2-METHYLNAPHTHO[1,2-d]IMIDAZOLE-5,6-DICARBOXYLIC ACID ANHYDRIDE

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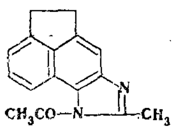
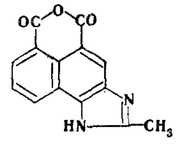
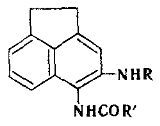
The literature data [1] on the preparation of heterocyclic derivatives of naphthalic anhydride by oxidation of the corresponding acenaphthene compounds have made it possible to assume that anhydrides of naphtho[1,2-d]imidazole-5,6-dicarboxylic acid may be obtained from acenaphtho[4,5-d]imidazoles. For this purpose, we carried out the synthesis (described in [2]) of 1-N-acetyl-2-methylacenaphtho[4,5-d]-imidazole (I) by heating 4,5-diaminoacenaphthene with acetic anhydride in benzene. Anhydride II was obtained by oxidation of I by the method in [1].



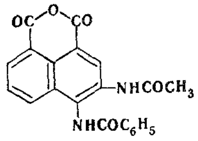
I



II



III–V



VI

III R=COCH$_3$, R'=CH$_3$; IV R=H, R'=C$_6$H$_5$; V R=COCH$_3$, R'=C$_6$H$_5$

However, a detailed study of I showed that its structure corresponds to 4,5-diacetyldiaminoacenaphthene (III), and the IR spectrum confirmed the presence of absorption bands in the region (1620-1670 cm^{-1}) corresponding to the stretching vibrations of an amide carbonyl group [3]. In addition, there are two absorption bands in the region of the stretching vibrations of the NH group (3080 and 3240 cm^{-1}). The stretching vibrations of the NH group in the IR spectrum of II are found at 3220 cm^{-1}, the absorption bands of the amide carbonyl vanishes, and an intense absorption, which can be assigned to the stretching vibrations of the carbonyl groups of naphthalic anhydride, appears at 1720-1760 cm^{-1}. Consequently, closing of the imidazole ring occurs under more severe conditions during oxidation of the $-CH_2-CH_2$ group. However, imidazole ring closing is not observed in the oxidation of 4-amino- (IV) and 4-acetamido-5-benzamidoacenaphthene (V), apparently because of the steric effect of the phenyl group. 3-Acetamido-4-benzamido-1,8-naphthalic anhydride (VI) was isolated as the major product in the oxidation of IV and V.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer.

4,5-Diacetamidoacenaphthene (III). This compound was obtained by the method in [2] from 4.2 g (23 mmole) of diaminoacenaphthene and 8 ml of acetic anhydride in 24 ml of benzene. Recrystallization from acetic acid gave 2.1 g (34.4%) of a product with mp 262-263° (mp 263° [2]). Found: C 71.6; H 5.9;

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N 10.4%. $C_{16}H_{16}N_2O_2$. Calculated: C 71.7; H 6.0; N 10.4%.

4-Amino-5-benzamidoacenaphthene (IV). A solution of 44 g (232 mmole) of stannous chloride in 44 ml of HCl was added to a solution of 11.6 g (36 mmole) of 4-nitro-5-benzamidoacenaphthene in 250 ml of alcohol, and the mixture was refluxed for 2 h. It was then cooled, and the precipitate was removed by filtration, reprecipitated from pyridine, and recrystallized from dimethylformamide to give 7 g (66.6%) of a product with mp 251-252°. Found: N 9.6%. $C_{19}H_{16}N_2O$. Calculated: N 9.7%.

4-Acetamido-5-benzamidoacenaphthene (V). A 4.4-g (80 mmole) sample of iron powder was added to 8.8 g (27 mmole) of 4-nitro-5-benzamidoacenaphthene in 88 ml of glacial acetic acid, after which the mixture was refluxed for 2 h and treated with water. The precipitate was removed by filtration and recrystallized from dilute alcohol to give 8 g (87.6%) of a product with mp 193-196°. Found: C 76.2; H 5.4; N 8.1%. $C_{21}H_{18}N_2O_2$. Calculated: C 76.3; H 5.5; N 8.5%.

2-Methylnaphtho[1,2-d]imidazole-5,6-dicarboxylic Acid Anhydride (II). A mixture of 1.7 g (6 mmole) of III, 17 ml of glacial acetic acid, and 8.5 g (28 mmole) of sodium dichromate was refluxed for 5 h and poured into water. The precipitate was removed by filtration, reprecipitated from 10% sodium acetate solution, and recrystallized from dimethylformamide to give 0.8 g (50%) of a product with mp 340-342°. Found: C 66.4; H 3.1; N 10.5%. $C_{14}H_8N_2O_3$. Calculated: C 66.7; H 3.2; N 11.1%.

3-Acetamido-4-benzamido-1,8-naphthalic Anhydride (VI). This compound was obtained by the method used to prepare II. A) From 18 g (62 mmole) of IV, 180 ml of glacial acetic acid, and 90 g (300 mmole) of sodium dichromate. The product was crystallized from dimethylformamide to give 7.7 g (33%) of VI with mp 315°. Found: C 67.7; H 3.8; N 7.7%. $C_{21}H_{14}N_2O_5$. Calculated: C 67.4; H 3.8; N 7.5%.

B) From 11.3 g (34 mmole) of V, 113 ml of glacial acetic acid, and 56.5 g (189 mmole) of sodium dichromate. The yield of product with mp 315° was 7 g (54.7%). Found: C 67.4; H 3.8; N 7.6%. $C_{21}H_{14}N_2O_5$. Calculated: C 67.4; H 3.8; N 7.5%. The IR spectra of the products of oxidation of IV and V were coincident.

LITERATURE CITED

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3. L. Bellamy, Infra-red Spectra of Complex Molecules, Methuen (1958).