CONDENSATION OF CARBAZOLE WITH ACETONE IN THE PRESENCE OF TRIFLUOROACETIC ANHYDRIDE. A SINGLE STAGE SYNTHESIS OF 1,1,3-TRIMETHYL-1H-PYRIDO[j,k]CARBAZOLE

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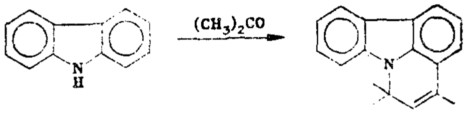
The acid catalyzed reaction of carbazole with aliphatic aldehydes has been well investigated and can lead to oligomers of poly-9-(alken-1-yl)carbazoles or 9,9'-dicarbazolyldialkyl ethers [1, 2] or to 9-(1-alkoxyalkyl)carbazoles [3] in the presence of alcohols. Attempts to involve ketones in these reactions have been unsuccessful up to this time.

We now report the first example of the reaction of carbazole with a ketone under mild conditions. In the presence of trifluoroacetic anhydride carbazole readily condensed with acetone to form 1,1,3-trimethyl-1H-pyrido[j,k]carbazole:



In the ^{13}C NMR spectrum the signal for the quaternary C_1 was found at comparatively low field (55.8 ppm) which confirmed the proposed structure and excluded an alternative double bond isomer position.

<u>1,1,3-Trimethyl-1H-pyrido[j,k]carbazole.</u> Trifluoroacetic anhydride (20 ml, 143 mmole) was added slowly (10 h) with stirring to a solution of carbazole (5 g, 30 mmole) in acetone (90 ml, 1.4 mole) and the stirring continued for a further 10-12 h. The product was diluted with benzene (20 ml), washed with water (3 × 300 ml), the organic layer removed and dried with $CaCl_2$. The solvent was distilled off and the oily residue dissolved in heptane (7 ml) and the product mixture separated on an Al_2O_3 column (3 × 60 cm. activity II) using heptane as eluent. 1,1,3-Trimethyl-1H-pyrido[j,k]carbazole (3.6 g, 66%) was obtained with mp 113-114.5°C (from heptane) and Rf 0.5 (benzene:hexane 1:1), IR Spectrum (Nujol): 1620, 1590 (C=C), 835, 755 cm^{-1} (C–H). It was strongly triboluminescent in the visible region. PMR Spectrum (CCl_4): 1.70 (6H, s, 1-CH_3), 2.05 (3H, s, 3-CH_3), 5.22 (kH, s, =CH), 6.8-7.3 (4H, m, 5-, 8-, 9-, and 10-H), 7.55 (1H, d, J_{45} = 7 Hz, 4-H), 7.65 (1H, d, J_{78} = 7 Hz, 7-H), 7.90 ppm (1H, d, J_{56} = 7 Hz, 6-H).

Elemental analytical data agreed with that calculated.

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