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A NEW SYNTHETIC ROUTE TO N,O,BIS-DIMETHYLPHENYLSILYL AMINO ACID

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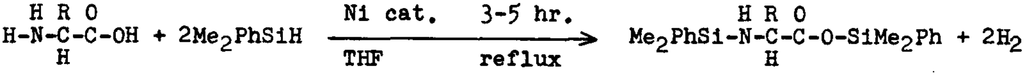
There have appeared some papers which dealt with trimethylsilyl derivatives of amino acid by using $\equiv$Si-Cl, $\equiv Si_2NH$,1) $\equiv Si\text{-}NHCOCH_3$2) and $\equiv Si_2NCOCH_3$3) as silylation reagents.

In our preceding papers which comprized reactions between hydrosilanes and phenols4) or thiophenols,5) we have reported that dehydrocondensation between the above reactants proceeded very smoothly with use of the catalyst formed from the reaction of $\equiv$Si-H with $NiCl_2$.

In the present, we have obtained N-silylamino acids silyl ester from several -amino acid and dimethylphenylsilane using above catalyst in satisfactory yield, and this reaction is a novel and an effective method for the preparation of N,O,bis-triorganosilyl amino acids.

Synthesis was carried out according to the following reaction.



$$\mathrm{H\text{-}\overset{H}{\underset{H}{N}}\text{-}\overset{R}{C}\text{-}\overset{O}{C}\text{-}OH + 2Me_2PhSiH \xrightarrow[\text{THF}\qquad\text{reflux}]{\text{Ni cat.}\quad\text{3-5 hr.}} Me_2PhSi\text{-}\overset{H}{N}\text{-}\overset{R}{\underset{H}{C}}\text{-}\overset{O}{C}\text{-}O\text{-}SiMe_2Ph + 2H_2}$$

A typical preparation will be detailed as follows: To a suspension consisted 11.7 g(0.1 mol) of L-valin, 34 g(0.25 mol) of Me_2PhSiH and 100 ml of THF was added 1.8 g of the above described nickel catalyst under nitrogen atmosphere, and the mixture was refluxed with stirring. After two hours reaction, the evolution of theoretical amount 450 ml(0.2 mol) of hydrogen was recognized.

After the removal of Ni catalyst by centrifugation, THF and unreacted silane was removed by distillation. Fractional distillation of the residual liquid product under reduced pressure gave 24.6 g(64 %) of N-dimethylphenylsilyl L-valine dimethylphenylsilyl ester boiling at 131-137°C/0.03 mmHg which was identified by IR spectra, 3380 cm^{-1}(NH), 1720 cm^{-1}(C=O), 1430 cm^{-1}(Si-Ph) and 1250 cm^{-1}(Si-Me) and elemental analysis.

The results obtained by the reaction with several amino acids are given in the Table 1.

Table 1 The reaction of amino acids with dimethylphenylsilane

Amino acid	b.p °C	Yield	Elemental Analysis % (Calcd)				n_D^{20}	d^{20}	MRd6)
	(mmHg)	%	C	H	N	Si			(Calcd)
Glycine	135-141 (0.1)	62	63.72 (62.93)	7.69 (7.34)	3.75 (4.08)	16.3 (16.4)	1.5183	1.0191	102.21 (101.68)
			calcd. for $C_{18}H_{25}NO_2Si_2$						
L-Alanine	140-148 (0.05)	66	63.57 (63.82)	7.48 (7.61)	3.80 (3.92)	15.6 (15.7)	1.5181	1.0295	105.31 (106.31)
			calcd. for $C_{19}H_{27}NO_2Si_2$						
L-Valine	131-137 (0.03)	64	65.40 (65.41)	8.06 (8.10)	3.43 (3.63)	14.6 (14.6)	1.5142	1.0111	114.88 (115.57)
			calcd. for $C_{21}H_{31}NO_2Si_2$						
L-Leucine	135-138 (0.02)	92	66.30 (66.11)	8.28 (8.32)	3.34 (3.51)	13.8 (14.1)	1.5106	1.0002	119.64 (121.45)
			calcd. for $C_{22}H_{33}NO_2Si_2$						
L-Phenyl-alanine	176-178 (0.08)	75	69.15 (69.23)	7.41 (7.27)	3.04 (3.23)	12.8 (13.0)	1.5423	1.0523	129.78 (130.55)
			calcd. for $C_{25}H_{31}NO_2Si_2$						

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