

Fig. 1.—Multilayer heat capacities of methane adsorbed on rutile.

begin to exhibit bulk properties. The maxima are interpreted as indicating a rearrangement in the adsorbed film corresponding to melting in the bulk phase. Morrison<sup>2</sup> suggests that the melting point is lowered because a distortion of the normal lattice makes solidification more difficult, and that the spreading of the effect over a temperature range might be due to the small thickness of the adsorbed films. The graphs show two noticeable differences between argon and methane. For argon, bulk properties begin between 1.6 and 2.9 monolayers; for methane they begin between about three and four monolayers. There is quite a difference in the shape of the 1.6 monolayer curve of argon and the one and two monolayer curves of methane. The argon curve is practically a straight line with only a small slope. The methane curves rise steeply to about 85°K., level off between 85 and 95°K., and then rise rather sharply again. The three monolayer curve of methane more closely approximates the argon curve in shape between 80 and 95°K. Mastrangelo<sup>5</sup> proposes that the shifts in the helium maxima are caused by pressure effects—high pressures at low coverages, and lower pressures at higher coverages. However, this will not explain the shifts for argon and methane, because their melting points are raised by increases in pressure. It is interesting to notice that the heat capacities of methane and argon adsorbed in the monolayer region are above or nearly the same as those of the liquid phases above the melting

(5) S. V. R. Mastrangelo, *J. Chem. Phys.*, **18**, 806 (1950).

point; but one monolayer of nitrogen has heat capacities decidedly below those of the bulk liquid phase.<sup>6</sup>

If the differential heat capacities ( $\overline{C}_{N_2}$ ) at 5.3 monolayers are plotted, using the data of 4.8 and 5.8 monolayers, the integral

$$\int_{72}^{90.6} (\overline{C}_{N_2} - C_{\text{psolid}}) = 230 \text{ cal.}$$

which is very nearly equal to the heat of fusion of methane (*cf.* ref. 2).

This work has been sponsored in part under ONR Contract No. 182(00), Project NR 057 173, and in part under AEC Contract No. AT(30-1)-824.

(6) J. A. Morrison and G. J. Szasz, *ibid.*, **16**, 280 (1948).

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### Synthesis of Poly-N<sup>β</sup>-benzyl-*dl*-asparagine

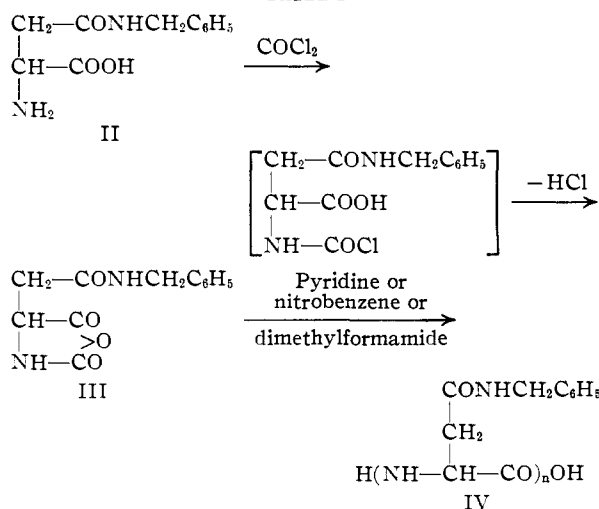
BY MAX FRANKEL, Y. LIWSCHITZ AND A. ZILKHA

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In continuation of previous work on syntheses of polyfunctional polyamino acids and derivatives,<sup>1</sup> the synthesis of poly-N<sup>β</sup>-benzyl-*dl*-asparagine is reported in the present paper.

This polymer was prepared by the following series of reactions (Table I), starting from N<sup>α</sup>,N<sup>β</sup>-dibenzylasparagine (I),<sup>2,3</sup> which was catalytically hydrogenolyzed to N<sup>β</sup>-benzyl-*dl*-asparagine (II). This on being suspended in dioxane and treated with phosgene, yielded the N-carboxy anhydride (III), probably through N<sup>α</sup>-chloroformyl-N<sup>β</sup>-benzylasparagine. III represented a white crystalline, comparatively stable compound, decomposing at 225°.

TABLE I



(1) M. Frankel and A. Berger, *Nature*, **163**, 213 (1949); *J. Org. Chem.*, **16**, 1513 (1951); M. Frankel, M. Breuer and S. Cordova, *Experientia*, **VIII**, 299 (1952); M. Frankel and M. Halmann, *J. Chem. Soc.*, 2735 (1952); M. Frankel, M. Harnik and Y. Levin, *Experientia*, **VIII**, 98 (1952); E. Katchalski, I. Grossfeld and M. Frankel, *This Journal*, **69**, 2584 (1947); **70**, 2094 (1948).

(2) F. H. McMillan and N. F. Albertson, *ibid.*, **70**, 3778 (1948).

(3) M. Frankel, Y. Liwshitz and Y. Amiel, *ibid.*, **75**, 330 (1953).

As, in this instance, the method of thermal polymerization *in alto vacuo* was not feasible because of the high decomposition temperature, polymerization was carried out in solution, using pyridine,<sup>4</sup> nitrobenzene<sup>5</sup> and dimethylformamide as solvents.

III, on being dissolved in dry pyridine or nitrobenzene, polymerized rapidly and the solution turned into a gel. Owing to the sparse solubility even of low-chain polymers of N<sup>β</sup>-benzyl-*dl*-asparagine (IV) in these solvents, the resulting substances had an average chain length of 10 to 13 only. As these were, however, soluble in dimethylformamide, polymerization was carried out in the latter solvent leading to polymer preparations with an average chain length of 24 units (molecular weight about 5000), which were already insoluble in dimethylformamide and precipitated on standing.

The above polymers were soluble in hot glacial acetic acid, but practically insoluble in water, as well as in dilute mineral acids and alkali. A positive biuret reaction could, therefore, be obtained only on prolonged contact of the substance with the reagent solution, or when adding some dimethylformamide which dissolved lower fractions. On boiling with ninhydrin solution, the solid particles of the substance attained a blue color.

Attempts to remove the benzyl group have, so far, not been successful.

#### Experimental

Microanalyses are by Drs. Weiler and Strauss. Melting points were determined in a Fisher-Johns apparatus.

**N-Carboxy Anhydride of N<sup>β</sup>-Benzylasparagine (III).**—N<sup>β</sup>-Benzylasparagine (II) was obtained from N<sup>α</sup>,N<sup>β</sup>-di-benzylasparagine (I),<sup>3</sup> by hydrogenolysis with a palladium chloride on carbon catalyst (30%) in glacial acetic acid at 60°. A 10% catalyst<sup>2</sup> gave only poor results. After reduction, the organic material which adhered to the catalyst was extracted with cold formic acid. Removal of the latter *in vacuo* gave II in 77% yield.

Eight grams of II (which had been dried at 100°), was suspended in 250 ml. of dry dioxane in a three-necked flask to which a reflux condenser, a gas inlet tube and a stirrer had been attached. Phosgene was bubbled into the suspension and stirring commenced, while the bath temperature was maintained at 55°. After about 30 minutes, a clear solution resulted. Excess of phosgene and the dioxane were removed *in vacuo* at 40° and the resulting white crystalline substance was washed with ether and dried over phosphorus pentoxide. The yield was 7 g. (78.5%).

*Anal.* Calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>: C, 58.1; H, 4.8; N, 11.3. Found: C, 58.0; H, 4.8; N, 11.4.

**Polymerization of the N-Carboxy Anhydride of N<sup>β</sup>-Benzylasparagine (III) in Pyridine.**—III was dissolved in varying amounts of pyridine (which had been dried by reflux with potassium hydroxide) and left at room temperature (*cf.*, Table II). The solutions became gradually more viscous while CO<sub>2</sub> was evolved and finally turned into gels. The polymers were isolated, after different periods of time, by precipitating them through addition of ether or water. They were then filtered, washed with some more ether or water respectively and dried *in vacuo*. The average chain length of all polymeric preparations was determined by analysis of amino-nitrogen in a Van Slyke manometric apparatus.

**Polymerization in Nitrobenzene.**—The procedure was similar to the above and polymers were precipitated by the addition of ether.

**Polymerization in Dimethylformamide.**—Polymerization was carried out at temperatures of about 5° and isolation of the polymer effected by addition of water.

(4) V. Go and H. Tani, *Bull. Chem. Soc. (Japan)*, **14**, 510 (1939); W. E. Hanby, S. G. Waley and J. Watson, *Nature*, **161**, 132 (1948); *J. Chem. Soc.*, 3289 (1950).

(6) W. E. Hanby, S. G. Waley and J. Watson, *ibid.*, 3009 (1950).

Results are summarized in Table II.

TABLE II

Amt. III, g.	In pyridine			In nitro- bz.	In dimethyl- formamide	
	1	0.5	1	3	5	1
Sol., ml.	4	20	15	20	40	10
Isold. after, days	15 min.	9	19	18	24 hr.	21
Amino {						
Calcd.	0.62	0.68	0.68	0.52	0.75	0.29
Found	0.62	0.67	0.71	0.53	0.75	0.30
N, % {						
Calcd.	64.3	64.1	64.1	64.3	64.1	64.5
Found	63.1	63.9	62.8	62.6	64.2	62.0
Carbon, % {						
Calcd.	5.9	5.9	5.9	5.9	5.9	5.9
Found	5.8	5.9	6.0	5.9	6.6	6.0
Hydrogen, % {						
Calcd.	13.6	13.6	13.6	13.6	13.6	13.6
Found	14.2	12.9	13.6	13.5	13.3	13.1
Nitrogen, % {						
Calcd.	11	10	10	13	9	24
Found						
Chain length						

**Hydrolysis of Poly-N<sup>β</sup>-benzyl-*dl*-asparagine.**—0.019 g. of the polymer ( $n = 24$ ) was boiled under reflux with 5 ml. of hydrochloric acid (6 N) for 19 hours. The resulting clear solution was transferred quantitatively into a 25-ml. volumetric flask, neutralized with 6 N sodium hydroxide solution against methyl orange and water added up to the 25-ml. mark. Aliquot parts of this solution were analyzed for free amino-nitrogen and values of 13.0% obtained (theor. 13.7%). This indicated complete hydrolysis to aspartic acid and benzylamine. Confirmation of this fact was obtained by paper partition chromatography of the hydrolysate (phenol-water as mobile phase), giving the characteristic spots for aspartic acid and benzylamine.

(6) As is generally known, analyses of polymers, especially as regards carbon, are not always satisfactory (see for instance ref. 5 and C. S. Marvel, Cooke and J. C. Cowan, *THIS JOURNAL*, **62**, 3497 (1940)).

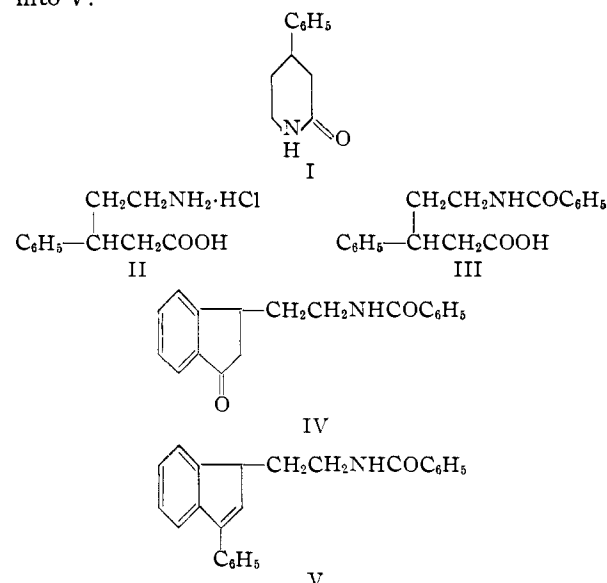
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### Syntheses from 4-Phenyl-2-piperidone<sup>1</sup>

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Having developed a method for preparing 4-phenyl-2-piperidone (I),<sup>2</sup> we considered it of some interest to investigate various chemical transformations of the substance. The present note describes conversion of I through II, III and IV, into V.



(1) From the M.S. Thesis of R. W. DeNet, December, 1947.

(2) C. F. Koelsch, *THIS JOURNAL*, **65**, 2459 (1943).