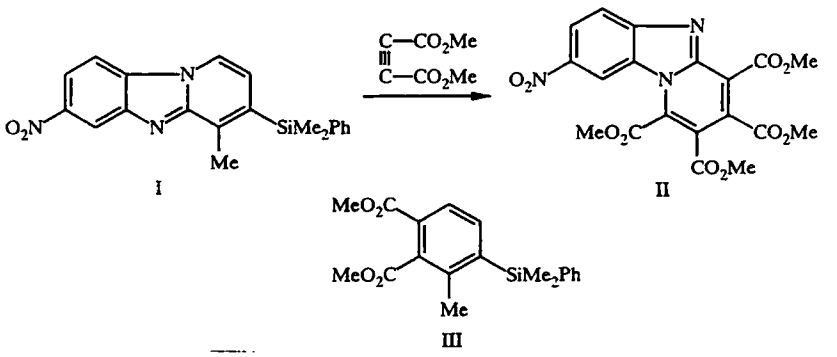
Chemistry of Heterocyclic Compounds, Vol. 33, No. 8, 1997

CLEAVAGE OF 7-NITRO-4-METHYL-3-DIMETHYLPHENYL-SILYLPYRIDO[1,2-*a*]BENZIMIDAZOLE BY DIMETHYL ACETYLENEDICARBOXYLATE IN BENZENE

A. V. Varlamov, E. A. Savitkina, A. I. Chernyshev, and A. P. Krapivko

Pyrido[1,2-*a*]benzimidazole is known to form adducts with two or three molecules of dimethyl acetylenedicarboxylate — 9,10,11,12-tetramethoxycarbonylbispyrido[1,2-*a*:2′,1′-*b*]benzimidazoline and 6,7,9,10,11,12-hexamethoxycarbonyl-5,8-ethenylenebispyrido[1,2-*a*:2′,1′-*b*]benzimidazoline respectively [1]. When we treated 7-nitro-4-methyl-3-dimethylphenylsilylpyrido[1,2-*a*]benzimidazole (I) with a 30-fold excess of dimethyl acetylenedicarboxylate in benzene at 20°C we obtained 8-nitro-1,2,3,4-tetramethoxycarbonylpyrido[1,2-*a*]benzimidazole in 50% yield. The silicon-containing fragment was shown by chromatomass spectrometry to be removed as the substituted benzene (III):



It proposed that the reaction begins with addition of dimethyl acetylenedicarboxylate at atom $N_{(5)}$ accompanied by aromatization of the pyridine unit. This is followed by fission of the $N-C_{(1)}$ bond by nucleophilic attack by a second dimethyl acetylenedicarboxylate molecule. It cannot be excluded that an intermediate in this unusual rearrangement is the adduct of compound I with two molecules of dimethyl acetylenedicarboxylate.

8-Nitro-1,2,3,4-tetramethoxycarbonylpyrido[1,2-*a*]benzimidazole (II, $C_{19}H_{15}N_3O_{10}$), yellow crystals, m.p. 196-197°C (benzene), R_f 0.4 (silufol, 3:1 ethyl acetate–heptane). ^{1}H NMR spectrum (200 MHz, $CDCl_3$): 3.97, 3.99, 4.10, 4.30 (12 H, 4 s, CO_2Me), 8.16 (1 H, d, J_{67} = 8 Hz, 6-H), 8.54 (1 H, dd, J_{76} = 8, J_{79} = 2 Hz, 7-H), 8.66 ppm (1 H, d, J_{97} = 2Hz, 9-H). Mass spectrum, *m/z* (I_{rel}, %): 445 (M^+, 100), 414 (35, $M-CH_3OH$), 387 (12, $M-CO_2CH_2$), 329 (70, $M-2CO_2CH_2$), 271 (49, $M-3CO_2CH_2$), 213 (21, $4-CO_2CH_2$).

The authors express their thanks to GKRF via VO for financial assistance for this study (NTP "Fine organic synthesis," Grant FT-15).

REFERENCE

1. N. S. Prostakov, A. V. Varlamov, I. V. Shendrik, A. P. Krapivko, and N. I. Golovtsov, Khim. Geterotsikl. Soedin., No. 2, 239 (1986).

Russian University for Brotherly Peoples, Moscow 117198. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1137-1138, August, 1997. Original article submitted April 25, 1997.

 0009-3122/97/3308-0994$18.00