BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2477—2479 (1966)

Studies of Acenaphthene Derivatives. XII.[1] On the Red Substance Obtained from Acenaphthenequinone and Ammonia

By Otohiko TSUGE and Masashi TASHIRO

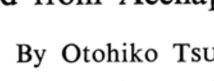
The Research Institute of Science and Industry, Kyushu University, Hakozaki, Fukuoka

(Received March 17, 1966)

In order to elucidate the chemical structure of red crystals (A) obtained from the reaction of acenaphthenequinone (I) with ammonia, the reaction of I with ammonia, formamide or benzylamine was reinvestigated. It has been made clear again that the compound A is not acenaphthazine (II) but acenaphtho[1, 2-b]isoimidazole-2-spiro-2′-acenaphthenone (III), and that Schönberg's assumption of the structure of the compound A is incorrect. That reaction of I with benzylamine afforded II as yellow needles in a good yield. Also, it has been found that the reaction product (B) of I with formamide is a mixture of almost equal amounts of II and III.

The previous work[2] of this series has shown that the chemical structure of the red compound A, the reaction product of acenaphthenequinone (I) with ammonia, is neither acenaphthenequinonimide anhydride ($C_{24}H_{12}ON_2$)[3] nor acenaphthazine (II),[4] but acenaphtho[1, 2-b]isoimidazole-2-spiro-2′-acenaphthenone (III).

II



III

Recently, Schönberg and Singer[5] obtained a red substance identical with the compound A by the reaction of I with formamide in the presence of acetic acid;[6] they objected to our proposed structure III for the compound A as a misconception resulting from the treatment of an impure substance. On the basis of its analyses, a study of its infrared spectrum,[7] and its being similar to phenanthrazine, they concluded that the compound A is acenaphthazine (II), whose structure was early suggested by Schönberg and Nedzati.[4]

In the preceding paper,[1] however, it has been shown that II is formed as yellow needles in the reaction of I with primary aliphatic amines, such as methyl-, ethyl- and benzylamine, and the reaction course of the formation of II was also suggested.

Consequently, we are compelled to reexamine our assignment of III for the compound A to see whether it is attributable to the results of the treatment of an impure substance, and to see whether II is the main product in the reaction of I with ammonia or formamide.

In the reaction of I with ammonium carbonate in acetic acid, red crystals (A) are formed.[2] The crude product just after the reaction and the product purified by means of recrystallization from pyridine or by means of sublimation over iron powder are in agreement with the formula $C_{24}H_{12}ON_2$ (III), but not with Schönberg's formula $C_{24}H_{12}N_2$ (II), and the infrared spectrum of the crude product, which showed the absorption band at 1704 cm⁻¹ assigned to the carbonyl group, was also almost the same as that of the purified

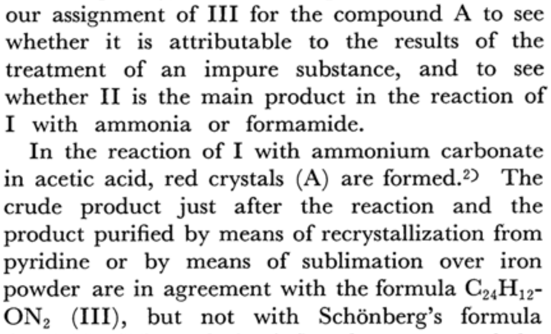


Fig. 1. Infrared spectra of the crude and purified II and III in KBr disk.

a: II obtained from the reaction of I with formamide

b, c: Substance purified three or five times by sublimation respectively

---

1) Part XI: O. Tsuge and M. Tashiro, This Bulletin, **38**, 399 (1965).

2) O. Tsuge and M. Tashiro, ibid., **36**, 970 (1963).

3) C. Graebe and E. Gfeller, *Ann.*, **276**, 1 (1893).

4) A. Schönberg and F. Nedzati, *Ber.*, **54**, 238 (1921).

5) A. Schönberg and E. Singer, *Chem. Ber.*, **98**, 3436 (1965).

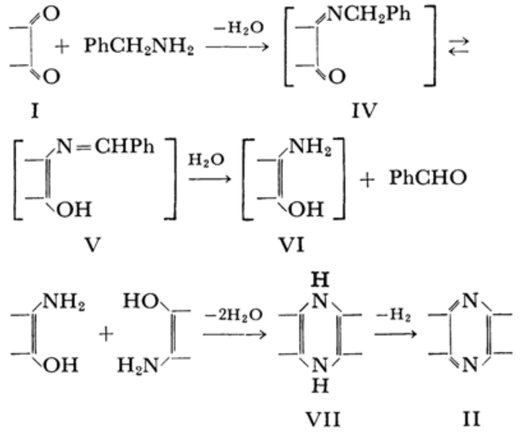
6) It has been reported that the crude product was contaminated by an oxygen-containing substance.[5]

7) Although it was shown that its infrared spectrum did not exhibit any carbonyl bond, its spectrum was not given.

product. These observations indicate that our substance is a pure and single compound.

The reaction of I with an excess amount of benzylamine afforded II, benzal benzylamine and *N*-benzylnaphthalimide. Unlike III, II is yellow needles, and it is more easily purified by sublimation than III. As benzal benzylamine is the condensation product of benzaldehyde[8] and benzylamine, it is resonable to conclude that the reaction proceeds through the previously-proposed course.[1]

As Chart 1 shows, *N*-benzylacenaphthenequinonimine (IV) rearranges to the Schiff base (V), which in turn hydrolyzes to yield benzaldehyde and 1, 2-aminoacenaphthenole (VI). The self-condensation of VI leads to the formation of dihydroacenaphthazine (VII), which easily dehydrogenates to II. On the other hand, benzaldehyde reacts with benzylamine to form benzal benzylamine.



$PhCHO + PHCH_2NH_2 \longrightarrow PhCH{=}NCH_2Ph$

Chart 1

The infrared and ultraviolet spectra of II and III are given in Figs. 1 and 2 respectively. The infrared spectrum of III exhibited the sharp band at 1704 cm^{-1} ascribed to the carbonyl group. In view of its elemental analyses and the results of oxidation[2] as well as its infrared spectrum, the compound A may be said to be in accord with the structure of III.

The infrared spectrum of the crude product (B) just after the reaction of I with formamide is also shown in Fig. 1. On the basis of its infrared spectrum, which revealed all the distinctive bands of II and III (as are shown in Fig. 1) and of the ultraviolet spectra (cf. Fig. 2), it may be supposed that the product B is a mixture of II and III.

If the product B was extracted with chloroform and if the chloroform-extract was then recrystallized from pyridine, a red substance whose infrared spectrum was superimposed on that of III was obtained. On the other hand, the more repeatedly the purification of the product B was done by sublimation, the weaker the strength of the band at 1704 cm^{-1} ascribed to the carbonyl group became; finally yellow needles, m. p. 438°C, the infrared spectrum of which was the same as that of II, were obtained.

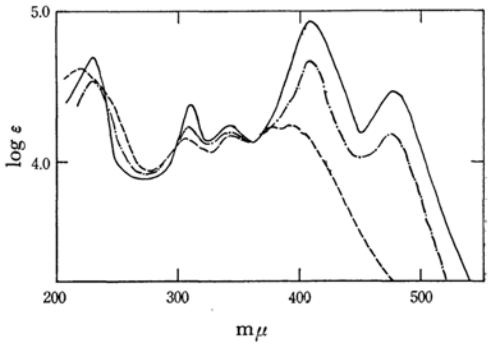


Fig. 2. Ultraviolet spectra of II, III and product B in concentrated sulfuric acid.
—— II
---- III
—.— Product B

The infrared spectra of the product B as purified by recrystallization and by sublimation are also shown in Fig. 1.

The quantitative estimation of II and III in the product B was established by using the ratio method,[9] which was carried out by the measurement of the absorbances, a_1 and a_2, for the bands at 1320 and 1704 cm^{-1}, respectively. Thus, samples of a mixture consisting of specified amounts of II and III were prepared, and the absorbances, a_1 and a_2 were measured according to the baseline

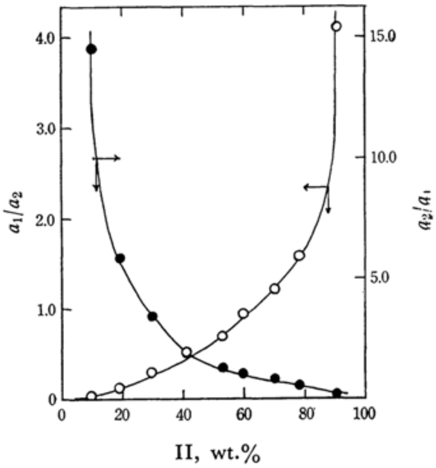


Fig. 3. Calibration curves.

---

[8] Benzaldehyde was isolated and identified as 2, 4-dinitrophenylhydrazone.[1]

[9] S. Takagi, "Experiment and Calculation of Quantitative Analyses" (in Japanese), Vol. III, Kyoritsu, Tokyo (1961), p. 91.

method. The calibration curves plotting the relationship between a_1/a_2 or a_2/a_1 and the concentration (wt. %) of II are shown in Fig. 3.

According to the calibration curves thus obtained, it was found that the product B consisted of II (45%) and III (55%). In the reaction of I with formamide known as the Leukart reaction, I reacts with the ammonia which is formed in the reaction process to give III, besides the usual reaction.

Experimental

The Reaction of I with Ammonium Carbonate in Glacial Acetic Acid.—As has been described previously,[2] a mixture of I (1.0 g.) and ammonium carbonate (13.0 g.) in glacial acetic acid (30 ml.) was refluxed for 1 hr. to afford red crystals (0.38 g.). These crude red crystals were washed with hot acetic acid and with acetone, and then dried in vacuo.

Some of the crystals were recrystallized from pyridine, and another part was purified by sublimation over iron powder. The infrared spectrum of the crude product was almost the same as that of the purified product. The elemental analytical data of the red crystals are given in Table I.

Table I. Elemental analytical data of red crystals

Sample	Found, % C	Found, % H	Found, % N
Crude	83.97	3.33	8.39
	83.81	3.39	8.35
Recrystallized from pyridine	83.97	3.36	8.36
	83.78	3.28	8.40
Sublimated	84.07	3.18	8.47

Calcd. for $C_{24}H_{12}N_2$ (II): C, 87.79; H, 3.68; N, 8.53%.

Calcd. for $C_{24}H_{12}ON_2$ (III): C, 83.71; H, 3.51; N, 8.14%.

The Reaction of I with Benzylamine.—A mixture of I (16 g.) and benzylamine (25 g.) was heated at 80°C for 1 hr. During this time the mixture turned brown. After it had cooled, the mixture was washed with benzene (250 ml.); 6.1 g. of brown crystals were left (m. p. over 400°C). Recrystallization from nitrobenzene or sublimation over iron powder afforded acenaphthazine (II) as yellow needles, m. p. 438°C (decomp.).

Found: C, 87.79; H, 3.65; N, 8.75. Calcd. for $C_{24}H_{12}N_2$: C, 87.79; H, 3.68; N, 8.53%.

After the benzene washings had been dried over sodium sulfate and the benzene had then been removed, distillation in vacuo gave 8.6 g. of a colorless oil (138°C/3 mmHg) and a residue. The distillate was proved, by a study of its infrared spectrum, to be identical with the benzal benzylamine which was prepared from benzaldehyde and benzylamine. On the other hand, the residue was washed with a small amount of hot isopropyl alcohol; this left pale yellow crystals which, on recrystallization from isopropyl alcohol, afforded 3.0 g. of *N*-benzylnaphthalimide as pale yellow needles, m. p. 195—195.5°C.[1]

The Reaction of I with Formamide.—A mixture of I (2.5 g.), formamide (40 ml.), and glacial acetic acid (1 ml.) was heated at 170—180°C for 20 min. The same treatment as has been previously used[2] gave 1.5 g. of red crystals, which were found to be a mixture of II (45%) and III (55%) by the spectroscopic determination. The crude product (300 mg.) was extracted with chloroform (300 ml.), leaving insoluble red crystals which consisted of II (55%) and III (45%). The chloroform extract was concentrated in vacuo to afford red crystals (100 mg.) which were a mixture of II (40%) and III (60%). The fractional recrystallization of the crystals from pyridine gave almost pure III as red needles; their infrared spectrum is also given in Fig. 1.

The chloroform-insoluble crystals were purified by sublimation over iron powder. The more repeatedly sublimation was done, the greater was the relative amount of II in the crystals (Table II).

Table II. Variation in the relative amounts of II and III with sublimation

Number of times	Composition (wt. %) II	Composition (wt. %) III
1	64	36
2	70	30
3*	83	17
4	85	15
5*	~100	

* Infrared spectra are given in Fig. 1.

Schönberg et al.[5] may have failed to recognize that II is red crystals, because II as red crystals appears to be contaminated with a trace amount of III.

Also, the reaction in the absence of acetic acid gave red crystals which consisted of II (55%) and III (45%).

The Spectroscopic Determination of II and III in Compound B.—The infrared absorption measurements were made with a Koken IR-S double-beam spectrophotometer equipped with a sodium chloride prism.

Potassium chloride disks containing II and III, in which the weight percentages of III were 10.0, 21.7, 30.0, 39.8, 47.9, 59.7, 70.1, 80.7 and 90.2% respectively, were prepared. The absorbances, a_1 and a_2, for the bands at 1320 and 1704 cm^{-1} respectively were measured by the baseline method.

The calibration curves obtained by the ratio method are shown in Fig. 3.

The authors are indebted to the staff of the Analytical Service Centre of this university and Mr. Eiji Shiozaki of this laboratory for their microanalyses.