The Reaction of Glycine Cobalt Complex with Acetaldehyde

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Considerable progress in the chemical synthesis of threonine has recently been made by Sato, Okawa and Akabori by means of a Knoevenagel-type condensation of acetaldehyde with the active methylene groups of glycine copper complex[1]. As a continuation of their study we have investigated a similar type of reaction using acetaldehyde and glycine cobalt complex. The triglycino-cobalt was reported to occur in two isomeric forms, namely α- and β-form[2]. These two isomers can be obtained separately owing to the difference of their specific gravities.

A 0.02 g. portion of glycine cobalt complex was allowed to react with 0.1 cc. of acetaldehyde in the presence of 0.1 cc. of 6% aq. sodium carbonate as a condensing catalyst in a sealed tube. After suitable periods of time the total yields of products (threonine+allothreonine) and the ratios of threo- to allo-form in the products were determined by the dinitrofluorobenzene method[3] and a simplified ninhydrin method, respectively.

In general, the yields, especially when the β-form complex was used, were poor, while the threo/allo ratios obtained were much higher than those observed in the case of the copper complexes (threo/allo =1.8). The highest ratio was obtained when the condensation was carried out at 70°C for 2 hr. using the α-isomer. Under this condition the total yield (allo+threo) was 32%, (see Table I).

The poor yield may be due to remarkable stability of glycine cobalt complex, and the changes in the threo/allo ratios with reaction temperature and/or time (see Tebles I and II) suggest that the stabilities of cobalt threonine and cobalt

Table I
Influence of reaction temperature on the threo/allo ratio at a reaction time of 2hr.

Reaction Temp.	α-form			β-form		
	threo, %	allo, %	threo/allo	threo, %	allo, %	threo/allo
50°C	77	23	3.4	78	22	3.5
70°C	88	12	7.6	81	19	4.2
90°C	76	24	3.1	70	30	2.3

Table II
Influence of reaction time on the threo/allo ratio at 70°C

Reaction Time	α-form			β-form		
	threo, %	allo, %	threo/allo	threo, %	allo, %	threo/allo
1/2 hr.	78	22	3.5	74	26	2.9
1 hr.	82	18	4.5	75	25	3.0
2 hr.	88	12	7.6	81	19	4.2
4 hr.	85	15	5.6	78	22	3.5

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[1] M. Sato, K. Okawa and S. Akabori, This Bulletin, **30**, 937 (1957).

[2] H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909).

[3] J. C. Perrone, *Nature*, **167**, 513 (1951).

allothreonine complexes are different. Moreover, as can be seen in Tables I and II, the ratios obtained with the α-form appear to be slightly higher than those obtained with the β-form.

The effect of catalysts other than sodium carbonate was also examined and only potassium carbonate was effective. Disodiumhydrogenphosphate and sodium acetate were completely inactive. The detailed results on this reaction will be reported elsewhere.

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