SYNTHESIS OF 4-(3-METHYLPYRAZOLYL-1)NAPHTHALIC ANHYDRIDE

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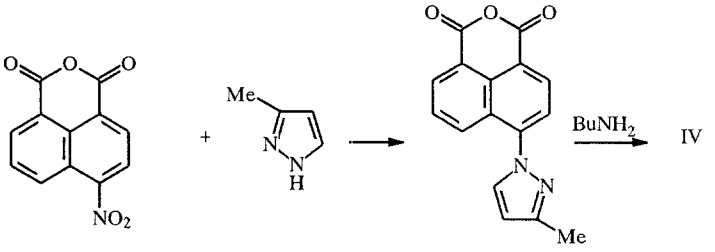
Heating 4-nitronaphthalic anhydride in an excess of 3(5)-methylpyrazole gives only 4-(3-methylpyrazolyl-1)naphthalic anhydride, which is converted by butylamine into the known N-butylimide of 4-(3-methylpyrazolyl-1)naphthalic acid.

It is known that 3(5)-methylpyrazole reacts with 1-nitroanthraquinone with prolonged heating to form 1-(3-methylpyrazolyl-1)anthraquinone (I) [1].

We have discovered that the reaction of 3(5)-methylpyrazole with 4-nitronaphthalic anhydride (II), in which the nitro group is activated by an electron-accepting group, proceeds much faster and leads similarly to only one of two possible isomers, 4-(3-methylpyrazolyl-1)naphthalic anhydride (III). The structure of the latter was confirmed by the close agreement of the chemical shifts of the pyrazole ring protons in the PMR spectra of I [1] and III, as well as by synthesis from anhydride III of the N-butylimide of 4-(3-methylpyrazolyl-1)naphthalic acid (IV), which has previously been obtained from the N-butylimide of 4-hydrazinonaphthalic acid by cyclization [2].



II III

EXPERIMENTAL

The PMR spectrum of III was recorded on a Bruker-200 spectrometer in $CDCl_3$ with HMDS internal standard. Data from C, H, N elemental analysis agreed with the calculated values.

4-(3-Methylpyrazolyl-1)naphthalic Anhydride (III, $C_{16}H_{10}N_2O_3$). For 8.5 h at 150°C were heated 2.19 g (1,mmole) of 4-nitronaphthalic anhydride and 16 ml (20 mmole) of 3(5)-methylpyrazole, until the starting anhydride had disappeared (by TLC). Methylpyrazole was evaporated under vacuum and the residue washed with diethyl ether (2 × 50 ml) and dried. Yield 2.19 (79%) of compound III, mp 208-210°C. PMR: 2.35 (3H, s, 3′-CH_3); 6.36 (1H, d, 4′-H); 7.68 (1H, d, 5′-H); 7.70 (1H, d, 3-H); 7.77 (1H, m, 6-H); 8.58 (2H, d, d-H, 5-H); 8.80 ppm (1H, d, 7-H).

N-Butylimide of 4-(3-Methylpyrazolyl-1)naphthalic Acid (IV). Into a solution of 1.0 g (3.6 mmole) of III in 50 ml ethanol was poured a solution of 1.0 g (13 mmole) of butylamine in 20 ml water and the mixture was refluxed 1.5 h until anhydride III had disappeared (by TLC). After cooling and dilution with water, the precipitate was filtered off and dried. Yield 1.04 g (82%) of IV, mp 144-145°C; mp was 145°C in [2].

LITERATURE CITED

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2. C.-W. Schellhammer and W. Wagner, German Patent 1,469,220; *Ref. Zh. Khim.*, 15H279P (1977).

D. I. Mendeleev Moscow Chemical—Technological Institute, Moscow 125190. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, p. 194, February, 1992. Original article submitted January 29, 1991.

 0009-3122/92/2802-0158$12.50