated at 150 °C under argon. TLC showed complete conversion to naphthalide **10** in 13 min.

3-Phenylnaphthalide (11). Method A. To a refluxing solution of 521 mg (2 mmol) of ketol **4** in 10 mL of anhydrous *tert*-butyl alcohol under argon was added 4.0 mL (0.4 mmol) of 0.1 M sodium *tert*-butoxide in *tert*-butyl alcohol in three portions over a period of 16 h. TLC showed that the only product formed was naphthalide **11**. Water (60 mL) was added to the hot solution to saturation, and crystallization was allowed. The solid was collected, washed, and dried to give 445 mg (85%) of product, mp 113–114 °C. Recrystallization from ethanol–water gave analytically pure naphthalide **11**: mp 113–114 °C; IR 1725, 1710 (shoulder) cm^{-1}; mass spectrum (10 eV), *m/e* (rel intensity) 260 (100), 155 (18). Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.28; H, 4.73.

Method B. To a solution of ~0.1 g of ketol **4** in 1 mL of DMF was added a few drops of 10% NaOH. TLC of the basic reaction mixture showed that the reaction is rapid, and after approximately 15 min, 1 mL of water was added to saturation and crystallization was allowed.

In a similar experiment, a few drops of 50% KOH was added to a solution of ketol **4** in Me_2SO. The mixture was diluted with water, seeded, and allowed to crystallize. The fluorescent solid was collected (after 3 days), and the pH of the mother liquor was at least pH 11. The IR spectrum (Nujol) demonstrated that the product was naphthalide **11**.

Method C. To a solution of 0.1 g of hydroxy ketone **4** in 0.2 mL of dry DMF was added 0.1 g of DBU. After 2 h on the steam bath, TLC showed essentially complete conversion to naphthalide **11**.

3-Mesitylnaphthalide (12). Method A. To a stirred solution of 3.0 g (10 mmol) of ketol 2-hydroxy-2-mesitylacenaphthenone[6] (**5**) in 60 mL of reagent grade benzene at room temperature was rapidly added 2.0 g of commercial potassium *tert*-butoxide. After 5 min, 10 mL of water was added and the mixture was worked up to give a solid, which was recrystallized from CCl_4 to give 2.5 g (83%) of pure naphthalide **12**: mp 210–211 °C; IR (C_2Cl_4) 1732 cm^{-1}; UV (hexane) 214 nm (ϵ 47 000), 245 (24 800), 312 (7800), 329 (5800); NMR;[8] mass spectrum (low eV), *m/e* (rel intensity) 302 (80), 147 (100) (exact mass *m/e* 147.0809, $MesCO^+$). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.35; H, 6.04.

Method B. To a heterogeneous mixture of two KOH pellets and 2 mL of Me_2SO was added approximately 20 mg of pure ketol **5**. A dark color formed on the surface of the KOH but was continuously swept into solution and dispelled by stirring. After 2 min, TLC showed quantitative conversion into naphthalide **12**.

Method C. Potassium hydride (oil dispersion) was added to a solution of ketol **5** in benzene. Hydrogen evolution was vigorous, and in a few minutes TLC showed naphthalide **12** as the major component.

3-Tipylnaphthalide (13). Ketol 2-hydroxy-2-tipylacenaphthenone[6] (**6**) was treated with potassium *tert*-butoxide in benzene solution analogously to the reaction of ketol **5** above (which gave homologue **12**). TLC showed conversion into a fluorescent product, presumably naphthalide **13**, which, however, was not further characterized or isolated.

3-Methylnaphthalide (14). Method A (Unsuccessful). A solution of 0.1 g of ketol **7** and 35 mg of potassium *tert*-butoxide in 10 mL of dry *tert*-butyl alcohol was refluxed for 41 h. As observed by TLC, no reaction had occurred in that time.

Method B. A solution of ketol **7** in a 1:1 (v/v) mixture of DBU and DMF was heated on the steam bath. TLC indicated approximately 50% conversion to a fluorescent product after 19 h and indicated only a trace of starting material remaining after 70 h. The major product was the fluorescent species, presumably naphthalide **14**, which, however, was not further characterized or isolated.

Comparison of Solvents. Solutions of 20 mg of potassium *tert*-butoxide in 4.0 mL of purified Me_2SO, benzene, or *tert*-butyl alcohol under argon were prepared, and into each was rapidly injected a solution of 50 mg of ketol **5** in 1.0 mL of the respective solvent. At various times t the reactions were quenched by injection of an aliquot into an excess of water, and the extent of reaction was observed by TLC. The reaction times t required for the starting material to be unobservable were as follows: $t < 8$ s (for Me_2SO solvent), $180 < t < 360$ s (benzene), $t > 4000$ s (*tert*-butyl alcohol).

Reaction of Naphthalides 8, 10, and 11 with NaH. For each experiment, an excess of 50% NaH (oil dispersion) was placed in 2 mL of dry DMF (stored over 4A molecular sieves); no hydrogen was evolved. To this mixture was added approximately 10 mg of the analytically pure naphthalide, and hydrogen was immediately evolved at a moderate rate and deep colors were generated. The colors were as follows: **8**, deep green; **10**, blue; **11**, green. The colored solutions were unstable and decayed shortly to give brown or black mixtures.

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Registry No.—**1**, 69517-48-2; **2**, 69517-49-3; **3**, 69517-50-6; **4**, 68556-40-1; **5**, 59261-60-8; **6**, 59261-61-9; **7**, 69517-51-7; **8**, 69517-52-8; **9**, 69517-53-9; **10**, 69517-54-0; **11**, 69517-55-1; **12**, 69502-46-1; **13**, 69517-56-2; **14**, 69517-57-3; hydrocyanic acid, 74-90-8; acenaphthenequinone, 82-86-0; phenyl bromide, 108-86-1; methyl bromide, 74-83-9; naphthalide-3-carboxylic acid, 5762-28-7; acenaphthenequinone–sodium bisulfite addition product, 69517-58-4.

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