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# REACTION OF THIAZOLO[2,3-b]BENZOTHIAZOLIUM SALTS WITH CARBON-NUCLEOPHILES AND SYNTHESIS OF THE DERIVATIVES OF PYRROLO[2,1-b]BENZOTHIAZOLE

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Carbon-nucleophiles such as malononitrile and 1-morpholino-1-cyclohexene attacked at the bridge-headed $>C=\overset{+}{N}<$ bond of thiazolo[2,3-b]benzothiazolium perchlorates (1) to give pyrrolo[2,1-b]benzothiazoles (2) through re-cyclization and re-aromatization of the intermediate 2-methylidene-3-(2-mercaptovinyl)-2,3-dihydrobenzothiazole and 1,2-dihydropyrrolo[2,1-b]benzothiazole systems. As 1-phenyl-2,3-tetramethylenepyrrolo[2,1-b]benzothiazole (2a) exhibited some anti-inflammatory activity, the homologous materials were prepared. On reaction with cuprous cyanide p-bromophenyl derivative (2b) furnished the benzonitrile (2c), which was converted into the compounds with various aliphatic substituents at the para position of the phenyl moiety. On reaction with methylmagnesium iodide and subsequent hydrolysis 2c was converted into the acetophenone (2d), which furnished acetic acid derivatives by Willgerodt-Kindler reaction. Treatment with triphenylphosphonium methylide 2d gave 2-phenylpropylene (2e), which was also prepared from 2d by the reaction of methylmagnesium iodide and subsequent dehydration reaction. Hydroboration of 2e afforded 2-phenylpropanol (2f), which was oxidized with chromic acid into the propionic acid derivative (3g), the sulfur atom being oxidized at the same time into sulfoxide. The de-oxygenation of the corresponding ethyl ester (3h) was carried out with $PBr_3$ to give α-substituted propionic acid ester (2h). Oxidation of 2a with chromic acid, with m-chloroperbenzoic acid or with sodium periodate furnished the corresponding sulfoxide (3a), which was also reduced back to the starting material (2a) with $PBr_3$. The infrared spectra of the sulfoxides (3a,g,h) showed an intense absorption at 1660-1690 $cm^{-1}$, indicating that the S-oxide group induced the enamine-type polarization of the $>C=C<$ bonds of the pyrrole ring.