From these data, it is disclosed that, except the ultrasonic treatment which brought about no apparent influence on the physical state of the lipovitellin molecule, all the treatments similarly yielded a smaller component of which molecular weight corresponds to about one half (0.47~0.54) of the original lipovitellin. It is worth to note that the treatment B, C and D all irreversibly give rise to such a monomer-like component as reversibly formed in alkaline medium (A). Particularly, an oxidation treatment by means of hydrogen peroxide yielded the 6S component solely, without leaving the original 10S component (though a significant amount of insoluble denaturant was yielded at the same time).

Therefore, it is supposed that hen lipovitellin in a dimer form is easily split into its monomer, reversibly or irreversibly, by certain treatments, though the mechanism is not clear yet. In this respect, it is recalled that the frog lipovitellin exists in two molecular forms, 11S and 6S components, in the course of its embryonal development (detected at the rotation stage) as reported previously,[2] whereas in unfertilized egg it is present only as a dimer form. Significance of such a dimer-monomer dissociation with reference to the utilization of lipoproteins during the course of development remains to be clarified.

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UDC 542.941 : 547.554.04

Minoru Sekiya and Masayasu Tomie : Reaction of Amide Homologs. XVII.[*1] Catalytic Hydrogenolysis of N,N′-Benzylidenebisamides.

(*Shizuoka College of Pharmacy*[*2])

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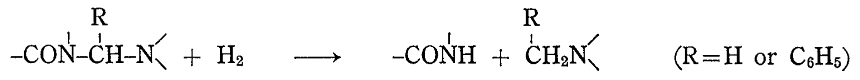
Previously, facile hydrogenolysis of N-amidomethyl[1,2] or N-α-amidobenzyl compound[1] attached to secondary amine has been reported from this laboratory to proceed as in the following, generally by catalytic hydrogenation under high hydrogen



$$-\mathrm{CON}-\overset{\mathrm{R}}{\mathrm{C}}\mathrm{H}-\mathrm{N}\langle + \mathrm{H_2} \longrightarrow -\mathrm{CONH} + \overset{\mathrm{R}}{\mathrm{C}}\mathrm{H_2N}\langle \qquad (\mathrm{R}=\mathrm{H} \text{ or } \mathrm{C_6H_5})$$

pressure at elevated temperature using Raney nickel catalyst. However, in the study[2] on the scope of the reaction for variety of N-amidomethyl compounds, N,N′-methylenebisamides have been shown to resist to the hydrogenolysis under the above conditions and N,N′-benzylidenebisamides were shown as well. Lately, it was found that the hydrogenolysis of N,N′-benzylidenebisamide was effected in acidic environment chiefly to afford N-benzylamide and amide. The conditions were that the hydrogenation was carried out in acetic acid under high hydrogen pressure at elevated temperature using palladium-on-charcoal catalyst.

A series of N,N′-benzylidenebisamides, *i.e.*, N,N′-benzylidenebisformamide, -bisacetamide, -bispropionamide, and -bisbenzamide were elected. Table I shows the

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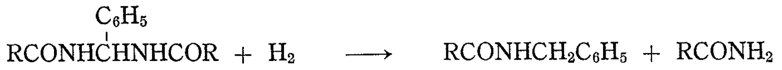
[*1] Part XVI : M. Sekiya, N. Yanaihara : This Bulletin, **15**, 108 (1967).

[*2] Oshika, Shizuoka (関屋 実, 冨江正泰).

1) M. Sekiya, K. Ito : This Bulletin, **11**, 892 (1963).

2) *Idem* : *Ibid.*, **14**, 996 (1966).

results of the hydrogenation of these compounds and a brief for general procedures. In every run, isolation of the main product, N-benzylamide indicated the following hydrogenolysis reaction, side-formation of amide being also confirmed.



$$\mathrm{RCONH}\overset{\mathrm{C_6H_5}}{\overset{|}{\mathrm{C}}}\mathrm{HNHCOR} + \mathrm{H_2} \longrightarrow \mathrm{RCONHCH_2C_6H_5} + \mathrm{RCONH_2}$$

As can be also seen from the Table, as by-product toluene was more or less obtained in every run. This formation appeared to involve further hydrogenolysis of the product, N-benzylamide, which is referred to as the well-known hydrogenolysis of benzylamine analogs. The hydrogenation of N,N′-benzylidenebisformamide was distinguished from others for side-formation of relatively small amounts of N,N-dibenzylformamide and of tribenzylamine as shown in the Table.

Table I. Catalytic Hydrogenolysis[a] of N,N′-Benzylidenebisamides

Substrate	Reaction temp. (°C)	Reaction period (hr.)[b]	Product	Yield (%)	By-product
N,N′-Benzylidene-bisformamide	130～145	1.7	N-Benzyl-formamide	41	Toluene N,N-Dibenzylformamide Tribenzylamine
N,N′-Benzylidene-bisacetamide	75～ 85	4.5	N-Benzyl-acetamide	75	Toluene
N,N′-Benzylidene-bispropionamide	75～ 85	3.7	N-Benzyl-propionamide	63	〃
N,N′-Benzylidene-bisbenzamide	75～ 85	2.7	N-Benzyl-benzamide	75	〃

a) Substrate: 0.09 mole of N,N′-benzylidenebisamide; solvent: 178 ml. of AcOH; catalyst: palladium-on-charcoal prepared from 0.16 g. of $PdCl_2$ and 1.6 g. of charcoal; initial hydrogen pressure: 80 kg./cm^2 at room temperature.

b) Period up to the time when the rate of hydrogen absorption went remarkably down.

Experimental

Material——The following bisamides, which were prepared from benzaldehyde and the corresponding amides, and carefully purified, were used: N,N′-Benzylidenebisformamide[3] (m.p. 149～150°), N,N′-benzylidenebisacetamide[4] (m.p. 256～257°), N,N′-benzylidenebispropionamide[5] (m.p. 225～226°), N,N′-benzylidenebisbenzamide[6] (m.p. 228°).

General Procedure for Catalytic Hydrogenolysis of N,N′-Benzylidenebisamides——In a 300 ml. autoclave, 0.09 mole of N,N′-benzylidenebisamide and 178 ml. of AcOH were placed and palladium-on-charcoal prepared from 0.16 g. of $PdCl_2$ and 1.6 g. of charcoal was added. Under 80 kg./cm^2 (at room temperature) of initial hydrogen pressure, the whole was heated and constantly shaken at requisite temperature, when uptake of hydrogen set in. After the hydrogen absorption had gone remarkably down, shaking and heating were continued more 30 min. Then, after standing overnight, catalyst was removed from the reaction mixture by filtration.

Hydrogenolysis of N,N′-Benzylidenebisformamide——The reaction mixture obtained from the general procedure (reaction temperature 130～145°; reaction period 1.7 hr.) was submitted to distillation under reduced pressure, whereupon AcOH, $HCONH_2$, and $AcNH_2$ were distilled off. The AcOH distillate was found to contain a small amount of toluene. The distillate, to which H_2O was added, was basified with KOH and a liberated oil was collected by extraction with ether. This was identical with an authentic toluene by comparison of the IR spectra. The residual liquid was further distilled fractionally under higher reduced pressure.

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3) K. Bülow: Ber., **26**, 1972 (1893).
4) H. Hellmann, G. Aichinger, H.P. Wiedemann: Ann., **626**, 35 (1959).
5) G.S. Bhatnager, K.C. Pandya: C.A., **41**, 3774 (1947); J.B. Polya, T.M. Spotswood: Rec. trav. chim., **70**, 269 (1951).
6) F.D. Chattaway, A.E. Swinton: J. Chem. Soc., **1912**, 1208.

The fraction, b.p$_{0.4}$ 130~134°, m.p. 56°, weighing 5.0 g., was identical with an authentic sample of N-benzylformamide by comparison of the IR spectra and by mixed melting point test. Crystallization from ether gave crystals, m.p. 60°. *Anal.* Calcd. for C_8H_9ON : C, 71.09; H, 6.71; N, 10.39. Found : C, 69.87; H, 6.72; N, 10.38. The second fraction, b.p$_{0.4}$ 160~164°, was shown to be composed of N,N-dibenzylformamide and tribenzylamine. The fraction was dissolved in dry benzene and dry HCl was introduced into the solution, whereupon tribenzylamine hydrochloride precipitated. Filtration gave crystals, m.p. 214~221°, weighing 0.3 g. This was identical with an authentic sample by comparison of the IR spectra and by mixed melting point test. Recrystallization from EtOH gave crystals, m.p. 226~227°. *Anal.* Calcd. for $C_{21}H_{22}NCl$: C, 77.87; H, 6.85; N, 4.32. Found : C, 77.79; H, 6.71; N, 4.01. The benzene solution was washed with $KHCO_3$ and dried over Na_2SO_4. Removal of benzene gave solid residue, m.p. 47~49°, weighing 4.0 g. This material was identical with an authentic N,N-dibenzylformamide by comparison of the IR spectra and by mixed melting point test. Crystallization from ether gave crystals, m.p. 51~52°. *Anal.* Calcd. for $C_{15}H_{15}ON$: C, 79.97; H, 6.71; N, 6.22. Found : C, 79.90; H, 6.60; N, 6.29.

Hydrogenolysis of N,N′-Benzylidenebisacetamide——From the reaction mixture obtained from the general procedure (reaction temperature 75~85°; reaction period 4.5 hr.) AcOH and $AcNH_2$ were distilled off under reduced pressure. The AcOH distillate was shown to contain a small amount of toluene, which was isolated and identified in the same manner as in the experiment with N,N′-benzylidenebisformamide. The residue was further distilled under higher reduced pressure to give a solid distillate, b.p$_2$ 151~154°, m.p. 58~59°, weighing 10.1 g. This material was identical with an authentic N-benzylacetamide by comparison of the IR spectra and by mixed melting point test. Crystallization from ether gave crystals, m.p. 61°. *Anal.* Calcd. for $C_9H_{11}ON$: C, 72.45; H, 7.43; N, 9.39. Found : C, 72.66; H, 7.42; N, 9.50.

Hydrogenolysis of N,N′-Benzylidenebispropionamide——From the reaction mixture obtained from the general procedure (reaction temperature 75~85°; reaction period 3.7 hr.) AcOH and propionamide were removed by distillation under reduced pressure. The former distillate was shown to contain a small amount of toluene, which was isolated and identified in the same manner as in the experiment with N,N′-benzylidenebisformamide. The residue was further distilled under higher reduced pressure to give a solid distillate, b.p$_{12}$ 151~156°, m.p. 48~50°, weighing 9.3 g. This material was identical with an authentic N-benzylpropionamide by comparison of the IR spectra and by mixed melting point test. Crystallization from benzene-petr. ether gave crystals, m.p. 50~51°. *Anal.* Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.51; H, 7.89; N, 8.41.

Hydrogenolysis of N,N′-Benzylidenebisbenzamide——From the reaction mixture from the general procedure (reaction temperature 75~85°; reaction period 2.7 hr.) AcOH was removed by distillation under reduced reduced pressure. From the AcOH distillate a small amount of toluene was isolated in the same manner as in the experiment with N,N′-benzylidenbisformamide. Further distillation under higher reduced pressure gave a fraction of benzamide and then a solid fraction, b.p$_2$ 200~201°, m.p. 105~107°, weighing 14.3 g. The latter fraction was identical with an authentic N-benzylbenzamide by comparison of the IR spectra and by mixed melting point test. Crystallization from benzene gave crystals, m.p. 107°.

The authors are indebted to Mr. K. Narita of this college for elementary analyses.

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UDC 546.271.04 : 547.834.2.07

Takehisa Kunieda and Shun-ichi Yamada : Chemistry of Sodium Borohydride and Diborane. III.[*1] Synthesis of (+)-Lupinine by Hydroboration Reaction.

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(Received July 4, 1966)

Although the chemistry of lupinine, the simplest compound among the so-called lupine alkaloids, has been studied in detail,[1] no report has been found concerning the synthesis of optically active lupinine from optically active compound.

[*1] Part II : This Bulletin, **14**, 1389 (1966).

[*2] Hongo 7, Tokyo (国枝武久, 山田俊一).

1) N. J. Leonard : "The Alkaloids" edited by R. H. F. Manske, Vol. VII, 263 (1960), Academic Press, New York and London.