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SYNTHESIS OF 2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL ESTERS OF ACIDS WITH PHYTOHORMONAL ACTIVITY. NEW MODIFICATION OF THE KOENIGS—KNORR METHOD

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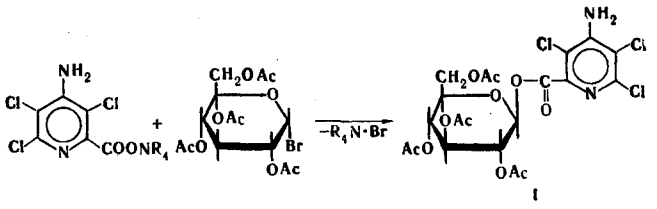
2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl esters were synthesized by the reaction of tetralkylammonium salts of 4-amino-3,5,7-trichloropicolinic, 2,4-dichlorophenoxyacetic, and β-indolylacetic acids with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide. According to the PMR spectral data, substitution occurs stereospecifically to give the β anomers.

Glucopyranosyl esters of acids with phytohormonal activity are attracting attention as metabolites of phytohormones [1].

Glucopyranosyl esters can be obtained by the Koenigs—Knorr method [2, 3] or modifications of it based on the reaction of acetobromoglucose with silver [4], mercury [5], or amine [6] salts of acids. However, these methods are not universal and are often accompanied by low yields and the formation of mixtures of anomers that are difficult to separate [7].

Our attempts to synthesize a previously unknown ester of aminopicolinic acid (I) by the Koenigs—Knorr method and some of its modifications were unsuccessful. For the synthesis of this compound we propose a new modification of the Koenigs—Knorr method based on the reaction of acetobromoglucose with the tetraalkylammonium salt of 4-amino-3,5,6-trichloropicolinic acid:



R=CH3, C4H9

According to the PMR spectral data, the reaction proceeds stereoselectively to give the β anomer. The signal of the anomeric proton in the PMR spectra appears at 6.25 ppm in the form of a doublet with splitting constant J = 8 Hz. A similar splitting constant of an ano-

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meric proton was also observed for esters of 2,4-dichlorophenoxyacetic acid (II) and β-indolylacetic acid (III), which were synthesized by the proposed method. This J value is usually characteristic for a β anomer [6].

EXPERIMENTAL

The PMR spectra were recorded with a Varian T-60 spectrometer. The mass spectra were recorded with an LKB-9000 spectrometer at 70 eV and 100°C. The products were chromatographed on Silufol UV-254 plates; the spots were developed with a mixture of 4% 2,3,5-triphenyltetrazolium chloride and 4% sodium hydroxide in methanol with brief heating at 120°C.

1-O-(4-Amino-3,5,6-trichloropicolinyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranose (I). A) A 0.01-mole sample of 4-amino-3,5,6-trichloropicolinic acid was added to a solution of 0.01 mole of tetramethylammonium hydroxide in 6 ml of water, and the resulting solution was evaporated in vacuo. The residue was washed with hot acetone and dried in a vacuum desiccator to give tetramethylammonium 4-amino-3,5,7-trichloropicolinate, with mp 205°C (dec.). in 80% yield. A 411-mg (1 mmole) sample of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide was added to a suspension of 376 mg (1 mmole) of the salt obtained above in 20 ml of dioxane, and the reaction mixture was stirred at 80°C for 8 h. It was then cooled, and the precipitate was removed by filtration. The filtrate was evaporated *in vacuo*. and the residue was washed with CCl_4 and dissolved in ether. The solution was treated with hexane, and the precipitate was removed by filtration and dried in a vacuum desiccator to give I, with mp 134-135°C, R_f 0.74 [benzene–ethyl acetate (1:2)], and $[\alpha]_D^{20}$ +27° ($CHCl_3$, c 2.3), in 60% yield. PMR spectrum (in d_6-DMSO): 2.0 (12H, 4 CH_3COO), 4.2 (2H, 6-H), 4.32 (1H, 5-H), 4.85-5.5 (3H, 2-, 3-, and 4-H), and 6.25 (1H, d, J = 8 Hz, proton attached to C_1). Mass spectrum, m/z (%): 570 (3), 331 (40), 283 (49), 266 (15), 240 (49), 224 (53), 197 (100), 162 (11). Found: C 42.2; H 3.7; N 4.7%. $C_{20}H_{21}Cl_3N_2O_{11}$. Calculated: C 42.1; H 3.6; N 4.8%.

B) The compound was similarly obtained in 57% yield, except that tetrabutylammonium hydroxide was used in place of tetramethylammonium hydroxide.

C) The synthesis was carried out by the Koenigs–Knorr method [2]. A 1.5-mmole sample of silver oxide was added to a mixture of 1 mmole of 4-amino-3,5,6-trichloropicolinic acid and 1 mmole of tetra-O-acetyl-α-D-glucopyranosyl bromide in 20 ml of dry dioxane, and the reaction mixture was stirred in the dark at 20°C for 24 h. The precipitate was removed by filtration and washed with ethyl acetate. The filtrate was evaporated *in vacuo*, and the syrupy product in the residue was found to be free of I, according to the mass-spectral data.

D) The synthesis was carried out by the modification in [4]. A mixture of 1 mmole of the silver salt of 4-amino-3,5,6-trichloropicolinic acid and 1 mmole of acetobromoglucose in 50 ml of dioxane was stirred at 45-50°C for 4 h, after which it was cooled, and the precipitate was subjected to centrifugation. The supernatant material was evaporated, and the syrupy product in the residue was found to be free of I, according to the mass-spectral data.

E) The synthesis was carried out by the modification in [6] from 1 mmole of 4-amino-3,5,6-trichloropicolinic acid, 1 mmole of acetobromoglucose, and 0.14 ml of triethylamine in 10 ml of acetone, but I could not be isolated from the reaction mixture.

1-O-(2,4-Dichlorophenoxyacetyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranose (II). This compound was obtained under the conditions of example A from 1 mmole of tetramethylammonium 2,4-dichlorophenoxyacetate and 1 mmole of 2,3,4,6-tetra-O-acetylglucopyranosyl bromide in 20 ml of dioxane. A product with mp 125-127°C, R_f 0.5 [benzene–ethyl acetate (4:1)], and $[\alpha]_D^{20}$ +47° ($CHCl_3$, c 2) was obtained in 70% yield. PMR spectrum (in $CDCl_3$): 5.8 ppm (1H, d, J = 7 Hz, glucose 1-H). According to [6], this compound had mp 127°C.

1-O-(β-Indolylacetyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranose (III). This compound was obtained under the conditions of example A from 0.2 mole of tetramethylammonium β-indolylacetate and 0.2 mmole of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide in 4 ml of acetonitrile, except that the reaction was carried out at 20°C for 48 h. The precipitate was then removed by filtration, and the filtrate was evaporated *in vacuo*, The residue was dissolved in 2 ml of a mixture of benzene and ethyl acetate (1:1) and chromatographed with a column filled with Woelm 02753 silica gel (Federal Republic of Germany) in the same system. The eluent, which contained a product with R_f 0.65 on a Silufol plate in a chloroform–ethyl acetate system (2:1), was evaporated in vacuo, and the residue was dissolved in ether and precipitated by the addition of hexane to give III, with mp 118-120°C, in 55% yield. PMR

spectrum (in d_6-DMSO): 5.6 ppm (1H, d, J = 7 Hz, glucose 1-H). According to the data in [8], this compound had mp 120-121°C.

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SYNTHESIS OF PYRIDINE AND QUINOLINE DERIVATIVES OF FERROCENE FROM β-CHLORO-β-FERROCENYLACROLEIN

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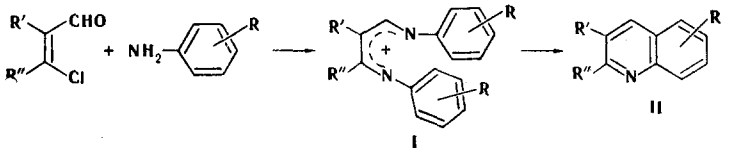
UDC 547.828'832.5'257.2.07

2-Ferrocenylquinolines that contain a hydroxy or methoxy group in the 7 position were obtained by the reaction of β-chloro-β-ferrocenylacrolein with m-anisidine and with m-aminophenol. The introduction of aniline in this reaction leads to the formation of β-ferrocenyl-β-phenylaminoacrolein anil hydrochloride, which cannot be converted to 2-ferrocenylquinoline. 2,3,6-Trisubstituted pyridines that contain a ferrocenyl substituent in the 6 position were obtained by condensation of β-chloro-β-ferrocenylacrolein with β-dicarbonyl compounds.

It is known [1] that β-chloroacroleins are convenient starting compounds for the synthesis of a number of five-, six-, and seven-membered heterocycles. In particular, β-chloro-β-ferrocenylacrolein was previously used for the synthesis of ferrocene-containing pyrazoles [2], pyrimidines [2], pyrylium salts, and the corresponding pyridines [3].

It has been shown [4] that quinoline derivatives II are readily formed via the following scheme in the reaction of β-chloroacroleins with aromatic amines:



I II

However, in an attempt to synthesize 2-ferrocenylquinoline by the reaction of β-chloro-β-ferrocenylacrolein with aniline we isolated only intermediately formed immonium salt Ia (R, R' = H, R'' = ferrocenyl), which is not converted to the corresponding quinoline even when it is refluxed in acetic acid. The introduction in the meta position of the aniline ring of electron-donor substituents facilitates intramolecular electrophilic attack in immonium salt I, which leads to the formation of quinolines II with splitting out of an aniline fragment. In fact, brief refluxing of β-chloro-β-ferrocenylacrolein with m-anisidine or m-aminophenol in benzene leads to the formation of the corresponding quinoline derivatives IIb (R = 7-OCH_3, R' = H, R'' = ferrocenyl) and IIc (R = 7-OH, R' = H, R'' = ferrocenyl). It is apparent that intermediately formed immonium salt I can be converted to a quinoline via two pathways; α-

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