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Unusual Products of the Leuckart Reaction of 1-Acenaphthenone

Jiro TATSUGI, and Michio OKUMURA

Department of Applied Chemistry, Aichi Institute of Technology, Yakusa, Toyoda 470-03

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Synopsis. In the reaction between formamide and 1-acenaphthenone, 1,1′-biacenaphthenyliden-2-one was obtained instead of 1-acenaphthenamine which is expected to be formed by the Leuckart reaction. When formic acid was incorporated in the reaction, besides 1,1′-biacenaphthenyliden-2-one two new nitrogen-containing compounds were isolated; their structures were identified to be acenaphtho[1,2-*d*]pyrimidine and diacenaphtho[1,2-*b*: 1′,2′-*d*]pyridine by independent syntheses.

The reaction of 1-acenaphthenone (**1**) with formamide or ammonium formate gave exclusively a nitrogen-free product (**2**) (75% yield). When **1** was treated with a mixture of formamide and anhydrous formic acid, two new products (**3**) and (**4**) were obtained along with the liberation of CO_2 (Table 1). When using 80% formic acid in place of the anhydrous acid, the yield of **2** increased and those of **3** and **4** were reduced. The nitrogen-free product **2** decolorized bromine and permanganate solutions, suggesting the presence of unsaturated bonds. The IR spectrum of **2** showed the presence of a carbonyl group and its NMR spectrum showed a singlet at 4.70 ppm which is assignable to allylic methylene protons. This compound was identified to be the structure shown in the scheme by independent synthesis of the compound by the aldol condensation of **1** in the presence of caustic alkali.

Table 1. Reaction of 1-acenaphthenone with the mixture of formamide and anhydrous formic acid

1-Acenaphthenone **1** mol	$HCONH_2$ mol	HCOOH mol	Temp (°C)	Time (h)	Yields (%) **2**	**3**	**4**
0.02	0.46	none	150	3	75	—	—
0.01	0.23	0.23	150	3	31	28	9
0.01	0.23	0.18[a)]	150	3	69	9	1
0.01	0.23	0.23	55	18	—	—	—
0.01	0.23	0.23	100	3	6	trace	—
0.01	0.23	0.23	110	3	13	6	—
0.01	0.23	0.23	125	3	26	10	2

a) *ca.* 80% HCOOH.

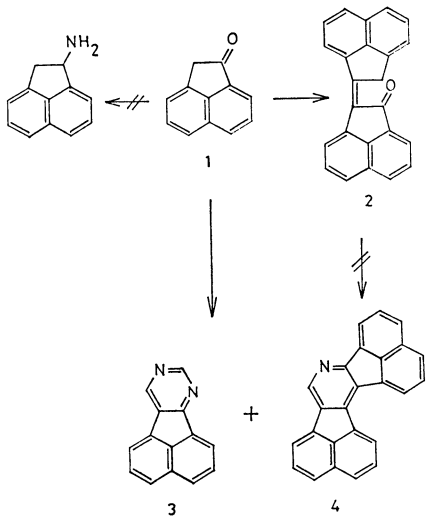

Fig. 1.

The compound **3** has an experimental formula of C_7H_4N; the structure is suggested to have a pyrimidine nucleus by the IR spectrum. Furthermore, the NMR spectrum in $CDCl_3$ is well interpreted to be acenaphtho-[1,2-*d*]pyrimidine. The authentic acenaphtho[1,2-*d*]-pyrimidine was independently prepared by the reaction of 2-formyl-1-acenaphthenone (**1a**) with formamidine (Fig. 2).

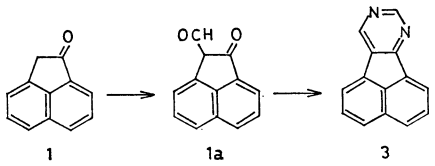

Fig. 2.

The admixture of **3** with the authentic sample showed no melting point depression and the R_f values of both compounds were the same.

The compound **4** was identified as diacenaphtho[1,2-*b*: 1′,2′-*d*]pyridine on the basis of its IR, UV, and mass spectra and elementary analysis. The independent synthesis of **4** was accomplished by converting 2-(ethoxymethylidene)-1-acenaphthenone into 2-(amino-methylidene)-1-acenaphthenone by dry ammonia and then condensing it with **1**. The authentic compound showed the same R_f value as that of **4** isolated from the Leuckart reaction products.

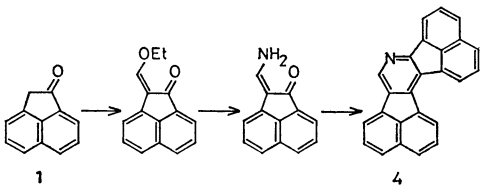

Fig. 3.

Recently, pyrimidine derivatives were isolated from the Leuckart reaction mixture in thiophene derivatives by Hill and Loev,[1)] and Srinivasan and Rampal,[2)] though the formation of the pyridine derivatives has not yet been reported.

The above mentioned **3** and **4** are new compounds which have not yet been reported in the literature.

In the reaction of **1** with formamide, which took place exclusively as an aldol condensation and showed no Leuckart reaction, formamide seemed to perform the

role of a protic solvent. In the presence of formic acid, however, the Leuckart reaction is in competition with the aldol reaction and gives **2**, **3**, and **4**, but no normal Leuckart reaction products. It may be assumed that **3** and **4** might result *via* an intermediate of the Leuckart reaction. It is worthy to note that **4** might be produced by the condensation of **2** with formamide as shown in Fig. 1. This can be ruled out since no **4** was isolated from the reaction mixture of **2** and formamide.

When 80% formic acid was used, the yield of **2** increased and those of **3** and **4** decreased. It is reasonable to consider that the presence of water favors the enolization of **1** and accelerates the aldol condensation by the dissociation of formic acid. Further experiments are necessary, however, to consider the reaction route of the formation of **3** and **4** in the Leuckart reaction conditions. This is now in progress.

Experimental

The melting points were determined on a Yanaco MP-type apparatus and are uncorrected. The IR spectra were taken in potassium bromide pellets on a Hitachi 215 grating spectrometer. The UV spectra were recorded on a Hitachi EPS-3T spectrophotometer. The NMR spectra were obtained on a JEOL JNM-C-60H spectrometer using TMS as internal standard.

Reaction of 1-Acenaphthenone ***1*** *with Formamide.* A mixture of **1** (3.36 g, 0.02 mol) and formamide (19.0 ml, 0.46 mol) was heated at 150 °C for 3 h. After cooling the reaction mixture, the precipitate was filtered and washed with methanol. The unchanged **1** was recovered from the methanol washing (13% recovery). Recrystallization of the crude product (2.53 g) from 300 ml of benzene (or chloroform) gave 2.38 g (75%) of **2**, yellow needles, mp 259—260 °C (lit, 262,[3] 258 °C[4]). IR (KBr): 1690 cm^{-1} (C=O). NMR ($CDCl_3$): δ=4.70 (2H, s) and 7.61—8.31 (12H, m). The mixed melting point with an authentic sample synthesized by Graebe's method[3] showed no depression.

The reaction of **1** with ammonium formate at 190 °C for 10 h gave a similar result.

Reaction of ***1*** *with Formamide and Formic Acid.* A mixture of **1** (1.68 g, 0.01 mol), formamide (9.5 ml, 0.23 mol), and anhydrous formic acid (8.5 ml, 0.23 mol) was heated at 150 °C for 3 h. In about 10 minutes evolution of carbon dioxide and precipitation of a colored product were observed. After heating at 150 °C for 30 min, the reaction mixture showed the presence of four spots (**1**, **2**, **3**, and **4**) on thin-layer chromatography (TLC). The colored product was separated by filtration and washed with methanol and then with ether. 0.66 g of yellow solid (two spots on TLC) was obtained. It was chromatographed by means of SiO_2 with chloroform as eluent. The first fraction collected was recrystallized from benzene to afford 0.50 g (31%) of **2**. The second fraction was recrystallized from dioxine to give 0.15 g (9%) of **4**, yellow needles, mp>300 °C, IR (KBr): 1582, 1510, 1430, and 1358 cm^{-1}. UV (dioxane) max: 332.5 nm (log ε 4.63). Found: C, 91.63; H, 4.00; N, 4.20%. Calcd for $C_{25}H_{13}N$: C, 91.72; H, 4.00; N, 4.28%. MS *m/e*: 327. The filtrate was extracted with chloroform. The chloroform layer was washed with H_2O and dried over $MgSO_4$, and then the chloroform was evaporated. The residue was recrystallized from acetone to give 0.58 g (28%) of **3**, pale yellow needles, mp 154—155 °C. IR (KBr): 1582, 1542, 1425, and 1378 cm^{-1}. UV (EtOH) max: 234 nm (log ε 4.44). NMR ($CDCl_3$) δ=9.36 (1H, s), 9.32 (1H, s), and 7.75—8.57 (6H, m). Found: C, 82.55; H, 4.02; N, 13.77%. Calcd for $C_{14}H_8N_2$: C, 82.33; H, 3.95; N, 13.72%. Picrate: yellow needles, mp 210—212 °C.

2-Formyl-1-acenaphthenone ***1a.*** A 100-ml three necked flask was equipped with a stirrer and a reflux condenser to which is attached a drying tube containing soda lime. 1-Acenaphthenone **1** (1.68 g, 0.01 mol), ethyl formate (3 ml, 0.04 mol), dioxane (40 ml), and an ethanolic solution of sodium ethoxide prepared by dissolving sodium (1.0 g, 0.04 mol) in 10 ml of absolute ethanol were added to the flask and stirred at 0 °C under nitrogen atomosphere for 12 h. The precipitate was separated by filtration and dissolved in water. The water-insoluble part **2** was filtered off. The filtrate was extracted by ether to remove the unreacted **1**. The aqueous layer was acidified with 1 M-HCl to precipitate **1a**, which was filtered, washed thoroughly with water, and dried. Recrystallization from benzene gave the purified product, 1.57 g (80%), mp 179—180 °C (lit, 180—182 °C[5]).

*Acenaphtho[1,2-*d*]pyrimidine* ***3.*** A solution of **1a** (0.98 g, 0.005 mol) and formamidine acetate (0.73 g, 0.007 mol) in 20 ml of ethanol was heated to reflux for 13 h and then the solvent was evaporated using a rotary evaporator. The residue was dissolved in 50 ml of chloroform, washed with 1M-sodium hydroxide solution, and dried over anhydrous sodium sulfate. Evaporation of chloroform gave a pale yellow residue, which was recrystallized from THF to yield 0.8 g (79%) of authentic **3**, mp 154—155 °C.

*Diacenaphtho[1,2-*b*: 1′,2′-*d*]pyridine* ***4.*** A mixture of **1** (1.68 g, 0.01 mol) and triethyl orthoformate (2.0 g, 0.014 mol) was mixed with 30 ml of acetic anhydride and heated to reflux for 12 h with stirring. The reaction mixture was then poured into ice-water and stirred at room temperature to decompose the acetic anhydride and then extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was extracted with hexane. The hexane extract was evaporated and dried *in vacuo*. The residue was dissolved in absolute ethanol and then treated with dry ammonia. The ethanol solution was evaporated to dryness. The residue and **1** (0.84 g, 0.005 mol) and were dissolved into HMPA (10 ml). The solution was heated at 150 °C for 5 h under nitrogen atmosphere. It was cooled to room temperature to precipitate a solid product, which was filtered, washed with ethanol, and recrystallized from dioxane to give purified **4**.

Attempted Reaction of ***2*** *with Formamide.* A mixture of **2** (0.795 g, 0.0025 mol) and formamide (9.5 ml, 0.23 mol) was heated at 150 °C for 3 h. After cooling the reaction mixture, the precipitate was filtered and washed with methanol. 0.771 g (97%) of the unchanged **2** was recovered. The expected product **4** was not formed.

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