THE ACYLATION OF AMINO ACIDS BY tert-ALKYL PYROCARBONATES

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The acylation of amino acids with pyrocarbonates has been studied by a number of authors [1, 2] and has found practical application in biochemistry [3]. It has been found [2] that pyrocarbonates react very readily with the amino groups of amino acids in aqueous organic solutions at pH > 7 with the quantitative formation of N-alkoxycarbonyl derivatives. The reaction of tert-alkyl pyrocarbonates (Ia, b) with amino acids has not previously been studied. We have found that when di-tert-alkyl pyrocarbonates (Ia, b) are stirred with solutions of triethylammonium or sodium salts of amino acids in aqueous isopropanol (1 : 1) a reaction begins after a short induction period (3-5 min) and is accompanied by the spontaneous heating of the reaction mixture. N-tert-Alkoxycarbonyl derivatives of amino acid salts (IIa, b) are formed.

$$(ROCO)_2O + H_2NCHCOO^- \longrightarrow ROCONHCHCOO^- + ROH + CO_2$$

(R′ on the amino acid salt; R′ on the product)

I a, b — IIa, b

a) R = tert $-C_4H_9$

b) R = $(CH_3)_2-C-CH_2C_6H_5$

The yields of N-tert-alkoxycarbonyl derivatives of the amino acids are high and are determined only by the losses on isolation. The constants of the N-tert-butyloxycarbonyl derivatives obtained (BOC-glycine, -L-alanine, -L-leucine, -L-phenylalanine, and -L-proline) correspond to those given in the literature.

N-Benzyl-isopropyloxycarbonyl derivatives of amino acids (IIb) (BPOC-amino acids) have now been prepared for the first time. BPOC-glycine was obtained with a yield of 57%, mp 108-109°C; BPOC-L-leucine with a yield of 63%, mp 93-95°C, $[\alpha]_D^{20} - 26 \pm 1°$ (c 1; C_2H_5OH). BPOC-L-proline is an oil.

The elementary analyses corresponded to the calculated figures.

LITERATURE CITED

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