

of the 2+3 mixture with water is even more favorable (practically no loss of yield).

Z/E-Isomeric mixtures of 2, R¹=H, R≠H, can be quantitatively converted with hydrogen chloride in ether^[1] into the Z-isomers suitable for the enantioselective hydrogenation^[2]. The alkaline saponification of 2 also proceeds smoothly and in high yield to give N-acetyldehydroamino acids^[4].

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A Facile, Generally Applicable Synthesis of N-Acetyldehydro- α -amino Acids

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Dehydroamino acids are used as educts for the synthesis of α -amino acids. Thus, a series of amino acids could be prepared e.g. by addition of acidic compounds such as malonic acid derivatives, indole, imidazole, and thiols to dehydroamino acids^[1]. Of particular synthetic significance is the enantioselective hydrogenation of N-acyldehydroamino acids or -amino acid esters in the presence of optically active metal complexes as catalysts which produce, respectively, amino acids or amino acid esters in very high optical yield^[2].

Until now the known syntheses of dehydroamino acids are either involved, not generally applicable, or rely upon amino acids as starting materials^[1].

The recently postulated intermediary 2-iminopropionic acid ester was trapped, by careful acylation, as the N-acetyldehydroalanine ester in the alkoxide-catalyzed preparation of pyruvic acid ester from 2-azidopropionic acid ester^[3].

We have now obtained N-acetyl-2 and/or N,N-diacetyldehydro- α -amino acid esters 3 by warming the 2-azidocarboxylic acid esters 1 in acetic anhydride or acetic anhydride/acetic acid in presence of catalytic amounts of rhenium heptasulfide (Table 1). The azidocarboxylic acid esters 1 are almost quantitatively accessible from the corresponding α -halogen derivatives via azide exchange by a phase-transfer reaction with Aliquat 336 as catalyst. Exclusive formation of 2 can be achieved using a smaller Ac₂O/AcOH ratio, advantageously in presence of HCl. Work-up

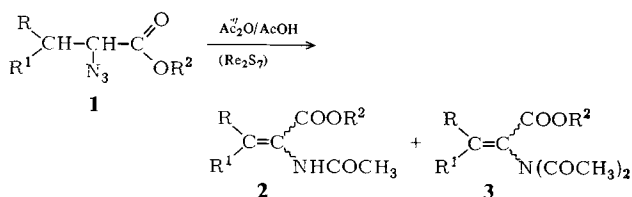


Table 1. N-Acetyl-2 and N,N-diacetyldehydroamino acid esters 3 from 2-azidocarboxylic acid esters 1. Solv. = solvent. A: in Ac₂O, B: in Ac₂O/AcOH (3/7), C: in Ac₂O/AcOH (2/3)/HCl, D: in Ac₂O/AcOH (1/1), E: in Ac₂O/AcOH (1/4)/HCl.

	1		R ²	Solv.	Yield [%]		2
	R	R ¹			2 + 3	Solv.	
a	H	H	Me	A	39 + 40	B	71
b	H	n-Pr	Me	A	20 + 75	C	91
c	H	Ph	Et	D	33 + 57	E	90
d	Me	Me	Me	A	93	C	90
e	H	PhS	Me			C	77

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