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C-ACYLATION OF ELECTRON-ENRICHED HETEROCYCLIC COMPOUNDS WITH KIRSANOV ISOCYANATE — A NEW METHOD FOR THE INTRODUCTION OF PHOSPHORUS-CONTAINING GROUPINGS INTO MOLECULES OF HETEROCYCLES

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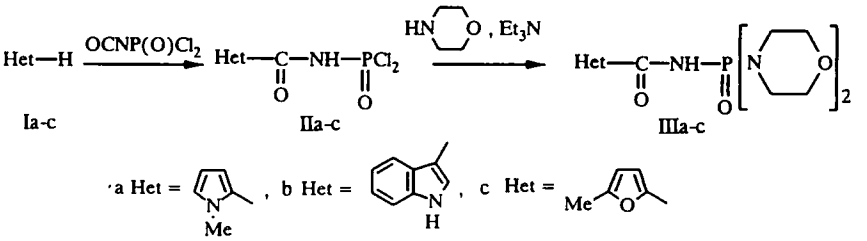
Arylsulfonyl isocyanates are utilized for the C-acylation of electron-enriched nitrogen heterocycles [1], whereby the most active is chlorosulfonyl isocyanate (Graf isocyanate), which acylates not only nitrogen-containing heterocycles, but also oxygen-containing heterocycles [2]. There is an example of the C-acylation of 2-methylindolizine with isocyanatodialkylphosphoric acids [3]. It could be assumed that the most active of the isocyanates of phosphorus acids in C-acylation reactions will be isocyanatophosphoric dichloride (Kirsanov isocyanate) [4]. In fact, N-methylpyrrole, indole, and 2-methylfuran react with Kirsanov isocyanate with the formation of N-hetarylamidophosphoric dichlorides (IIa, b), which are key substances in the synthesis of a great number of derivatives. The addition proceeds at the usual place of electrophilic attack in the named heterocycles. The dichlorides (IIa-c) obtained react with morpholine to give the corresponding diamidophosphates (IIIa-c).



The structure of the compounds obtained was confirmed by the data of elemental analysis for N, P, and Cl, the IR spectra, and ^{31}P and ^{1}H NMR. The IR spectra of the compounds obtained contain characteristic absorption bands of the C=O (1670-1680 cm^{-1}) and P=O (1200-1210 cm^{-1}) groups.

N-(1-Methylpyrrole-2-carboxy)amidophosphoric Dichloride (IIa). $C_6H_7Cl_2N_2O_2P$. To the solution of 0.1 mole of N-methylpyrrole in 10 ml of octane is added, with stirring and cooling using cold water, the solution of 0.1 mole of isocyanatophosphoric dichloride in 5 ml of octane. After 15 min, the resulting residue is filtered off by the dry method, washed with octane, and kept *in vacuo* at room temperature. The yield is 90%, and the mp is 130-132°C. The ^{31}P NMR spectrum (CH_2Cl_2) is characterized at 2.41 ppm. The PMR spectrum (DMSO-D_6) is as follows: 3.90 ppm (3H, s, NCH_3), 6.20 ppm (1H, m, 4-H Pyr), 7.22 ppm (1H, m, 3-H Pyr), 7.50 ppm (1H, m, 5-H Pyr), and 9.42 ppm (1H, m, NH).

N-(Indolyl-3-carboxy)amidophosphoric Dichloride (IIb). $C_9H_7Cl_2N_2O_2P$. This compound is obtained by analogy with (IIa). The yield is 89%. The mp is 150-155°C. The ^{31}P NMR spectrum (CH_2Cl_2) is characterized at 2.55 ppm. The PMR spectrum ($CDCl_3$) is as follows: 7.36 ppm (3H, m, 5-, 6-, 7-H Ind), 7.50 ppm (1H, m, 4-H Ind), 8.15 ppm (1H, s, 2-H Ind), 9.05 ppm (1H, broad s, CONH), and 11.80 ppm (1H, s, NH Ind).

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N-(Dimorpholylphosphato)amide of 1-Methylpyrrole-2-carboxylic Acid (IIIa). $C_{14}H_{23}N_4O_4P$. To the suspension of 0.1 mole of compound (IIa) in 50 ml of benzene is added, with stirring and cooling using cold water, 0.4 mole of morpholine in 10 ml of benzene. After 1 h, the residue is filtered off and dissolved in 10 ml of water. The product is extracted with 3 x 10 ml of methylene chloride. The solvent is evaporated. The yield is 82%, and the mp is 214-215°C. The ^{31}P NMR spectrum (CH_2Cl_2) is characterized at 10.38 ppm. The PMR spectrum (DMSO-D_6) is as follows: 3.07 ppm (8H, m, NCH_2), 3.52 ppm (8H, m, O-CH_2), 3.80 ppm (3H, s, NCH_3), 6.02 ppm (1H, t, J_{4H5H} = 3.5 Hz, 4-H Pyr), 7.01 ppm (1H, s, 3-H Pyr), 7.15 ppm (1H, d, J_{4H5H} = 3.5 Hz, 5-H Pyr), and 8.80 ppm (1H, d, J_{HP} = 7.6 Hz, NH).

N-(Dimorpholylphosphato)amide of Indolyl-3-carboxylic Acid (IIIb). $C_{17}H_{23}N_4O_4P$. This compound is obtained by analogy with (IIIa). The yield is 87%, and the mp is 180-183°C. The ^{31}P NMR spectrum (CH_2Cl_2) is characterized at 11.17 ppm. The PMR spectrum (DMSO-D_6) is as follows: 3.13 ppm (8H, m, NCH_2), 3.55 ppm (8H, m, OCH_2), 6.97 ppm (3H, m, 5-, 6-, 7-H Ind), 7.47 ppm (1H, m, 4-H Ind), 8.16 ppm (1H, s, 2-H Ind), 10.75 ppm (1H, broad s, CONH), and 11.82 ppm (1H, s, NH Ind).

N-(Dimorpholylphosphato)amide of 2-Methylfuryl-5-carboxylic Acid (IIIc). $C_{14}H_{22}N_3O_5P$. To the solution of 0.1 mole of 2-methylfuran in 10 ml of octane is added, with stirring, the solution of 0.1 mole of isocyanatophosphoric dichloride in 5 ml of octane. After 12 h, the solution of 0.4 mole of morpholine in 2 ml of octane is added to the reaction mixture with stirring and cooling using cold water. After 30 min, the product is isolated by analogy with (IIIa), and is recrystallized twice from ethyl ether. The yield is 30%, and the mp is 180-182°C. The ^{31}P NMR spectrum (CH_2Cl_2) is characterized at 9.90 ppm. The PMR spectrum (DMSO-D_6) is as follows: 2.34 ppm (3H, s, CH_3), 3.07 ppm (8H, m, NCH_2), 3.52 ppm (8H, m, OCH_2), 5.80 ppm (1H, m, NH), 6.20 ppm (1H, s, 4-H Fur), and 7.46 ppm (1H, s, 3-H Fur).

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