Syntheses of 3-Alkyl-naphtho(1.2-b)furan-2-carboxylic Acids

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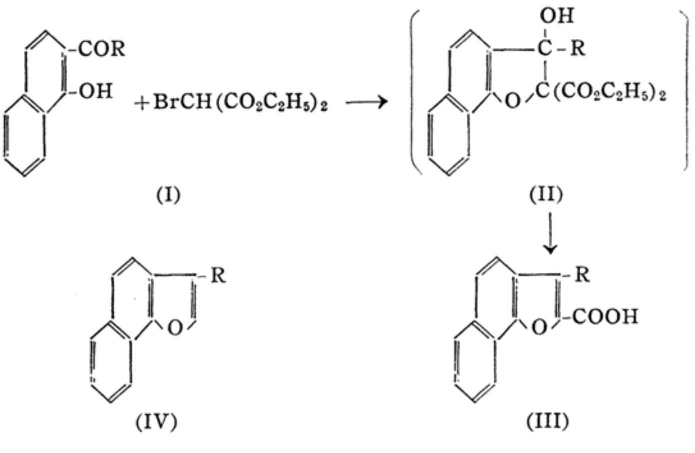
In connection with other synthetical works three 3-alkyl-naphtho(1.2-b)furan-2-carboxylic acids (III R=CH_3, C_2H_5, *n*-C_3H_7) were synthesized.

Search of literature revealed that of these three compounds only 3-methyl-naphtho(1.2-b)furan-2-carboxylic acid had been reported¹⁾, but those synthetical methods are not preferable because of the complexity and the poor yield. Tanaka²⁾ reported a new general synthetic method for coumarones (benzofurans), and by using this method he synthesized phenanthro(1.2-b)furan derivatives³⁾. For the syntheses of the substances mentioned above, his method was applied.

2-Aceto-1-naphthol (I, R=CH_3) and ethyl bromomalonate when refluxed in acetone in the presence of anhydrous potassium carbonate gave an oily substance, the structure of which is assumed to be II (R=CH_3). The last, without further purification, was hydrolysed with alcoholic potash and the carboxylic acid III(R=CH_3) was obtained. An attempt to decarboxylate the acid (III, R=CH_3) to 3-methyl-naphtho(1.2-b)furan (IV, R=CH_3) by refluxing in quinoline with copper powder²⁾ ended fruitless; by this procedure an oily substance with a peculiar smell of coumarones was obtained, but neither this oil nor its picrate showed satisfactory analytical value. As for the picrate, its analytical disagreement is likely due to its instability.

Starting from 2-propionyl- (I, R=C_2H_5) and 2-butyryl-1-naphthol (I, R=*n*-C_3H_7), the corresponding naphtho(1.2-b)furan-2-carboxylic acid (III, R=C_2H_5 and R=*n*-C_3H_7) were likewise synthesized in rather good yield (about 40%). Attempts to obtain the compounds IV (R=C_2H_5; C_3H_7) through decarboxylation of the corresponding acids III (R=C_2H_5; C_3H_7) were again unsuccessful just like the case III (R=CH_3) already mentioned.

The synthetic method used in the present paper is far superior to those described in the old literatures¹⁾·*⁾, so far as naphthofuran-2-carboxylic acids are concerned. The facts that the last acids hardly ever undergo decarboxylation are already stated in the literature¹ᶜ⁾. On the other hand benzofuran-2-carboxylic acids are smoothly²⁾ and phenanthro(1.2-b)furan-2-carboxylic acids are with difficulty decarboxylated³⁾. Since the different behavior of decarboxylation of these



(I) (II) (IV) (III)

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1) (a) A. Hantzsch, *Ber.*, **19**, 1303 (1886). (b) R. Stoermer, *Ann.*, **312**, 313 (1900). (c) St. v. Kostanecki and J. Tambor, *Ber.*, **42**, 908 (1909).

2) S. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 307 (1951); ibid., **73**, 282 (1952); *J. Am. Chem. Soc.*, **73**, 872 (1951).

3) S. Tanaka and S. Kawai, Unpublished work.

* Naphtho(2.3-b)furan derivatives were synthesized by Stoermer (see ref. (1b)) and K. Takeda, T. Schimada and K. Kitanouchi, *J. Pharm. Soc. Japan*, **70**, 268 (1950).

polynuclear benzofuran-2-carboxylic acids attracted the author's interest, the present writer wishes to re-examine the decarboxylation of other sorts of 3-alkyl-naphtho(1.2-b)furan-2-carboxylic acid in the future.

Experimental[4]

3-Methyl-naphtho(1.2-b)furan-2-carboxylic Acid (III, $R=CH_3$) 2-Aceto-1-naphthol (8 g.), ethyl bromomalonate (10.4 g.), freshly dehydrated potassium carbonate (8 g.) and anhydrous acetone (50 ml.) were mixed together and the whole was gently refluxed in a water bath for ten hr. After distilling off the main part of the solvent, the residue was mixed with water and acidified with dilute mineral acid and then extracted with ether. The ethereal extract was washed with water, dried and the ether was removed, giving a dark brown oily substance. Without purification it was dissolved in alcoholic potash (alcohol 80 ml., potassium hydroxide 8 g., water 4 ml.), and then refluxed on a steam bath for one hr. After removal of the solvent, the residue was dissolved in water, washed with ether, and acidified with mineral acid, yielding grayish white precipitates; yield, about 4 g. (41 %). Recrystallization from glacial acetic acid (with charcoal) gave III ($R=CH_3$) as faint yellow pillars of m.p. 255–256° (dec.)[5]. Its analysis does not show satisfctory coincidence with the theoretical ones, just as in the cases of many sorts of coumarone-2-carboxylic acids[2].

Anal. Found: C, 73.21; H, 4.56. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46 %.

Ethyl 3-Methyl-naphtho(1.2-b)furan-2-carboxylate The above-mentioned carboxylic acid (1 g.) was dissolved in absolute alcohol (10 ml.) containing 5 % of hydrogen chloride gas and the whole was refluxed in a water bath for five hr. After removal of the solvent, the residue was dissolved in ether, washed successively with aqueous sodium carbonate and water, dried and the ether was removed, leaving crystals (0.5 g.). The crude crystais were recrystallized from alcohol, giving ethyl ester as colorless flat columns of m.p. 107–108°[6].

Anal. Found: C, 75.10; H, 5.50. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55 %.

3-Ethyl-naphtho(1.2-b)furan-2-carboxylic Acid (III, $R=C_2H_5$) 2-Propionyl-1-naphthol (4.3 g.), ethyl bromomalonate (5 g.), potassium carbonate (3.1 g.) and acetone (60 ml.) were mixed together and the whole was refluxed in a water bath for ten hr. under exclusion of moisture. A similar treatment of the case with methyl derivative gave 2.2 g. (43 %) of crude crystals of carboxylic acid. Recrystallization from benzene gave III ($R=C_2H_5$) as colorless scales of m.p. 218–219°.

Anal. Found: C, 75.04; H, 4.94. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03 %.

3-*n*-Propyl-naphtho(1.2-b)furan-2-carboxylic Acid (III, $R=n\text{-}C_3H_7$) 2-Butyryl-1-naphthol (6 g.), ethyl bromomalonate (7.5 g.), potassium carbonate (5 g.) and acetone (65 ml.) were mixed together and the whole was refluxed in a water bath for ten hr. The same treatment as in the case with methyl derivative gave 3 g. (42 %) of the carboxylic acid. Recrystallization from chloroform (with charcoal) gave III ($R=n\text{-}C_3H_7$) as colorless needles of m.p. 203–204°.

Anal. Found: C, 75.35; H, 5.45. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55 %.

Attempted Decarboxylation of III— i) 3-Methyl-naphtho(1.2-b)furan-2-carboxylic acid (III, $R=CH_3$) (1 g.) and copper powder (0.1 g.) were refluxed in quinoline (10 ml.) on a wire gauze for 30 min. After cooling, ether (200 ml.) was added and the mixture was filtered from the copper. The ethereal solution was washed successively several times with 2-N-hydrochloric acid, water, aqueous sodium bicarbonate and then with water to remove quinoline and dried. This ethereal extract, when freed from the solvent, gave an oily substance. Distillation in vacuo gave an oil (0.5 g.), b.p. 66–70°/1 mm. A part of the oil solidified[7] on standing, and it has the characteristic smell of coumarones. There is a great difference between the analytical and the theoretical value.

The above-obtained semi crystals (0.2 g.) were dissolved in benzene (5 ml.) and to the solution was added picric acid (0.2 g.). The mixture was gently warmed on a steam bath for about 30 min. After cooling, yellow lustrous pillars were yielded, which showed m.p. 61–62° (dec.). Since the picrate thus obtained decomposed gradually in the recrystallization process, attempts to separate the picrate in pure state were unsuccessful.

ii) 3-Ethyl-, and 3-*n*-propyl-naphtho(1.2-b)-furan-2-carboxylic acids behaved analogously, their decarboxylation being difficult.

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[4] All melting points were un-corrected.

[5] See ref (1a) Hantzsch gave m. p. 243-245° (dec).

[6] See ref. (1a) Hantzcsh gave m. p. 108°.

[7] See ref. (1c). Kostanecki and Tambor gave m. p. 38°, b. p 302-304°/720 mm.