DISSERTATIONES

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The Reaction of Ureido Esters with Acid Anhydrides

A. Kornhauser

Tracer Laboratory, Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

The reaction of acetic anhydride with α - and β -ureido esters was studied. Some substituted ureido esters of the tipe RCH(NHCONHR') (CH₂)_nCO₂Et (R=H, CH₃, (CH₃)₂CHCH₂, C_6H_5 ; R' = C_6H_5 , $1-C_{10}H_7$, $n-C_4H_9$, $n-C_6H_{13}$, n=0 or 1) were prepared and subjected to the reaction with boiling acetic anhydride. It was shown that no cyclization to the expected dihydrouracils or dihydrooxazines occurred. Carbon dioxide and the corresponding N,N-diacetyl- and N-acetyl-aminoesters, and N,N-diacetyl- and N-acetyl-aminoesters were identified as the reaction products. N,N-Diacetyl- and N-acetyl-aminoesters were also prepared from the corresponding amino and N-carbonyl-esters. By analogous reactions with propionic anhydride N,N-dipropionyl- and N-propionyl-amino derivatives were obtained. A satisfactory separation of N,N-diacyl- from N-acyl-amino derivatives was achieved by chromatography on a charcoal-celite column.

The mechanism of the reaction was studied using 14 C. It was established that the carbon dioxide evolved in the reaction of acetic anhydride with ethyl β -[3-(1'-naphthyl)-ureido-2- 14 C]-butyrate originates from the carbonyl of the ureido group. As an intermediate in the reaction of β -ureido esters with acetic anhydride, a mixed carbaminic-carboxylic anhydride has been presumed. The IR- spectra of N,N-diacetyl- and N-acetyl-amino derivatives are given and discussed. The properties of

the obtained N,N-diacylamino esters are described. Ethyl N,N-diacetyl- β -amino butyrate was reduced with LiAlH₄ to N,N-diethyl-3-amino butanol-(1).

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A. KORNHAUSER

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- I. Kornhauser A.
- II. Tracer Laboratory, Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

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Acetic Anhydride
Butanol-1, 3-d ethylamino-,
Butyric acid, Et ester,
β-diacetylamino-,

Butyric acid, Et ester, β-dipropionylamino-,

p-diproprohylamino
Butyric acid, Et ester,
β-propionylamino-,
Diacetamides
LiAlH₄

δ-Methyl-hexanoic acid, Et ester, β-diacetylamino-,

Naphthylamine-1,
N,N-dipropionyl-,
Propionic acid, Et ester,
a-diacetylamino-, Propionic Anhydride Ureido esters, substituted-,