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103. Minoru Sekiya, Yukichi Harada, and Kozo Tanaka : Reaction of Amide Homologs. XX.*[1] Thermal Reaction of N,N′-Benzylidenebisamides with Formates and Formamide.

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Thermal reactions of some representative N,N′-benzylidenebisamides with the reagents, trimethylammonium formate given by $5HCO_2H \cdot 2N(CH_3)_3$, ammonium formate and formamide, were examined to see reaction nature and to elucidate distinctions among them. In the formate reaction reductive fission at the carbon-nitrogen bond of bisamide was mainly induced by oxidation of formic acid to carbon dioxide resulting in formation of the corresponding N-benzylamide and in the formamide reaction formation of N-benzylformamide was induced by self-oxidation of bisamide. Ammonium formate behaved in the reaction in a position between formate and formamide.

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As for formic acid reduction of N,N′-alkylidenediamine or its derivatives, the reduction of N,N′-benzylidenebispiperidine[1] and a variety of N-acylaminomethyl- or N-sulfonamidomethylamines[2] have been reported to result principally in the reductive fission at the carbon-nitrogen bond to yield alkylamine or its N-formylated compound $\left(>C\genfrac{}{}{0pt}{}{N<}{N<}\rightarrow>CHN< + HN<\right)$. Lately, our attention was drawn to N,N′-alkylidenebisamides, the formic acid reduction of which has not yet been investigated. Besides, it appeared noteworthy, in correlation with the formic acid reduction, that Sekiya, *et al.*[3] reported the formamide reaction of N,N′-benzylidenebisformamide, in which self-reduction-oxidation reaction proceeded to give N-benzylformamide as a principal product. As N,N′-alkylidenebisformamide is well known to be produced by heating aldehyde with formamide, investigation as to the formic acid or formamide reaction of this compound appeared to be also correlated with the so-called Leuckart reaction of aldehyde.

Using a variety of benzylidene analogs of N,N′-alkylidenebisamide as substrates, the formic acid reduction was found to be successfully carried out with the reagents, trimethylammonium formate, given by $5HCO_2H \cdot 2N(CH_3)_3$ (hereafter called TMAF) to give N-formylated amines. Extensive studies on the formamide reaction with the same bisamides were also made. Our objective in the present paper, by carrying out comparative studies between the formic acid and formamide reactions, was to define essential differences between both of the reactions and to gain information pertinent to the reaction mechanisms.

As the bisamide substrates were elected N,N′-benzylidenebisformamide, -bisacetamide and -bispropionamide, which appeared to be suitable for product isolation among bisamides. For comparative studies between the formic acid and formamide reactions, the reagents, TMAF, ammonium formate and formamide were employed and with each of the reagents the thermal reaction of each of the N,N′-benzylidenebisamides was carried out. TMAF, a constant boiling liquid of b.p$_{18}$ 91~93°, has been

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*[1] Part XIX. M. Sekiya, K. Ito, A. Hara, J. Suzuki : This Bulletin, **15**, 802 (1967).

*[2] Oshika, Shizuoka (関屋 実, 原田雄吉, 田中康三).

1) E. Staple, E.C. Wagner : J. Org. Chem., **14**, 559 (1949).

2) M. Sekiya, K. Ito : This Bulletin, **12**, 677 (1964).

3) M. Sekiya, K. Ito, A. Hara, J. Suzuki : *Ibid.*, **15**, 802 (1967).

Table I. Reactions[a] of N,N′-Benzylidenebisamide with Formates and Formamide

N,N′-Benzylidenebisamide	Reaction		Product and Yield (molar equiv.[b])				Conversion[c] (%)
	Temp. (°C)	Time (hr.)	N-Acylated prim. amine	N-Formylated sec. amine	tert. amine	Benzyl-alcohol	
With TMAF($5HCO_2H \cdot 2N(CH_3)_3$)							
N,N′-Benzylidenebisformamide	138～145	5.5	N-Benzylformamide 0.19	N,N-Dibenzylformamide 0.22	Tribenzylamine 0.02	0.24	93
N,N′-Benzylidenebisacetamide	138～145	5.0	N-Benzylacetamide 0.35	N,N-Dibenzylformamide 0.04	Tribenzylamine 0.08	0.25	92
N,N′-Benzylidenebispropionamide	138～145	5.0	N-Benzylpropionamide 0.20	N,N-Dibenzylformamide 0.12	Tribenzylamine 0.05	0.31	90
With Ammonium Formate							
N,N′-Benzylidenebisformamide	138～145	2.0	N-Benzylformamide 0.66	N,N-Dibenzylformamide 0.03	Tribenzylamine 0.05		87
N,N′-Benzylidenebisacetamide	138～145	3.5	N-Benzylformamide 0.79	N,N-Dibenzylformamide 0.02			83
N,N′-Benzylidenebispropionamide	138～145	5.5	N-Benzylformamide 0.76	N,N-Dibenzylformamide 0.01			78
With Formamide[d]							
N,N′-Benzylidenebisformamide[e]	165～170	10.0	N-Benzylformamide 0.42				42
N,N′-Benzylidenebisacetamide	165～170	10.0	N-Benzylformamide 0.43				43
N,N′-Benzylidenebispropionamide	165～170	10.0	N-Benzylformamide 0.47				47

a) In each run, 0.1 mole of N,N′-benzylidenebisamide substrate was used. General method and procedures are given in Experimental.
b) Tenfold molar amount of yield.
c) Percentage of the reductive conversion summing up the yields of the reduction amine products.
d) Particularly, in every run of these formamide reaction, resinous material was obtained as by-product, from which lophine and amaron were isolable.
e) Rewriting from the previously reported paper(ref. 3).

known[2~4] as a good formate reagent, which was elected with the expectation of pure formic acid reduction. Ammonium formate would be expected to behave as both formate and formamide, because this reagent could be led to the dehydration equilibrium at the elevated reaction temperature ($HCO_2NH_4 \rightleftarrows HCONH_2 + H_2O$). All the reactions were suitably carried out under the settled conditions in that 0.1 mole each of N,N′-benzylidenebisamide was heated with constant stirring along with each of the reagents, of which 2 moles as formic acid were used. In all cases of using TMAF and ammonium formate, the reaction temperature was maintained at 138~145°, while considerable evolutions of carbon dioxide and trimethylamine or ammonia were observed. In all cases of using formamide, higher temperature (165~170°) and longer reaction period (10 hours) were necessary, and almost no evolution of carbon dioxide but that of ammonia was observed. These settled conditions for the formamide reaction was just consisted with those for the previously reported[3] formamide reaction with N,N′-benzylidenebisformamide, as we had a mind to investigate extensively. Table I indicates all the results on the formation of the reduction products.

First of all, the formamide reaction was distinguished from the formate reactions by no carbon dioxide evolution in the course of the reaction as mentioned above. Formamide itself is not considered to behave as a reducing agent. In the previously reported paper,[3] it has been shown on the formamide reactions of N,N′-benzylidenebisformamide and also of certain N-benzylideneamines that the reduction to the N-formylated amine products is induced by the self-oxidation of the starting benzylidene compounds, the resinous by-product, from which lophine (2,4,5-triphenylimidazole), amaron (2,3,5,6-tetraphenylpyrazine), and cyaphenine (2,4,6-triphenyl-*s*-triazine) were isolable, being regarded as the mixture of the oxidation product. In each of the formamide reactions of N,N′-benzylidenebisacetamide and -bispropionamide was obtained the similar resinous by-product, which seemed to be the likely oxidation product. In close accord with the previously reported reaction[3] with N,N′-benzylidenebisformamide by means of column chromatography lophine and amaron were isolated as parts of the residue, though the whole component could not be clarified because of difficulties in obtaining pure material. However, it would be evident that the formation of lophine or amaron from N,N′-benzylidenebisamide indicates oxidation of divalent benzylidene to trivalent phenylmethylidyne.

Side formation of the resinous material was characteristic of the formamide reaction. In the TMAF reactions the evolution of carbon dioxide indicates the oxidation of formic acid by which the reduction induced and no resinous by-product was obtained in every case. In the ammonium formate reactions, which is in a position between the formate and formamide reactions because of the dehydration equilibrium, a nearly negligible amount of the resinous material was given.

As for the reduction amine products, variation in the sorts and in the composition was shown in each series of the reactions with TMAF, ammonium formate and formamide, as can be seen in Table I. The product compositions relatively complicated were determined by careful separation operations described in Experimental, which were established beforehand by preliminary test using authentic samples and to gain reasonable accuracy the experiments were repeated. The sorts of the reduction products and their composition, indicated in Table I, showed certain characteristics of the reaction with respect to each of the reagents, TMAF, ammonium formate and formamide. The TMAF reactions resulted in the formation of benzylalcohol, N-benzylamide retaining the original acyl group, N,N-dibenzylformamide and tribenzylamine,

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4) K. Ito: Yakugaku Zasshi, 86, 1166 (1966).

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on the other hand the formamide reactions resulted only in the formation of N-benzylformamide. The ammonium formate reaction resulted mainly in the formations of N-benzylformamide and N,N-dibenzylformamide. As for each of the reactions of N,N′-benzylidenebisamides, comparison of the amine product compositions was shown in Fig 1, where, per cent of molar equivalent amount of the amine products is plotted against each of the reactions of the three reagents. The characteristics of the formation of the amine products with respect to each reaction with the three reagents can be clearly illustrated. From composition of the amine products, especially from that of N-benzylamide and N,N-dibenzylformamide products, it would be deduced that the ammonium formate reaction is in a position between TMAF and formamide reactions because of the known dehydration equilibrium of the ammonium formate at elevated temperature. This has been also previously demonstrated[3] in the reaction of azomethines.

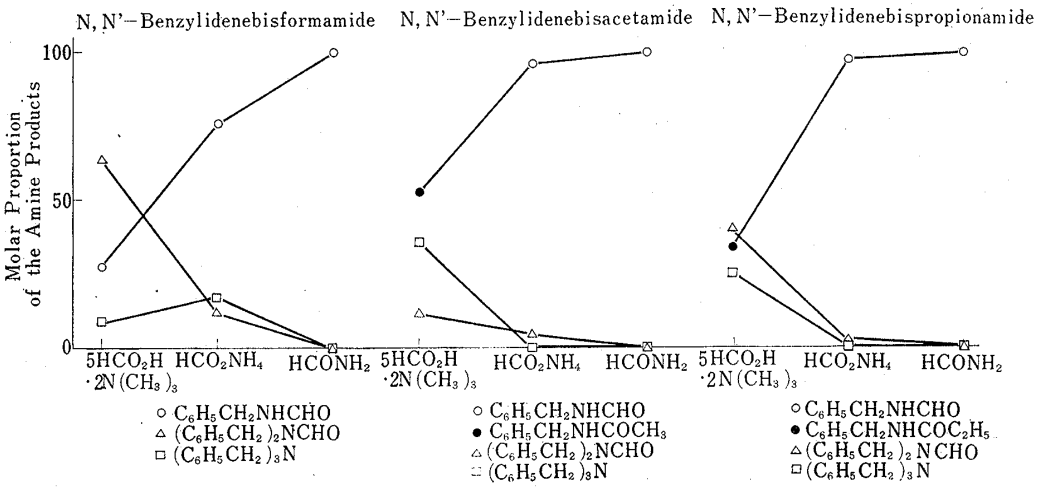
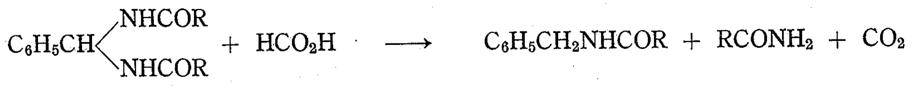


Fig. 1. Comparison of Amine Product Composition in the Reactions with TMAF, Ammonium Formate and Formamide

The comparative studies described above draw clear distinctions between the formate and formamide reactions in the reducing source and in the formation of the reduction amine products. When considered the formation of N-acylated benzylamine, the TMAF reaction was distinguished from the formamide reaction by the attaching acyl group of the product. In the former the product retained the acyl group of the starting bisamide and, in contrast, in the latter the starting acyl group was replaced by the formyl group. As to the TMAF reaction the retension of the acyl group is considered to be a clear evidence for occurrence of the reductive fission at carbon-nitrogen bond of the starting bisamide. Similar reductive fission have been known to occur in the formic acid reaction of the certain alkylidene diamine derivatives such as N,N′-benzylidenebispiperidine,[1] and N-acylaminomethyl or N-sulfonamidomethyl amine.[2] The reaction proceeded through the oxidation of formic acid to carbon dioxide as observed, then the formation equation of N-acylated benzylamine can be written as follows.



$$C_6H_5CH\begin{cases}NHCOR\\NHCOR\end{cases} + HCO_2H \longrightarrow C_6H_5CH_2NHCOR + RCONH_2 + CO_2$$

The TMAF reaction is also characterized by the formation of the others, benzylalcohol, and relatively less amounts of N,N′-dibenzylformamide and of tribenzylamine, as can be seen from Table I. The formation of benzylalcohol evidently implies hydrolysis of the starting bisamide to benzaldehyde followed by reduction with formic acid. Though source of water participating in the hydrolysis is hard to explain definitely, probably sensitivity of the reaction in regard to water would catch a trace of the water as an impurity of the TMAF (hygroscopic) or as a some side chain reaction product. Thus, the TMAF reaction is considered to proceed in the directions of both the reductive fission and the hydrolysis. Probably, the formation reaction of N,N-dibenzylformamide and of tribenzylamine may be considered to take place through some intermediate in the course of the latter.

On the other hand, as for the formamide reaction a distinction from the TMAF reaction was seen, as described in the foregoing, in the reducing source which was thought not to come from oxidation of formic acid but from the self-oxidation of N,N′-benzylidenebisamide. Moreover, with regard to the reduction amine product the reaction with N,N′-benzylidenebisacetamide and -dispropionamide resulted only in the formation of N-benzylformamide, in which the acyl group on the starting bisamides was replaced by the formyl group. In order to see whether N-benzylacetamide and -propionamide would undergo replacement of its acyl group by formyl group on heating with formamide, tests with both the compounds were carried out under the same condition as in the bisamide reaction. However, such replacement was hardly seen to occur in every case. In view of this fact, the course of the formamide reaction appeared to have some complication. Though it is hard to say the actual reaction course, it would be probable that $C_6H_5CH=NCOR$, which would be possible to be produced by deamidation of the starting bisamide, would be a likely intermediate, because this azomethine-like compound possessing carbon-nitrogen double bond is considered to react with formamide in a similar way to the previously reported reaction[3] of azomethine which has been generalized to result in the reductive cleavage at the carbon-nitrogen double bond to give the N-formylated primary amines. In contrast to the TMAF reaction, the predominant formation of N-formylated primary amine, N-benzylformamide, seems to be an important nature of the formamide reaction, as like as that previously reported reaction of azomethine.[3]

In relation to the Leuckart reaction of aldehyde, as N,N′-alkylidenebisformamide is known to be produced on heating mixture of aldehyde and formamide, the stages similar to the foresaid reactions of the bisformamide with formamide and with ammonium formate are considered to proceed as a possible pathway in the Leuckart reaction.

Experimental

Material——The following bisamides, which were prepared from benzaldehyde and the corresponding amides and carefully purified, were used: N,N′-Benzylidenebisformamide[5] (m.p. 149~150°), N,N′-benzylidenebisacetamide[6] (m.p. 256~257°), N,N′-benzylidenebispropionamide[7] (m.p. 225~226°).

General Procedure for Reaction of N,N′-Benzylidenebisamides with TMAF, Ammonium Formate, and Formamide——In a three-necked flask provided with a air condenser tube and a thermometer, 2 moles (as HCOOH) of TMAF (139 g.) or HCO_2NH_4 (126 g.) or $HCONH_2$ (90 g.) were weighed and 0.1 mole each of N,N′-benzylidenebisamides was added. The mixture was warmed by immersing in a preheated silicon-oil bath and during the course of the reaction, constantly stirred with magnetic stirrer. The primary suspensing mixture turned to a homogeneous liquid on heating.

In the cases of using TMAF or HCO_2NH_4 reaction temperature was maintained at 138~145°. The reaction was indicated by considerable evolution of CO_2 accompanied by $N(CH_3)_3$ in the TMAF reduction and by NH_3 in the HCO_2NH_4 reduction. There was passed a constant stream of air free from CO_2, and occasionally transfer of CO_2 was assured by $Ba(OH)_2$ solution. The reaction was continued until the CO_2 evolution was considerably subsided.

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5) K. Bülow: Ber., **26**, 1972 (1893).
6) H. Hellmann, G. Aichinger, H. P. Wiedemann: Ann., **625**, 35 (1959).
7) G. S. Bhatnager, K. C. Pandya: C. A., **41**, 3774 (1947); J. B. Polya, T. M. Spotswood: Rec. trav. chim., **70**, 269 (1951).

In every case of using $HCONH_2$, the temperature was maintained at 165~170° for a period of 10 hr. During the course, only a little evolution of CO_2 was observed, but evolution of NH_3 continuously.

Reaction of N,N′-Benzylidenebisformamide with TMAF——The reaction mixture from the general procedure (reaction period : 5.5 hr.) was submitted to distillation under reduced pressure, whereupon mostly excess of TMAF was first distilled off. This distillate was shown to contain benzylalcohol, which was isolated by the following procedure. The distillate, to which its equivalent amount of H_2O was added, was decomposed and then saturated with NaOH. The liberated small amount of oily material was extracted with benzene and the extract was dried over Na_2SO_4 and the benzene was removed. The residual liquid, weighing 2.6 g. (0.024 mole), exhibited IR spectrum identical with that of an authentic sample of benzylalcohol. This was converted to benzyl N-phenylcarbamate, m.p. 76~78°, which was also identified by comparison of the IR spectrum with an authentic sample. *Anal.* Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16. Found : C, 74.06; H, 5.76; N, 6.31.

The foregoing residual liquid was further distilled fractionally under higher reduced pressure. The fraction, b.$p_{2\sim3}$ 143~145°, m.p. 57°, weighed 2.6 g. (0.019 mole). This was identified as N-benzylformamide by comparison of the IR spectrum and mixed melting point test with an authentic sample. 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, 71.28; H, 6.61; N, 10.32. The second distillate, b.$p_{2\sim3}$ 166~172°, was shown to be composed of N,N′-dibenzylformamide and tribenzylamine. Successful separation of each component was performed in the manner previously described.[3] The mixture was dissolved in dry benzene and dry HCl was introduced, whereupon tribenzylamine hydrochloride precipitated and was collected by filtration and weighed 0.6 g. (0.02 mole), showing m.p. 215~221°. This exhibited an IR spectrum identical with an authentic sample. 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 aq. $KHCO_3$ and dried over Na_2SO_4, and the solvent was removed. The residue, weighing 4.9 g. (0.022 mole), solidified on cool, showing m.p. 47~50°. This was identified as N,N-dibenzylformamide by comparison of the IR spectrum and mixed m.p. with an authentic sample. Recrystallization 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, 79.88; H, 6.79; N, 6.25.

Reaction of N,N′-Benzylidenebisacetamide with TMAF——In the reaction mixture (reaction period : 5 hr.) obtained from the general procedure tribenzylamine was crystallized on cool and collected by filtration. This weighed 1.8 g. (0.006 mole), and showed m.p. 89°, and was identified by comparison of the IR spectrum and mixed melting point test with an authentic sample, m.p. 92°. Distillation of the filtrate under reduced pressure gave a TMAF distillate, from which 2.7 g. (0.025 mole) of benzylalcohol was isolated in the same manner as in the experiment with N,N′-benzylidenebisformamide. Under higher reduced pressure, the residual liquid was further distilled fractionally. The first distillate, b.p_2 153~156°, m.p. 59°, weighing 5.2 g. (0.035 mole), was identified as N-benzylacetamide by comparison of the IR spectrum and mixed melting point test with an authentic sample. Recrystallization from ether gave crystals, m.p. 60~61°. *Anal.* Calcd. for $C_9H_{11}ON$: C, 72.45; H, 7.43; N, 9.39. Found : C, 72.13; H, 7.02; N, 9.50. The second distillate, b.$p_{2\sim3}$ 164~169°, was shown to be composed of N,N-dibenzylformamide and tribenzylamine. Separation of the components was carried out by the same manner as in the experiment with N,N′-benzylidenebisformamide, resulting in the following formation : 0.5 g. (0.002 mole) of tribenzylamine hydrochloride, m.p. 216~222°; 0.9 g. (0.004 mole) of N,N-dibenzylformamide, m.p. 50~52.

Reaction of N,N′-Benzylidenebispropionamide with TMAF——The reaction mixture from the general procedure (reaction period : 5.0 hr.) was submitted to distillation under reduced pressure. First, a TMAF distillate was obtained, from which 3.3 g. (0.031 mole) of benzylalcohol was isolated in the same manner as in the experiment with N,N′-benzylidenebisformamide. After removal of the following distillate of propionamide, the residual liquid was fractionally distilled under higher reduced pressure. The first distillate, b.$p_{0.2\sim0.3}$ 144~155°, was shown to be composed with N,N-dibenzylformamide and N-benzylpropionamide. Separation of the components was successfully accomplished by the following procedure, of which preliminary test was made with authentic samples. The oily mixture was thoroughly shaked with 8% aq. AcOH at room temperature. An insoluble oily material was extracted with benzene and the solution was washed with aq. $KHCO_3$ and dried over Na_2SO_4. After removal of benzene, the residue solidified, showing m.p. 49~51°. This material, weighing 1.1 g. (0.005 mole), was identified as N,N-dibenzylformamide by comparison of the IR spectrum and mixed melting point test with an authentic sample. The AcOH solution was basified and saturated with $KHCO_3$ and the liberated oily material was extracted with benzene. The solution was dried over Na_2SO_4 and benzene was removed. Redistillation of the residual oil gave a solid material, m.p. 48~49°, weighing 3.2 g. (0.020 mole), which was identified as N-benzylpropionamide by comparison of the IR spectrum and mixed melting point test with an authentic sample. *Anal.* Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03; N, 8.58. Found : C, 73.41; H, 7.76; N, 8.41.

The second distillate, b.$p_{0.2\sim0.3}$ 156~166°, was shown to be composed of tribenzylamine and N,N-dibenzylformamide. Separation of the components was carried out in the same manner as described in the experiment with N,N′-benzylidenebisbormamide resulting in the following formation : 1.7 g. (0.005 mole) of tribenzylamine hydrochloride, m.p. 218~223°, 1.6 g. (0.007 mole) of N,N-dibenzylformaide, m.p. 48~50°.

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Reaction of N,N′-Benzylidenebisformamide with Ammonium Formate——From the reaction mixture obtained from the general procedure (the reaction period: 2 hr.), a mixture of H_2O, HCO_2NH_4 and $HCONH_2$ was distilled off under reduced pressure, when a part of tribenzylamine 0.8 g. (0.0025 mole) also vaporized in the distillate as a suspensing state. The residual liquid was then carefully fractionated under higher reduced pressure (no residue remained). The fractions were similar to those of the experiment with TMAF and worked up by the same procedure giving the following products: N-Benzylformamide, m.p. 56~58°, 8.9 g. (0.066 mole); tribenzylamine hydrochloride, m.p. 214~223°, 0.8 g. (0.0025 mole); dibenzylformamide, m.p. 46~49°, 0.6 g. (0.003 mole).

Reaction of N,N′-Benzylidenebisacetamide with Ammonium Formate——After removal of H_2O, HCO_2NH_4 and $HCONH_2$ by distillation from the reaction mixture obtained from the general procedure (the reaction period: 3.5 hr.) the residual liquid was carefully fractionated under reduced pressure (distillation residue 0.4 g.). The first distillate, b.p$_{0.2}$ 126~130°, m.p. 56~59°, weighing 10.7 g. (0.079 mole), was identical with an authentic N-benzylformamide by comparison of the IR spectrum and mixed melting point test. The second distillate, b.p$_{0.4}$ 161~165°, was composed of N,N-dibenzylformamide. To remove contamination of trace of N-benzylformamide, the distillate washed with 5% AcOH and extracted with benzene. Drying the extract over Na_2SO_4 and subsequent evaporation gave a solid residue, m.p. 46~49°, weighing 0.4 g. (0.002 mole), which was shown to be nearly pure N,N-dibenzylformamide by comparison of the IR spectrum and by mixed melting point test.

Reaction of N,N′-Benzylidenebispropionamide with Ammonium Formate——Similar reaction products to those of the experiment with N,N′-benzylidenebisacetamide were obtained in this case. The reaction mixture from the general procedure (reaction period: 5.5 hr.) was worked up by the same procedure as in the experiment, giving following products: N-Benzylformamide, m.p. 57~59°, 10.3 g. (0.076 mole); N,N-dibenzylformamide, m.p. 45~49°, 0.3 g. (0.001 mole); distillation residue 0.5 g.

Reaction of N,N′-Benzylidenebisformamide with Formamide——The following is the rewriting from the previously reported paper.[3] From the reaction mixture obtained from the general procedure excess of $HCONH_2$ was distilled off under reduced pressure. The residual liquid was further distilled under higher reduced pressure to give a solid distillate, b.p$_2$ 140~143° and m.p. 56~59°, weighing 5.9 g. (0.044 mole). This material was identical with an authentic N-benzylformamide by comparison of the IR spectrum and by mixed melting point test. The remained resinous residue weighed 7.7 g. This separated into two parts, a material (4.1 g.) soluble in $CHCl_3$ and charcoal-like material insoluble in any solvent. The former was chromatographed through silica gel column using $CHCl_3$ as an eluent. From the eluated fractions, 2.9 g. of lophine, m.p. 275~277°, and 0.2 g. of amaron, m.p. 245~246°, were isolated, which was identical with authentic samples obtained in the preceding paper by comparison of the IR spectra and by mixed melting point tests. The remained part, which appeared to be composed of a few kinds of materials, was not further investigated, because of difficulties in obtaining pure material.

Reaction of N,N′-Benzylidenebisacetamide with Formamide——The reaction mixture from the general procedure was worked up by the same procedure as in the experiment with N,N′-benzylidenebisformamide. By the distillation under reduced pressure, N-benzylformamide, m.p. 56~58°, weighing 5.8 g. (0.043 mole), was obtained. The distillation residue weighed 7.6 g. of which 4.8 g. was soluble in $CHCl_3$. The chromatography through silica gel gave 0.4 g. of amaron, m.p. 245~247°, and 0.7 g. of lophine, m.p. 274~276°. Both the materials were identical with authentic samples obtained in the preceding paper[3] by comparison of the IR spectra and by mixed m.p. test.

Reaction of N,N′-Benzylidenebispropionamide with Formamide——The reaction mixture from the general procedure was worked up by the same procedures as in the experiment with N,N′-benzylidenebisformamide. N-benzylformamide, m.p. 56~58°, weighing 6.3 g. (0.047 mole) was obtained. The distillation residue weighed 6.7 g. of which 5.1 g. was soluble in $CHCl_3$. The chromatography gave 0.4 g. of amaron, m.p. 244~246°, and 0.72 g. of lophine, m.p. 274~277°.

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