KRATKA SAOPĆENJA SHORT COMMUNICATIONS

The Bromination of 2-Furanilide

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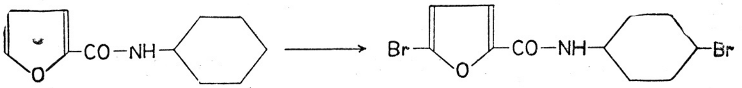
In connection with studies of the reactions of some thioamides, to be published later[1], we were led to investigate the bromination of 2-furanilide, hitherto not mentioned in the literature.

It was found that substitution takes place in both the benzene and furan nuclei, when 2-furanilide (I)[2] is brominated with three molecules of bromine, and a well crystallized dibromo-product, melting after purification at 154—155^0, is obtained in a 40% yield. To this product structure II was attributed, in agreement with the known substitution rules.



I II

The presumed structure (II) is supported by the fact that by cleavage of the bromination product with concentrated hydrochloric acid, under conditions which were found to be useful for the cleavage of some bromoanilides of benzoic acid[3], a small amount of p-bromoanaline was obtained. To furnish a final proof for structure II, the p-bromoanilide of 5-bromo-2-furoic acid was prepared in an unambiguous way from 5-bromo-2-furoyl chloride[4] and p-bromoaniline in pyridine. A colorless crystalline product was obtained in a 56% yield which by the appearence of the crystals, the melting point (154—155^0) and the mixed melting point showed to be identical with the product, obtained by bromination of 2-furanilide.

EXPERIMENTAL*

Bromination of 2-furanilide

In a 250-ml. three-necked, round-bottomed flask fitted with a stirrer, a reflux condenser and a dropping funnel, 6.0 g. (0.032 mole) of 2-furanilide[2] (m. p. 123—124^0) dissolved in 110 ml. of chloroform were placed. From the dropping funnel a mixture of 15.3 g. (4.9 ml., 0.096 mole) of bromine and 5 ml. of chloroform was then slowly added with stirring, and the reaction mixture was refluxed on a water bath for about 40 minutes. After evaporation of the chloroform under diminished pressure, the remaining dark red oil was dissolved in about 22 ml. of boiling 96% ethanol. The hot alcoholic solution was filtered, transferred to an Erlenmeyer flask and cooled to yield 4.4 g. (40%) of almost colorless crystals melting unsharply at 142—

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* The melting points are uncorrected

143°. After two recrystallizations from 96% ethanol pure *p-bromoanilide of 5-bromo-2-furoic acid* (II) was obtained in form of colorless, shiny plates, m. p. 154—155°. The analytical sample was dried under P_2O_5, *in vacuo*, at 100°, for 2 hours.

Anal. 25.711 mg. subst.: 36.0 mg. CO_2 and 4.2 mg. H_2O
4.316 mg. subst.: 0.157 ml. N_2 (28°, 750 mm)
$C_{11}H_7O_2NBr_2$ (345.01) calc'd.: C 38.29; H 2.05; N 4.06%
found: C 38.21; H 1.83; N 4.07%

Cleavage of the bromination product (II)

Two grams of the product obtained by bromination of 2-furanilide were heated in a sealed tube with 25 ml. of concentrated hydrochloric acid (sp. gr. 1.19) at 150—160° for 6 hours. The dark content of the tube was diluted with 30 ml. of water and extracted several times with ether. The ether solutions were collected and dried over anhydrous sodium sulfate. After removal of the solvent only a very small amount of a dark resinous oil was obtained, which could not be crystallized nor otherwise identified.

The aqueous solution was filtered, made strongly alkaline with an excess of sodium hydroxyde and repeatedly extracted with ether. After drying and distilling of the solvent a small quantity of a brown oil was obtained. It was treated with a few drops of concentrated hydrochloric acid to form immediately a crystalline salt, which was dissolved by heating and addition of some water. The solution was filtered still hot and made alkaline by addition of a few drops of concentrated aqueous sodium hydroxyde. From the milky emulsion formed a brownish oil separated which, when cooled, easily crystallized. Thus, 0.2 g. (about 20% of the theoretical amount) of p-bromoaniline, melting at 61—63° was obtained. The mixed melting point with an authentical sample of p-bromoaniline (m. p. 63—64°) gave no depression.

Synthesis of the p-bromoanilide of 5-bromo-2-furoic acid

The 5-bromo-2-furoyl chloride, used in the following experiment, was obtained from 5-bromo-2-furoic acid[5] by treatment with thionyl chloride[4]; yield 92%, b. p.$_{20}$ 102—103°, m. p. 53—54°.

To a solution of 5.2 g. (0.03 mole) of p-bromoaniline in 15 ml. of dry pyridine, 6.3 g. (0.03 mole) of 5-bromo-2-furoyl chloride dissolved in 15 ml. of dry benzene were dropwise added. During addition evolution of heat was observed and, as the reaction proceeded, colorless transparent crystals separated. After all acid chloride had been added, the reaction mixture was refluxed on a water bath for 30 minutes and allowed to stand at room temperature for 12 hours. Now 15 ml. of benzene and 20 ml. of water was added and the mixture transferred to a separatory funnel. After vigorous shaking the benzene layer was separated, washed with 20 ml. of water and dried over anhydrous sodium sulfate. The crude product remaining after evaporation of the solvent was crystallized from about 30 ml. of 96% ethanol. Almost colorless crystals (5.8 g., i. e. 56%) melting at 153—154° were obtained. Recrystallization from ethanol gave colorless shiny plates, m. p. 154—155°. This product showed to be identical with a sample of II prepared by bromination of 2-furanilide; a mixed melting point showed no depression.

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IZVOD

Bromiranje 2-furanilida

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Ustanovljeno je da kod bromiranja 2-furanilida (I) sa tri molekule broma u kloroformu dolazi do stvaranja bezbojnog, lijepo kristaliziranog dibrom-produkta s talištem 154—155° (iskorištenje 40%), kojemu se pripisuje konstitucija *p-bromanilida 5-brom-2-furankarbonske kiseline* (II). U prilog takve strukture govori činjenica, da se cijepanjem spoja s pomoću koncentrirane solne kiseline dobiva mala količina p-bromanilina. Da bi se pružio siguran dokaz konstitucije, izvršena je jednoznačna sinteza p-bromanilida 5-brom-2-furankarbonske kiseline iz 5-brom-2-furoil-klorida[4] i p-bromanilina. Tako dobiveni produkt (iskorištenje 56%) pokazao se u svakom pogledu identičnim sa produktom II, dobivenim bromiranjem 2-furanilida.

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