Studies of Acenaphthene Derivatives. IX[1]. *The Reaction of Acenaphthenequinone with Ammonia*

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In the course of the investigation of the reaction of acenaphthenequinone (I) with various amines, the reaction of I with ammonia was studied.

Many years ago, Graebe and Gfeller[2] found that the treatment of I with aqueous ammonia at 100°C in a sealed tube afforded red crystals (II) (m. p. over 300°C) with the formula $C_{24}H_{12}ON_2$, for which acenaphthenequinoneimide anhydride (IIa) was assumed. Later, Schönberg and Nedzati[3] suggested that acenaphthazine (IIb) (m. p. 400°C (decomp.)), with the formula $C_{24}H_{12}N_2$ for II, would be more reasonable than IIa because of its formation by the reduction of acenaphthenequinone dioxime (III) with a very poor yield and its having properties similar to those of phenanthrazine as well as because of the elemental analyses. In a similar manner, Charrier and Ghigi[4] obtained naphthalimide in addition to II, whose structure was not reexamined.

Furthermore, Schiedt[5] reported that IIb (m. p. 438°C) was produced by the heating of I with formamide in the presence of glacial acetic acid at 170°C. However, its structure was not characterized.

Although the structure of acenaphthazine for II seemed to be reasonable, the authors were doubtful about the reduction procedure of III and the purification method of II carried out by Schönberg and Nedzati[3]. They recognized that IIb was formed by the condensation of 1, 2-diaminoacenaphthene (IV) and I, which had been produced by the reduction, accompanied by the simultaneous hydrolysis of III, as is depicted in Chart 1. However, it can also be considered that this product was formed by the reaction of I produced by hydrolysis with ammonia, since they treated the reaction mixture with aqueous ammonia for a long time. Further, even if I reacted with IV, IIb was not the only possible product. Furthermore, the purification of II was carried out by sublimation with iron powder.

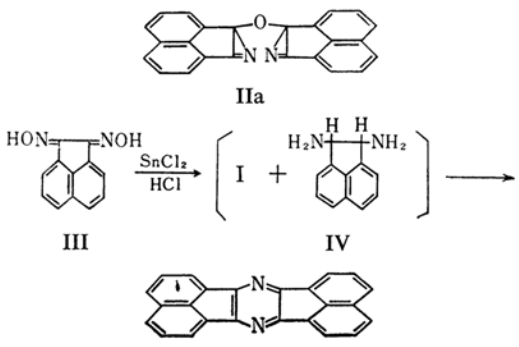


Chart 1

This paper deals with the results of a reexamination of the structure of II and of the reaction of I with ammonia under various conditions.

Results and Discussion

Reaction by Graebe's Procedure.—The reaction of I with 21% aqueous ammonia at 100°C in a sealed tube according to Graebe's procedure afforded red crystals (II) (m. p. 382°C), naphthalimide (V), and a new colorless compound (VI) (m. p. 286~287°C).

The elemental analytical data of II was in agreement with the formula $C_{24}H_{12}ON_2$ given by Graebe and Gfeller[2] but not with Schönberg's formula, $C_{24}H_{12}N_2$[3]. Its infrared spectrum exhibited the sharp bands at 1704 and 1616 cm^{-1} ascribed to the carbonyl group[6] and the C=N bond respectively, but it did not reveal any bands for the amino group (Fig. 1.). Also, the infrared spectrum of the compound purified by sublimation was exactly the same as that of the original substance. As no suitable solvent of II could be found, its molecular weight was not determined.

In order to elucidate the structure of II more clearly, the following experiments were carried out. It is obvious that II contains two acenaphthene rings in the molecule, because the oxidation of II (1 mol. as $C_{24}H_{12}ON_2$) with sodium dichromate in glacial acetic acid

1) Part VIII: H. Saikachi, O. Tsuge and M. Tashiro, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **80**, 584 (1960).
2) C. Graebe and E. Gfeller, *Ann.*, **276**, 1 (1893).
3) A. Schönberg and F. Nedzati, *Ber.*, **54**, 238 (1921).
4) G. Charrier and E. Ghigi, *Atti accad. Lincei*, **16**, 262 (1932).
5) B. Schiedt, *J. prakt. Chem.*, **157**, 203 (1941).
6) The infrared spectra of one acenaphthene or acenaphthenequinone exhibited sharp bands at 1724 or at 1727, 1742 and 1776 cm^{-1} respectively for the carbonyl group.

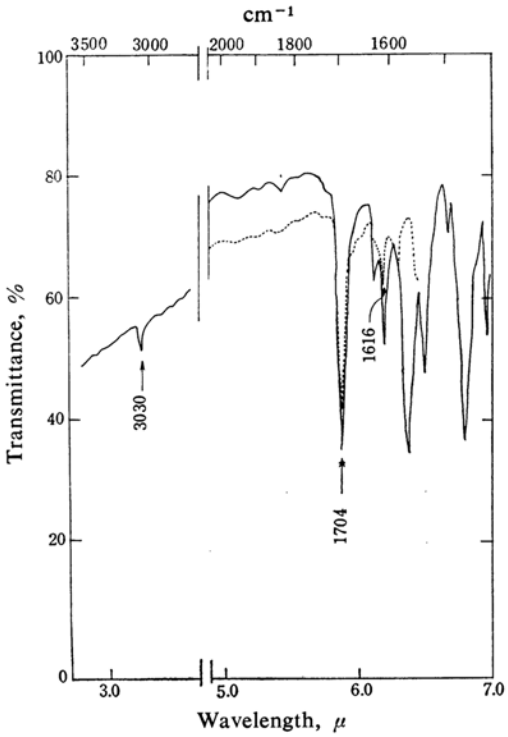


Fig. 1. Infrared spectra of II.
—— In hexachlorobutadiene mull
------ In Nujol mull

afforded naphthalimide (V) (ca. 1.5 mol.) and naphthalic anhydride (VII) (ca. 0.5 mol.) (Chart 2). The reduction of II with zinc dust in acetic acid gave a labile orange substance which was purified as the picrate. In the infrared spectrum of the orange product just after the reduction, there was no band due to the carbonyl group, but there were two bands, at 3120 and 1618 cm^{-1}, which may be ascribed to the hydroxyl group and the C=N bond respectively. However, this compound could not be identified.

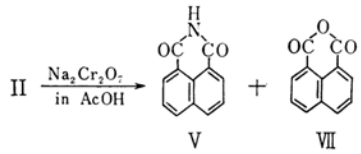


Chart 2

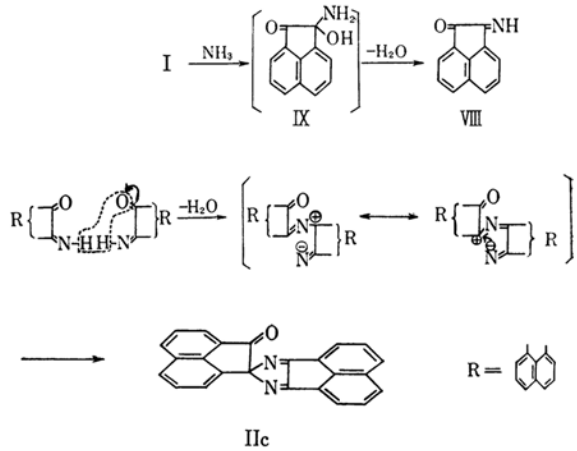
In addition, II was obtained quantitatively by the heating of the acenaphthenequinone monoimine (VIII) which had been obtained by the reaction of I with ammonia in ethanol, as will be described below.

Weiss[7] discovered that the reaction of benzil with ammonium acetate in the presence of acetic acid resulted in isoimidazole derivatives.

7) M. Weiss, *J. Am. Chem. Soc.*, **74**, 5193 (1952).

Accordingly, these observations are accommodated much better by the structure of acenaphtho [1,2-b] isoimidazole-2-spiro-2'-acenaphthenone (IIc) than by IIa or IIb. IIc is assumed to be formed by the self-condensation of the VIII which was produced by the dehydration of the ammonia-adduct (IX) of I as depicted in Chart 3.

On the other hand, VI accorded with the formula $C_{24}H_{13}O_3N$, which is the result of the



IIc

Chart 3

elemental analysis and the molecular weight measurement. The infrared spectrum of VI showed the absorption bands at 1721 or 1698 and 1658 cm^{-1} assigned to the carbonyl group or the amide I band respectively. The bands at 3077 cm^{-1} for the aromatic C–H bond and at 2933 cm^{-1} ascribed to the aliphatic C–H bond were also observed[8] (Fig. 2.). Its ultraviolet spectrum is very similar to that of *N*-phenylnaphthalimide, as is shown in Fig. 3.

These observations indicate that this compound is *N*-(2-oxo-acenaphthenyl)naphthalimide (VI).

It has previously been well-known that the treatment of I with alkali gives naphthaldehyde and naphthalic acid[9]. Consequently, VI is assumed to be formed by the condensation of the ammonia-adduct (IX) and naphthaldehyde, as is depicted in Chart 4.

Furthermore, the formation of V and VII can be illustrated naturally, as Chart 4 shows. The effect of the reaction time on the yields of these compounds was examined. The results are listed in Table I.

As is shown in Table I, IIc was formed as

8) The infrared spectrum of IIc did not show any absorption due to the aliphatic bonds, but it did show a band at 3030 cm^{-1} for the aromatic C-H bond. Also, *N*-phenylnaphthalimide exhibited the bands at 1701 and 1664 cm^{-1} assigned as the amide I bands in its infrared spectrum.

9) J. Cason and J. D. Wordie, *J. Org. Chem.*, **15**, 608 (1950).

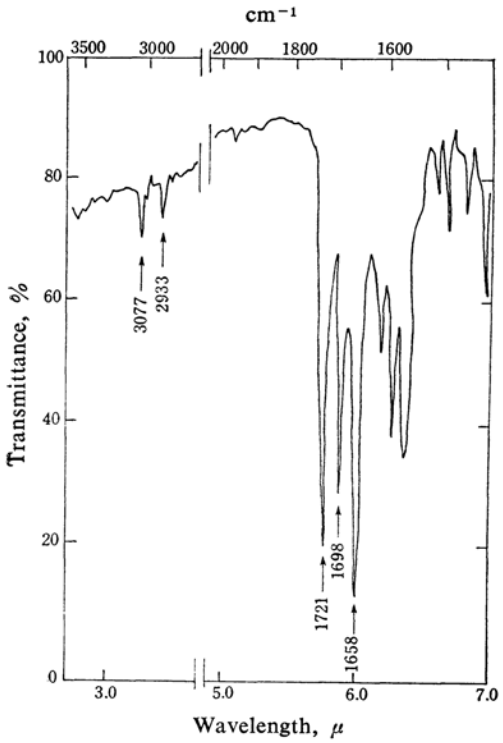


Fig. 2. Infrared spectrum of VI in hexachlorobutadiene mull.

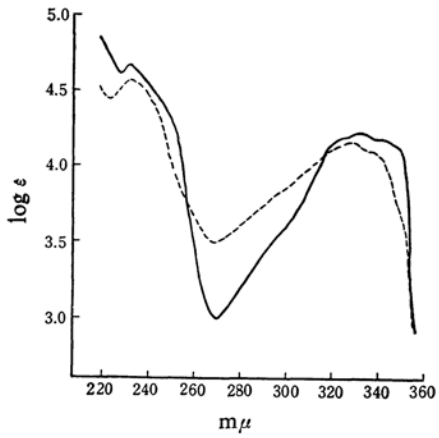


Fig. 3. UV spectra of VI and *N*-phenylnaphthalimide in dioxane.
—— VI
------ *N*-Phenylnaphthalimide

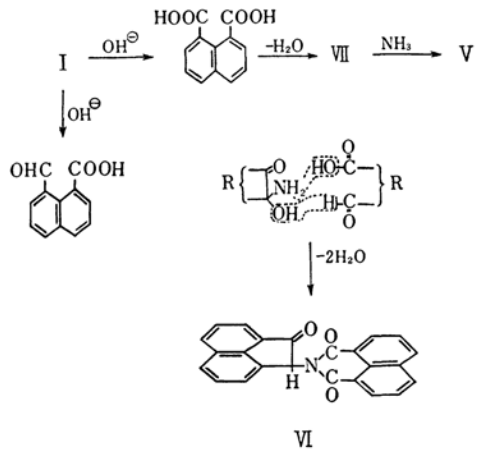


Chart 4

Table I. Reaction of I with aqueous ammonia*

Time	Product			Recovered
	IIc	V	VI	I
hr.	%		%	%
1.0	37.7	+**	19.0	40.0
2.0	57.2	+	21.0	21.3
3.0	64.6	+	22.2	—
4.0	65.6	+	21.5	—
6.0	65.2	+	21.7	—

* Mixtures of I (5.0 g.) and 21% aqueous ammonia (50 ml.) were heated at 100°C in a sealed tube for the specified periods
**+ : Trace amount

Table II. Reaction of I with ammonia gas in water*

Time	Product			Recovered
	IIc	V	VI	I
hr.	%	%		%
2.0	11.4	5.0	+	72.0
3.0	11.4	5.9	+	60.4
6.0	37.9	11.8	+	30.0
7.0	51.7	22.1	+	—
10.0	65.2	22.3	+	—

* Ammonia gas was violently passed through the suspension of I (5.0 g.) in water (50 ml.) at 70~80°C for the specified periods.

the main product, accompanied by a considerably large amount of VI. The yields of these compounds were nearly constant, even if the reaction time was longer than 3 hr.

The Reaction with Ammonia in Water or Ethanol.—Ammonia gas was violently passed through the suspension of I in either water or ethanol. The results are shown in Tables II and III.

In the case of the reaction of I with ammonia gas in water, also, IIc, V and VI were obtained, as is shown in Table II. However, more V was formed than VI, and the rate of the formation of IIc was slower than in Graebe's procedure mentioned above.

The reaction of I with ammonia gas in ethanol gave V as the main product, accompanied by IIc and an unknown compound

TABLE III. REACTION OF I WITH AMMONIA GAS IN ETHANOL*

Time	Product			Recovered
	IIc	V	VIII	I
hr.	%	%	%	%
0.5	1.9	22.3	1.6	46.0
1.0	7.0	46.2	5.0	25.0
2.0	14.4	51.7	12.6	20.5
4.0	13.9	49.7	13.4	16.0

* Ammonia gas was violently passed through the suspension of I (5.0 g.) in ethanol (50 ml.) under reflux for the specified periods.

(VIII) (m. p. 343°C (decomp.)) in almost identical yields. As the heating of VIII gave IIc in a quantitative yield, it seems reasonable to assume that VIII is the intermediate of IIc.

Zincke[10] reported long ago that the reaction of phenanthrenequinone with ammonia afforded phenanthrenequinone monoimine, which in turn yields a red substance upon being heated. In addition, the infrared spectrum of VIII, which corresponds to the formula $C_{12}H_7ON$, revealed absorption bands at 3128 and 1605 or 1681 cm^{-1} for the -C=NH or the carbonyl group respectively[11].

On the basis of these facts, this compound is considered to be acenaphthenequinone monoimine (VIII) formed as shown in Chart 3. The observed shifts of these bands to a longer wavelength region seem to be due to the intermolecular chelation of VIII.

TABLE IV. REACTION OF I WITH AMMONIUM CARBONATE IN GLACIAL ACETIC ACID*

Time min.	$(NH_4)_2CO_3$/I**	Product	
		IIc %	V %
30	10	—	—***
30	20	19.0	37.0
30	30	25.4	45.3
30	40	33.8	48.1
30	100	44.4	47.9
15	50	33.8	50.0
30	50	39.1	50.0
45	50	38.6	49.4
60	50	39.1	49.2

* Mixtures of I (1.0 g.) and $(NH_4)_2CO_3$ of the indicated amounts in glacial acetic acid (30 ml.) were heated under reflux for the specified periods.
** Molar ratio
*** Recovery of I was almost quantitative.

10) Th. Zincke, *Ber.*, **12**, 1641 (1879).
11) Phenanthrenequinone monoimine prepared by the reaction of phenanthrenequinone with ammonia showed the infrared absorption bands at 3215 and 1605 or 1678 cm^{-1} due to the -C=NH or the carbonyl group respectively.

The reaction of I with ethanolic ammonia in a closed vessel at room temperature for ten days afforded IIc, VI and VIII in about 10, 35 and 45% yields respectively. Another reaction with liquid ammonia gave IIc, VI and naphthalic acid.

The Reaction of I with Ammonium Carbonate in Glacial Acetic Acid.—The treatment of I with ammonium carbonate in boiling glacial acetic acid gave IIc and V. The effect of reaction conditions on the yields of these compounds is summarized in Table IV. As is shown in Table IV, this simple procedure seems to be the most promising route to IIc.

Furthermore, the heating of I with formamide and glacial acetic acid at 170~180°C afforded a red substance which was confirmed to be identical with IIc by a comparison of their infrared spectra. Also, another reaction of 2, 2-dichloroacenaphthenone with ammonium carbonate in glacial acetic acid afforded IIc.

Experimental[12,13]

The infrared spectra of all compounds were measured in hexachlorobutadiene mull. Acenaphthenequinone (I) was prepared by the oxidation of acenaphthene[14] in the form of yellow needles (m. p. 244~245°C).

The Reaction of I with Aqueous Ammonia by Graebe's Procedure.—A mixture of I (5.0 g.) and 21% aqueous ammonia (50 ml.) was heated in a sealed tube at 100°C for 1 hr. After it had cooled, the reaction mixture was poured into water and the precipitate was extracted by boiling acetic acid (100 ml.), leaving red crystals. Those red crystals were washed with ethanol and dried to give 1.78 g. (m. p. 375~376°C). Recrystallization from pyridine or sublimation afforded acenaphtho[1, 2-b]-isoimidazole-2-spiro-2'-acenaphthenone (IIc) as red needles (m. p., 382°C).

Found: C, 83.61; H, 3.56; N, 8.42. Calcd. for $C_{24}H_{12}ON_2$: C, 83.71; H, 3.51; N, 8.13%.

The precipitate obtained by the pouring of the extract and washings into water was heated with 40% sodium bisulfite (200 ml.) for 10 min. The hot solution was then filtered by suction. The filtrate was treated with concentrated sulfuric acid as usual to recover I (2.0 g.). The sodium bisulfite solution-insoluble residue was washed with hot water and ethanol, and then dried to afford 0.95 g. of colorless crystals melting at 260~270°C. On the fractional recrystallization of the colorless crystals from acetic acid, two compounds were obtained: one with an m. p. of 300°C and the other with an m. p. of 286~287°C. The former was in a trace amount and was proved to be identical with naphthalimide (V) by the admixed melting point with an authentic sample. The latter was *N*-(2-oxo-acenaphthenyl) naphthalimide (VI) as colorless prisms in a large amount.

12) All melting points are uncorrected.
13) The microanalyses were carried ont by M. Shidō of Kyushu University, to whom the authors are indebted.
14) "Organic Syntheses", **24**, 1 (1944).

Found: C, 79.43; H, 3.69; N, 3.82; mol. wt. (Rast), 362.5. Calcd. for $C_{24}H_{13}O_3N$: C, 79.32; H, 3.61; N, 3.85%; mol. wt., 363.35.

$\lambda_{max}^{Dioxane}$ mμ (log ε): 231 (4.69), 330 (4.23)[15].

The effect of reaction conditions on the yields of these products is shown in Table I.

The Oxidation of IIc.—Sodium dichromate (6.0 g.) was added slowly to a suspension of IIc (2.0 g., 5.8 mmol.) in glacial acetic acid (50 ml.) at 80°C.

After being refluxed for 1 hr., the reaction mixture was poured into water and allowed to stand overnight. The precipitate was then collected and extracted with a 10% aqueous sodium carbonate solution. The insoluble residue was washed with water and dried to afford 1.7 g. (8.6 mmol.) of colorless crystals (m. p. 287~279°C). On recrystallization of these crystals from acetic acid, colorless needles (m. p., 300°C) were obtained and proved to be identical with V. The sodium carbonate-extract was acidified with dilute hydrochloric acid, and the deposited precipitate was collected, washed with water, and dried to give 0.62 g. (3.1 mmol.) of a white solid (m. p. 267~269°C). Recrystallization of this from concentrated nitric acid gave colorless needles (m. p. 274°C) which were identical with naphthalic anhydride.

The Reduction of IIc.—A suspension of IIc (0.5 g.) and zinc dust (1.0 g.) in a mixture of acetic anhydride (20 ml.) and glacial acetic acid (6 ml.) was heated under reflux for 20 min.; additional zinc dust (1.0 g.) was then added to the reaction mixture and it was refluxed for another 30 min. The hot solution was filtered by suction, and the filtrate was poured into water to give a labile orange precipitate which tended to decompose on heating.

Purification of the orange substance was accomplished through its picrate. This picrate was obtained (0.45 g.) as a yellow solid (m. p. 270°C (decomp.)) which, on recrystallization from dioxane, gave a yellow crystalline powder (m. p. 275°C (decomp.)). (Found: C, 63.90; H, 3.73; N, 12.51%). This compound could not be identified.

The Reaction of I with Ammonia Gas in Water.—Ammonia gas was violently passed through a suspension of I (5.0 g.) in water (50 ml.) at 70~80°C for 6 hr. The reaction mixture was poured into water, and the precipitate was collected. The same treatment as in Graebe's procedure gave the starting material, I (1.5 g.), IIc (1.79 g.), V (0.64 g.) and VI in a small amount. The results of other experiments, along with various reaction conditions, are listed in Table II.

The Reaction of I with Ammonia Gas in Ethanol.—a) Ammonia gas was violently passed through a suspension of I (5.0 g.) in boiling ethanol (50 ml.) for 4 hr. The same treatment as in the above-mentioned procedure gave the starting material, I (0.8 g.). The sodium carbonate-insoluble residue was extracted with hot glacial acetic acid and then with hot chloroform[16], (40 ml.×2) remaining a white solid (0.67 g.; m. p. over 300°C). (Recrystallization from pyridine gave acenaphthene monoimine (VIII) as colorless prisms (m. p. 343°C (decomp.)).

Found: C, 79.69; H, 4.16; N, 7.75. Calcd. for $C_{12}H_7ON$: C, 79.54; H, 3.89; N, 7.73%. Hydrochloride of VIII, Found: N, 6.99. Calcd. for $C_{12}H_8ONCl$: N, 6.43%.

The acetic acid-extract was concentrated in vacuo to afford V (2.69 g.), and from the chloroform-extract IIc (0.66 g.) was obtained. The results of other reactions in ethanol are shown in Table III.

b) A mixture of I (2.0 g.) and ethanol (50 ml.) containing ammonia (ca. 0.4 g.) was stirred in a closed vessel at room temperature for ten days.

After the reaction mixture had been poured into water, the precipitate was collected, washed with water, dried, and extracted with hot chloroform (50 ml.×2). The recrystallization of the insoluble white solid (0.9 g.) (m. p. 343°C (decomp.)) whose infrared spectrum was superimposed on that of VIII obtained above was undertaken. The chloroform-extract was evaporated, and the residue was further extracted with hot glacial acetic acid to give insoluble red crystals IIc (0.17 g.) and soluble colorless prisms VI (0.8 g.). The structures of these compounds were confirmed to be as described above.

The Reaction of I with Ammonium Carbonate in Glacial Acetic Acid.—The refluxing of a mixture of (1.0 g.) and ammonium carbonate (13.0 g.) in glacial acetic acid (30 ml.) resulted in the precipitation of red crystals within a few minutes. After the mixture had been refluxed for 1 hr., filtration gave red crystals (0.37 g.) (m. p. 377~378°C), the infrared spectrum of which was exactly the same as that of IIc. The filtrate was poured into water, and the precipitate was treated, as usual, with a 40% sodium bisulfite solution (50 ml.) to give I in a small amount. The sodium bisulfite-insoluble residue was washed with hot water and dried to give colorless crystals (0.53 g.), which were found to be identical with V from the admixed m. p. and infrared spectrum. The findings on the effect of reaction conditions on the yields of these compounds are summarized in Table IV.

The Reaction of I with Liquid Ammonia.—A mixture of I (10.0 g.) and liquid ammonia (120 ml.) was shaken in a dry ice-methanol bath for 7 hr.

After the ammonia had been removed at room temperature, the residue was washed well with water. The washings were acidified with dilute hydrochloric acid and dried to afford white crystals (3.0 g.) (m. p. 268~272°C) which, on recrystallization from concentrated nitric acid, gave colorless needles (m. p., 274°C). This compound was identical with VII. The treatment of the insoluble residue with a 40% sodium bisulfite solution, and then with hot acetic acid, as mentioned above, gave I (3.2 g.), IIc (2.0 g.), and VI (1.0 g.).

The Reaction of I with Formamide in the Presence of Acetic Acid.—A mixture of I (2.5 g.), formamide (40 ml.) and glacial acetic acid (1 ml.) was heated at 170~180°C in an oil bath for 20 min.

After being cooled, the mixture separated out crystals. Filtration gave red crystals (1.5 g.) (m. p.

15) *N*-Phenylnaphthalimide: $\lambda_{max}^{Dioxane}$ mμ (log ε); 231 (4.59), 329 (4.17).

16) IIc was soluble in boiling chloroform.

over 300°C) which, on recrystallization from pyridine, showed an m. p. of 382°C. The infrared spectrum and elemental analytical values were in agreement with those of IIc. (Found: C, 83.83; H, 3.60; N, 8.48%.)

The Reaction of 2, 2-Dichloroacenaphthenone with Ammonium Carbonate in Glacial Acetic Acid. —A mixture of 2, 2-dichloroacenaphthenone[17] (1.0 g.) and ammonium carbonate (26.0 g.) in glacial acetic acid (30 ml.) was refluxed for 30 min. After the mixture had been cooled, filtration afforded red crystals (0.4 g.) (m. p. 360~363°C) which, on recrystallization from pyridine, gave red needles (m. p. 382°C), the infrared spectrum of which was superimposed on that of IIc. The filtrate was not examined.

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17) 2, 2-Dichloroacenaphthenone was prepared by the reaction of I with PCl_5. (A. I. Tochilkin, *Zhur. Vsesoynz. Khim., Obshchestva im. D. I. Mendeleeva*, 6, 591 (1961).)