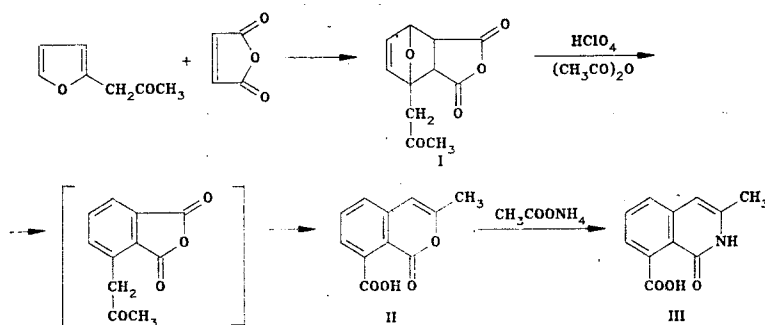


NEW APPROACH TO THE SYNTHESIS OF ISOCOUMARINS

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Isocoumarins are the least-studied compounds in the benzopyrone series, since the known methods for their preparation are extremely laborious. We have developed a new method for the synthesis of substituted isocoumarins that is based on the Diels-Alder reaction. Thus the adduct (I) of 2-acetyl-furan with maleic anhydride is converted to the previously unknown 3-methyl-8-carboxyisocoumarin (II) in 84% yield upon treatment with a 70% solution of perchloric acid in acetic anhydride.



Heterocycle II is formed as a result of aromatization of the six-membered ring of adduct I with subsequent recyclization of the intermediate 3-acetylphthalic anhydride. The structure of isocoumarin II was established on the basis of spectral data and was confirmed by conversion to isocarbostryl III by heating with ammonium acetate in acetic acid.

4-Acetyl-7-oxabicyclo[2.2.1]-2-heptene-exo-5,6-dicarboxylic Acid Anhydride (I). This compound, with mp 104-105°C, was obtained in 85% yield. PMR spectrum (CDCl<sub>3</sub>): 2.23 (3H, s, CH<sub>3</sub>), 3.17 (2H, s, CH<sub>2</sub>), 3.17-3.60 (2H, m, 5-H and 6-H), 5.26 (1H, s, 1-H), and 6.36-7.17 ppm (2H, m, 2-H and 3-H).

3-Methyl-8-carboxyisocoumarin (II). This compound had mp 199-201°C. PMR spectrum (CF<sub>3</sub>COOH), 2.33 (3H, s, CH<sub>3</sub>), 6.57 (1H, s, 4-H), and 7.50-7.87 ppm (3H, m, 5-H, 6-H, and 7-H).

3-Methyl-8-carboxyisocarbostryl (III). This compound, with mp 296-298°C, was obtained in 84% yield. PMR spectrum (CF<sub>3</sub>COOH): 2.67 (3H, s, CH<sub>3</sub>), 7.40 (1H, s, 4-H), 8.00-8.33 (2H, m, 5-H and 7-H), and 8.87-9.00 ppm (1H, m, 6-H).

The results of elementary analysis were in agreement with the calculated values.

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