phthalimido amides. Crystalline amides prepared are listed in Table VI.

Acknowledgment. The authors gratefully acknowledge the kind assistance of Dr. Raymond Cunningham, Mr. Frank Smith, and Mr. Charles Rauh of the Pharmacology Department of Lederle Laboratories Division of American Cyanamid Company, who performed the pharmacological tests. The authors are also indebted to Mr. Louis Branconne who performed the analysis. Finally they wish to thank the Lederle Laboratories Division of American Cyanamid Company for financial support of the work in the form of a research fellowship.

STILLWATER, OKLA.

[CONTRIBUTION FROM THE "LABORATORIO DE QUÍMICA BIOLÓGICA," FACULTAD DE CIENCIAS MÉDICAS AND THE "LABORATORIO DE QUÍMICA ORGÁNICA," FACULTAD DE CIENCIAS EXACTAS Y NATURALES]

Reaction of Ammonia with Some Acetylated and Benzoylated Monosaccharides. IV. Derivatives of L-Rhamnose

JORGE O. DEFERRARI AND VENANCIO DEULOFEU

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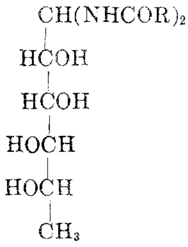
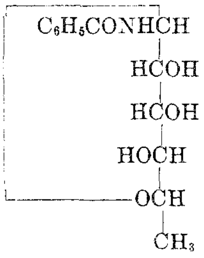
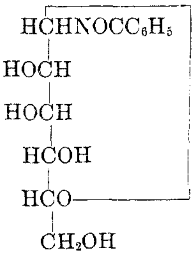
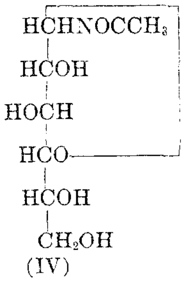
Tetrabenzoyl-L-rhamnose, on treatment with ammonia in methanol gave two products, *N,N'*-dibenzoyl-L-rhamnosylidenediamine and *N*-benzoyl-L-rhamnopyranosylamine. The products are analogous to those obtained previously from pentabenzoyl-D-mannose. Both tetraacetyl-L-rhamnose and pentaacetyl-7-desoxy-L-*glycero*-L-*gala*-heptononitrile, on treatment with ammonia in methanol, gave *N,N'*-diacetyl-L-rhamnosylidenediamine.

The formation of *N,N'*-diacetyl- and *N,N'*-dibenzoylhexosylidenediamines as the principal products, by the action of alcoholic ammonia on pentaacetyl- and pentabenzoylhexoses, is a general reaction which has been applied with success to derivatives of D-glucose,[1] D-mannose,[2] and D-galactose.[3] It has now been applied to tetraacetyl- and tetrabenzoyl-L-rhamnose, which is interesting for various reasons. In L-rhamnose, according to the mechanism of this reaction[4] only three acyl groups can participate in the intramolecular displacement and supply the elements for the formation of the amide molecules. Furthermore, L-rhamnose has the same steric relationship in the asymmetric carbon atoms as D-mannose. The benzoyl derivatives of this hexose, pentabenzoyl-D-mannose and hexabenzoyl-D-*glycero*-D-*gala*-heptononitrile, have a particular place in this reaction because they produce, at variance with the other hexoses, not only *N,N'*-dibenzoyl-D-mannosylidenediamine but also a cyclic monobenzamide compound, *N*-benzoyl-D-mannopyranosylamine.[2,5] Similar products were obtained when tetrabenzoyl-L-rhamnose was submitted to the ammonolysis. The principal one was *N,N'*-dibenzoyl-L-rhamnosylidenediamine (Ia) accompanied by *N*-benzoyl-L-rhamnopyranosylamine (II) in smaller amounts. L-Rhamnose was also present.


(Ia, R = C_6H_5)
(Ib, R = CH_3)


(II)


(III)


(IV)

That the *N*-benzoyl-L-rhamnosylamine and the *N*-benzoyl-D-mannosylamine (III) have a pyranose structure was determined by periodate oxidation. Each consumed two moles of periodate with production of one mole of formic acid; no formaldehyde was detected. For comparison purposes we studied the oxidation of *N*-acetyl-D-glucoforanosylamine (IV), to which a furanose structure was

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[1] V. Deulofeu and J. O. Deferrari, *J. Org. Chem.*, **17**, 1087 (1952).

[2] J. O. Deferrari and V. Deulofeu, *J. Org. Chem.*, **17**, 1093 (1952).

[3] J. O. Deferrari and V. Deulofeu, *J. Org. Chem.*, **17**, 1097 (1952).

[4] H. S. Isbell and H. L. Frush, *J. Am. Chem. Soc.*, **71**, 1579 (1949); V. Deulofeu and J. O. Deferrari, *Anales. Asoc. Quim. Argentina*, **38**, 241 (1950); R. C. Hockett, V. Deulofeu, and J. O. Deferrari, *J. Am. Chem. Soc.*, **82**, 1840 (1950).

[5] P. Brigl, H. Mühlschlegel, and R. Schinle, *Ber.*, **64**, 2921 (1931).

assigned by Hockett and Chandler,[6] on the basis of its oxidation with lead tetraacetate. Niemann and Hays[7] found that its periodate oxidation was anomalous, consuming no less than five moles of oxidant.

In experiments carried at 35°, we have found that one mole of periodate is consumed very fast, with production of one mole of formaldehyde and no formic acid. The oxidation is produced between carbon atoms 5 and 6 in agreement with structure (IV). The rapid reaction is accompanied by slow reactions that lead to the production of nearly 3 moles of formic acid. This is explained by the formation and subsequent oxidation of tartronic aldehyde.[8]

By ammonolysis in methanol of tetraacetyl-L-rhamnopyranose, only *N,N'*-diacetyl-L-rhamnosylidenediamine (Ib) was obtained, with 38.6% yield. The same compound was produced by Wohl's degradation of the pentaacetyl-7-deoxy-L-*glycero*-L-*gala*-heptononitrile, with almost the same yield (40.5%). The results are indentical with those obtained with pentaacetyl-D-mannose.

Our pentaacetyl-7-deoxy-L-*glycero*-L-*gala*-heptononitrile was prepared by acetylation of the 7-deoxy-L-*glycero*-L-*gala*-heptononitrile and by dehydration of the pentaacetyl-7-deoxy-L-*glycero*-L-*gala*-heptonoamide. The products were identical in the two cases, but their physical constants do not agree with those of the similar compound described by Mikšic.[9]

The 7-desoxy-L-*glycero*-L-*gala*-heptononitrile has a higher melting point when recrystallized from acetic acid than when recrystallized from methanol, as was observed by Zemplen[10] with D-glucononitrile.

The higher melting form exhibits a stable specific rotation when dissolved in water, while the lower melting form presents mutarotation of a complex nature, a difference which has also been described by Papadakis and coworkers[11] for the two similar forms of the D-glucononitrile. Wolfrom, Thompson, and Hooper[12] found the same type of mutarotation with *N*-methyl glucosaminonitrile, prepared in alcoholic solution.

The existence of two forms of each nitrile, differing in melting point and stability of rotation, seems to be a general property of these substances as we have found that it is also the case with D-*glycero*-D-*gala*-heptononitrile.

EXPERIMENTAL

*N,N'-Dibenzoyl-*L*-rhamnosylidenediamine* (Ia). Thirteen grams of tetrabenzoyl-α-L-rhamnopyranose[13] were dissolved, by shaking at room temperature, in 330 ml. methanolic ammonia, and the solution left standing for 24 hrs. It was then evaporated to dryness in vacuum at low temperature. The syrup obtained was dissolved in 40 ml. of ethanol and allowed to stand at 5° to deposit fine needles. The crystals were separated and well washed with ethanol. Yield: 0.95 g., m.p. 221–222.5°. The mother liquors were evaporated again to dryness in vacuum, and the residue dried in a desiccator. It was then extracted four times with 40 ml. of ethyl acetate to eliminate the benzamide. The ethyl acetate insoluble material was dissolved in the minimum amount of boiling water. By cooling, crystals appeared which were separated and found identical with the former product. Yield: 700 mg. m.p. 219° (total yield: 1.65 g.; 19%). For analysis the material was recrystallized once from ethanol and three times from water. Fine needles melting 222–223°. $[\alpha]_D^{26}$ + 14.4° (c, 0.693, pyridine).

Anal. Calcd. for $C_{20}H_{24}N_2O_6$: C, 61.84; H, 6.18; N, 7.21. Found: C, 61.25; H, 6.32; N, 6.29.

*N-Benzoyl-*L*-rhamnopyranosylamine*, (II). The aqueous mother liquors from the preparation of the second batch of crystals of *N,N'*-dibenzoyl-L-rhamnosylidenediamine were evaporated again to dryness and a crystalline residue obtained. This residue was suspended in a small amount of cold water, filtered, dried and treated first with boiling ethyl acetate and then with 2 ml. of warm ethanol. Rectangular prisms, melting at 237–238°, were obtained (yield: 110 mg.). Recrystallized five times from ethanol the material melted at 240–241°. $[\alpha]_D^{17}$ + 10.6 (c, 0.564, pyridine).

Anal. Calcd. for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.36. Found: C, 58.70; H, 6.15.

O-Tetrabenzoyl-N,N'-dibenzoylrhamnosylidenediamine. One gram of *N,N'*-dibenzoyl-L-rhamnosylidenediamine was dissolved in 12.5 ml. of pyridine, 3 ml. of benzoyl chloride was added, and the mixture was heated to 60–70° for 15 min. After 24 hr. standing at room temperature, it was poured into 200 ml. of ice water and extracted with chloroform. The chloroform solution was washed with cold 3*N* sulfuric acid, saturated sodium hydrogen carbonate solution and with water, and dried with sodium sulfate. By evaporation, a crystalline residue was obtained, that was recrystallized from 50 ml. of ethanol. Prisms melting 211–212°. Yield: 1.62 g. Recrystallized four times from ethanol, melted 213–213.5°. $[\alpha]_D^{14}$ −32.1° (c, 0.88, chloroform).

Anal. Calcd. for $C_{48}H_{40}N_2O_{10}$: C, 71.59; H, 4.97. Found: 71.40; H, 4.75.

Eight hundred milligrams of *O*-tetrabenzoyl-*N,N'*-dibenzoylrhamnosylidenediamine were dissolved with 20 ml. of methanolic ammonia and the solution, after standing 24 hr. at room temperature, was evaporated to dryness. The residue, by crystallization from ethanol yielded 380 mg. of material melting at 213–214°, and a second crop of 28 mg. Recrystallization of the material from water gave 320 mg. (83%) of *N,N'*-dibenzoyl-L-rhamnosylidenediamine, m.p. 222–223°. No *N*-benzoyl-L-rhamnopyranosylamine could be detected.

*O-Triacetyl-N-benzoyl-*L*-rhamnopyranosylamine.* The *N*-benzoyl-L-rhamnopyranosylamine (65 mg.) was boiled to dissolution, with 1.9 ml. of a mixture (1:1) of acetic anhydride and pyridine. After standing overnight, the solution was evaporated in a desiccator and 105 mg. of crystals melting at 205–220° were obtained. After four crystallizations from ethanol, m.p. 208° $[\alpha]_D^{20}$ +25.1° (c, 0.596, chloroform).

Anal. Calcd. for $C_{19}H_{23}NO_8$: C, 58.00; H, 5.85; N, 3.56. Found: C, 58.40; H, 5.81; N, 3.40.

L-*Rhamnose.* The water mother liquors and washings from the preparation of *N*-benzoyl-L-rhamnopyranosylamine were

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(6) R. C. Hockett and L. R. Chandler, *J. Am. Chem. Soc.*, **66**, 957 (1944).

(7) C. Niemann and J. T. Hays, *J. Am. Chem. Soc.*, **67**, 1302 (1945).

(8) P. Fleury, *Bull. soc. chim. France*, 1126 (1956).

(9) J. Mikšic, *Vestnik Králov. Ceské. Společnosti. Nauk.*, Cl. II, 18 pp. (1926); *Chem. Abstr.* **23**, 2941 (1926).

(10) G. Zemplen, *Ber.*, **60**, 171 (1927).

(11) P. E. Papadakis and H. J. Cohen, *J. Am. Chem. Soc.*, **60**, 765 (1939); P. E. Papadakis, *J. Am. Chem. Soc.*, **64**, 1950 (1942).

(12) M. L. Wolfrom, A. Thompson, and I. R. Hooper, *J. Am. Chem. Soc.*, **68**, 2343 (1946).

(13) R. K. Ness, H. G. Fletcher, and C. S. Hudson, *J. Am. Chem. Soc.*, **73**, 296 (1951).

evaporated again to dryness. The residue after purification weighed 300 mg. and melted at 92–95°. In water solution it exhibited mutarotation with an equilibrium $[\alpha]_D^{20}$ + 8.7°, in substantial agreement with $[\alpha]_D^{20}$ + 8.9° reported by Hudson and Yanovsky.[14] Identification was confirmed by preparation of the previously known[15] L-rhamnose-*p*-phenylhydrazone, m.p. 191°.

Pentaacetyl-7-deoxy-L-glycero-L-gala-heptonoamide. Twelve grams of 7-deoxy-L-*glycero*-L-*gala*-heptonoamide[16] was suspended in 150 ml. of a mixture of pyridine and acetic anhydride (1:1) and stirred at 65–70°. The amide dissolved in 1.5 hr. and heating was continued for 15 min. The solution was cooled and poured into 300 ml. of ice water. The acetylated amide was separated, washed with ice water, and dried. Yield: 22.8 g. (94%) of crude crystalline product that melted at 130–131°. Dried at 100° in vacuum it melted at 146°.

For analysis, a sample was recrystallized three times from ethanol, m.p. 146–147° (dried in vacuum 100°), $[\alpha]_D^{22}$ −20.1° (c, 1.48, chloroform).

Anal. Calcd. for $C_{17}H_{25}NO_{11}$: C, 48.68; H, 5.99. Found: C, 47.86; H, 6.13.

Pentaacetyl-7-deoxy-L-glycero-L-gala-heptononitrile. Five grams of pentaacetyl-7-deoxy-L-*glycero*-L-*gala*-heptonoamide, was heated to 80–85° for 30 min., with 15 ml. of phosphorus oxychloride. The excess of the phosphorus oxychloride was eliminated by distillation in vacuum, and the residue dissolved in a mixture of 50 ml. of ice water and 150 ml. of chloroform. The chloroform solution was washed with water, a saturated solution of sodium hydrogen carbonate, water again, dried with sodium sulfate, and evaporated in vacuum. The oily residue crystallized from a small amount of warm ethanol, 1.8 g. (37.6%) of prisms melting at 124–125°. Recrystallized from ethanol, it melted at 127–218° $[\alpha]_D^{25}$ −33.9°, (c, 1.16, chloroform). Mikšic[9] gives m.p. 85–86° $[\alpha]_D^{20}$ −76.4°.

Anal. Calcd. for $C_{17}H_{25}NO_{10}$: C, 50.87; H, 5.53; CN, 6.48. Found: C, 50.76; H, 5.80; CN, 6.56.

One gram of the nitrile was shaken with 4 ml. of a mixture (1:1) of acetic acid and acetic acid saturated with hydrogen bromide. After 2 hr., when the material had dissolved, the solution was left 5 hr. at room temperature and then poured into ice water. The solid that precipitated was separated and recrystallized from ethanol. The product, pentaacetyl-7-desoxy-L-*glycero*-L-*gala*-heptonamide, was identical with that already described.

7-Desoxy-L-glycero-L-gala-heptononitrile. Two grams of L-rhamnose hydrate was dissolved in 1.05 ml. of warm water. The solution was cooled to 0°, two drops of 12% ammonia in water added and then 0.5 ml. of anhydrous hydrogen cyanide. Crystallization was induced by scratching with a glass rod. After allowing crystallization to continue for 30 min., 1 ml. of hydrogen cyanide was added. After another 30 min. the suspension was diluted with 10 ml. ethanol, kept for 30 min. at 0°, filtered, washed with cold ethanol, and dried in a desiccator. Yield: 600 mg., m.p. 112–115°. Recrystallized from acetic acid (3.3 ml. acid per g. of nitrile), prisms melting at 139–141° were obtained $[\alpha]_D^{25}$ −10.0° (c, 2.08, water); when these crystals were recrystallized from absolute ethanol (10 ml. ethanol per g. of nitrile) prisms melting at 115–116° were obtained. $[\alpha]_D^{20}$ −9.9° (initial) → +10.8° (75 min.) → 0.7° (final) 150 min. (H_2O, c, 1.45).

Pentaacetyl-7-desoxy-L-glycero-L-gala-heptononitrile by acetylation of 7-desoxy-L-glycero-L-gala-heptononitrile. Two hundred and fifty milligrams of the free nitrile, m.p. 115–116°, was dissolved at room temperature in a mixture of 3 ml. of pyridine and 3 ml. of acetic anhydride. After 24 hr. the solution was poured into 25 ml. of ice water. The acetylated nitrile that separated in crystalline form was collected on a filter, washed and dried; m.p. 127–128°, unchanged by recrystallization from ethanol.

Twenty mg. of the free nitrile, m.p. 139–141°, was acetylated exactly as described for the low melting form. The acetylated nitrile recrystallized from ethanol melted at 126–127°. Both preparations gave no depression when mixed with a sample of pentaacetyl-7-desoxy-L-*glycero*-L-*gala*-heptononitrile melting at 127–128°.

N,N′-Diacetylrhamnosylidenediamine. (Ib) (a) *From pentaacetyl-7-desoxy-L-glycero-L-gala-heptononitrile.* Three grams of the acetylated nitrile was dissolved at room temperature in 180 ml. of methanolic ammonia (16%). After 48 hr., the solution was evaporated to dryness in vacuum at low temperature. The well-dried residue was mixed with 18 ml. of absolute ethanol and the insoluble solid filtered. A yield of 800 mg. (40.5%) of crystals, m.p. 230–231°, was collected. Recrystallized from 70% ethanol, long needles, melting at 239–240° were obtained; $[\alpha]_D^{22}$ + 23.1° (c, 0.497, H_2O).

Anal. Calcd. for $C_{10}H_{20}N_2O_6$: C, 45.45; H, 7.57; N, 10.60. Found: C, 44.67; H, 7.58; N, 10.62.

(b) *From tetraacetyl-L-rhamnose.* Three grams of a mixture of α- and β-tetraacetyl-L-rhamnose prepared by the method of Fisher, Bergmann, and Rabe,[17] were dissolved in 60 ml. of methanolic ammonia. After 24 hr. at room temperature, the solution was evaporated in vacuum and the crystalline residue suspended in 8 ml. of cold ethanol and filtered. After washing with methanol, 920 mg. (38.6%) of fine needles melting at 238–239° were obtained. A mixed melting point determination showed the material to be the same as the *N,N′*-diacetylrhamnosylidenediamine, prepared from pentaacetyl-7-desoxy-L-*glycero*-L-*gala*-heptononitrile.

D-*Glycero*-D-*gala-heptononitrile.* It was prepared according to Brigl, Mühlschlegel, and Schinle.[5] Recrystallization from acetic acid yielded crystals melting at 149°, $[\alpha]_D^{20}$ + 19.9° (H_2O, c, 1.25). From ethanol m.p. 122–123°, $[\alpha]_D^{20}$ + 21.4 (initial) → + 2.7° (55 min.) → + 13.1° (final, 165 min.) (H_2O, c, 1.25). Mikšic[9] gives m.p. 121–122° $[\alpha]_D$ + 31.4.

Oxidation of N-benzoyl-L-rhamnopyranosylamine and N-benzoyl-D-mannopyranosylamine with periodate. *N*-benzoyl-L-rhamnopyranosylamine (13.55 mg., 5×10^{-5} moles) was dissolved in 40 ml. of water, 5.0 ml. of 0.1*M* solution of sodium periodate added (5.0×10^{-4} moles) and then water to 50 ml. After 18 hr. at room temperature, 1.83 moles of periodate per mole of substance were consumed and 1.0 mole of formic acid was titrated. Formaldehyde could not be detected with dimethyldihydroresorcinol. After 23 hr., results were substantially the same.

Under the same conditions, 28.30 mg. (1×10^{-4} moles) of *N*-benzoyl-D-mannopyranosylamine consumed after 24 hr., 2.0 moles of sodium periodate and produced 1.0 mole of formic acid per mole. Formaldehyde could not be detected.

Oxidation of N-acetyl-D-glucofuranosylamine with periodate. *N*-Acetyl-D-glucofuranosylamine (88.4 mg.) was dissolved in water, 25 ml. of 0.1*M* solution of sodium periodate

TABLE I

OXIDATION OF *N*-ACETYL-D-GLUCOFURANOSYLAMINE WITH PERIODATE (35°) IN MOLES PER MOLE OF SUBSTANCE

Time, Min.	$NaIO_4$ Consumed	Formic Acid	Formaldehyde
15	1.19	0.00	1.00
75	1.49	0.10	—
135	2.16	0.32	0.958
205	2.56	0.84	—
275	3.01	1.13	—
1195	4.21	2.11	—
1690	5.23	2.76	0.998

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(14) C. S. Hudson and E. Yanovsky, *J. Am. Chem. Soc.*, **39**, 1032 (1917).

(15) A. W. van der Haar, *Anleitung zum Nachweiss, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren*, Geb. Borntraeger, Berlin, 1920, page. 184.

(16) E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 2455 (1934).

(17) E. Fischer, M. Bergmann, and A. Rabe, *Ber.*, **53** 2362 (1920).

added, the volume completed to 200 ml., and the resulting solution maintained at 35°. Samples were taken at intervals, the periodate consumed and the formic acid produced were titrated in the usual way. Formaldehyde was determined according to Reeves.[18] Results are given in the table below.

Acknowledgments. We thank Mr. Joseph F. Alicino, from The Squibb Institute for Medical Research, New Brunswick, N. J., for the microanalysis.

BUENOS AIRES, ARGENTINA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITÉ DE MONTRÉAL]

Preparation of L-Cystinyl and L-Cysteinyl Peptides Through Catalytic Hydrogenation of Intermediates

CASIMIR BERSE, ROGER BOUCHER, AND LUCIEN PICHÉ

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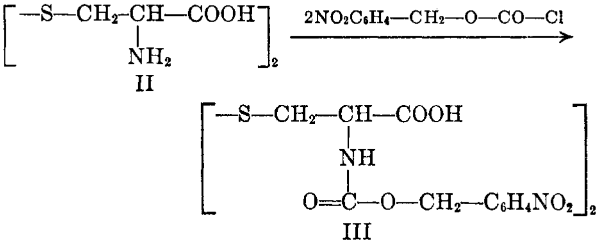
The preparation of peptides containing cystine or cysteine by the general method of catalytic hydrogenolysis of intermediates becomes possible if the classical carbobenzoxyl group is replaced by the more labile *p*-nitrocarbobenzoxyl radical to cover uncondensed α-amino groups. The hydrogenation procedure can be arrested at the cystine stage or allowed to proceed to cysteine. Likewise, if the *p*-nitrobenzyl radical is used to cover the thio group of cysteine, it can be removed by catalytic hydrogenation, whereas *S*-benzylcysteine intermediates are only cleaved by sodium in liquid ammonia. The preparation of L-cystinyldiglycine, L-cystinyldi-L-phenylalanine, and of L-cysteinyl-L-phenylalanine are proposed as typical examples.

Cystine has been reduced to cysteine by catalytic hydrogenation with palladium.[1,2] However, in attempting to hydrogenate dicarbobenzoxycystine according to the general Bergmann and Zervas procedure,[3] White[4] found that no reduction took place. It has indeed frequently been observed and it is now accepted that the efficiency of palladium or of platinum as a catalyst is sharply reduced whenever sulfur is present in the form of a dithio linkage as in cystine, of a thiol group as in cysteine, or of a thioether as in *S*-benzylcysteine. The exact limits of this incompatibility have not, however, been explored since Siffered and du Vigneaud's alternate method[5] of reduction of *N*-carbobenzoxyl and *S*-benzyl derivatives of cystine or of cysteine with sodium in liquid ammonia was adopted at an early period for the introduction of these two amino acids in synthetic peptides.

The authors have previously shown[6] that α-*p*-nitrocarbobenzoxy-L-arginyl derivatives are easily reduced to L-arginyl peptides by hydrogen at atmospheric pressure in the presence of palladium on carbon. In view of the increased ease of removal of the *p*-nitrocarbobenzoxyl radical which was noted as a result of labilization by the strong inductive effect of the nitro group, the authors were brought to use this radical to cover the basic amino groups of cystine and to investigate the possibility of its removal by catalytic hydrogenation under conditions where the carbobenzoxyl group is stable.

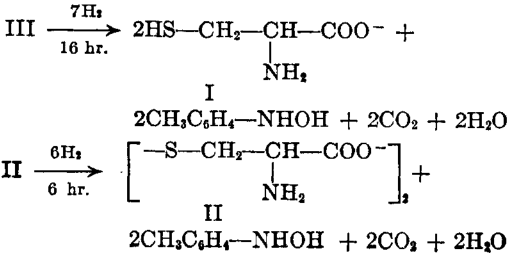
Di(*p*-nitrocarbobenzoxy)-L-cystine III was prepared by condensing *p*-nitrocarbobenzoxyl chlorocarbonate with L-cystine II in tetrahydrofuran or dioxane. The disubstituted cystine was submitted to catalytic hydrogenation at room temperature under atmospheric pressure in the presence of palladium black on carbon. In aqueous medium, when the disubstituted cystine was dissolved as the sodium salt, absorption of hydrogen proceeded rapidly at first, and continued until an equivalent of seven moles were consumed in about 16 hr. The products of reduction consisted of L-cysteine I and *p*-tolylhydroxylamine. If the hydrogenation process was arrested when 6 moles of hydrogen had been absorbed (about 6 hr.), L-cystine II and *p*-tolylhydroxylamine were obtained.



$$\left[-S-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH\right]_2 \xrightarrow{2NO_2C_6H_4-CH_2-O-CO-Cl} \left[-S-CH_2-\underset{\substack{| \\ NH \\ | \\ O=C-O-CH_2-C_6H_4NO_2}}{CH}-COOH\right]_2$$

II

III



$$\text{III} \xrightarrow[16\text{ hr.}]{7H_2} 2HS-CH_2-\underset{NH_2}{\underset{|}{CH}}-COO^- + 2CH_3C_6H_4-NHOH + 2CO_2 + 2H_2O$$

I

$$\text{III} \xrightarrow[6\text{ hr.}]{6H_2} \left[-S-CH_2-\underset{NH_2}{\underset{|}{CH}}-COO^-\right]_2 + 2CH_3C_6H_4-NHOH + 2CO_2 + 2H_2O$$

II

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