Studies on the High Pressure Reaction of Carbon Monoxide. II. Synthesis of Phthalimidine

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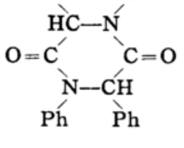
In Part I the reaction of Schiff bases and azobenzene derivatives with synthetic gas was described and it was found that in the case of azobenzene, no insignificant amount of diphenylurea had been formed besides aniline which was the main product.

With the object of obtaining more information on the cause of diphenylurea-formation as well as on the knowledge of reactivity of carbon monoxide with -N=N- bond, the authors studied the reaction with carbon monoxide alone instead of with synthetic gas as reported in Part I. There, it was found that new reactions took place which afforded phthalimidines when Schiff bases were subjected to the reaction with carbon monoxide under the cobalt catalyst, and quinazolones when azocompounds were used. The present paper describes the synthesis of phthalimidine.

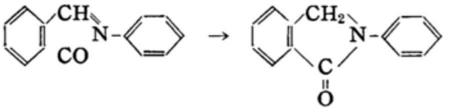
When benzaldehydeanil was dissolved in an aromatic hydrocarbon such as benzene or toluene and heated under carbon monoxide pressure of 100 to 200 atm. at 200~230°C in the presence of cobalt catalyst, it afforded white scaly crystals, m. p. 200°C.

The result of the analysis of these crystals indicated that it had an experimental formula ($C_{14}H_{11}ON$), indicating that 1 mol. of carbon monoxide had entered into every 1 mol. of benzaldehydeanil.

It appeared at the outset to have achieved the synthesis of amino acid in the form of anhydride and to have obtained tetraphenyldiketopiperazine of the following formula:

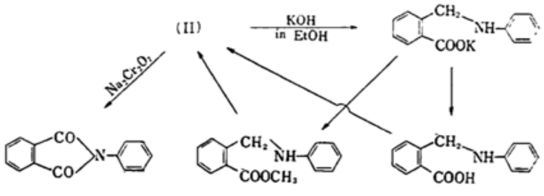


But a detailed study of this substance soon revealed that it was the derivative of phthalimidine (II) and was probably synthesized according to the following scheme:



(I) (II)

Compound II gave on hydrolysis an acid (III) which are so unstable on standing as to return to the original compound. In order to get a stable product, compound II was hydrolyzed with alkali and then the hydrolyzate was esterified directly with dimethylsulfate without acidification. Although the ester of III was separated as an oil, it also returned to its original compound II very easily.



(V) (IV) (III)

These behaviors did not correspond to the one of diketopiperazine.

The formation of phthalic anhydride by oxidation with potassium permanganate and the formation of *N*-phenylphthalimide by sodium bichromate-oxidation demonstrated eventually that compound II was a phthalimidine derivative as illustrated above.

A conclusive evidence was established by comparison with the authentic sample prepared by other means.

Thus a novel reaction was found, in which CO-attack had taken place on both the benzene rings and on the *N*-atom with simultaneous ring formation. In order to establish the necessary conditions for the achievement of this reaction, several runs were carried out and the results were shown in Table I. The essential features

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* Reported briefly in a previous communication: S. Murahashi, S. Horiie, *J. Am. Chem. Soc.*, 77, 6403 (1955).

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TABLE I. REACTION BETWEEN BENZALDEHYDEANIL WITH CO

Expt. No.	Anil g.	Catalyst	Solvent	CO Pressure atm.	Reaction temp., °C	Reaction time hr.	Yield g.
1	5	—	C_6H_6	200	220～230	6	—
2	5	$[Co(CO)_4]_2$	〃	〃	〃	〃	4.1
3	3	Co-acetylacetonate	〃	288	〃	〃	1.2
4	3	Co-ethylacetoacetate	〃	278	〃	〃	1.7
5	3	$CoCO_3$	〃	180	〃	6	2.0
6	5	$Fe(CO)_5$	〃	140	〃	〃	0.5
7	3	$Ni(CO)_4$	〃	330	〃	〃	—
8	5[a)]	$[Co(CO)_4]_2$[b)]	〃	200	〃	6	4.1
9	5	〃 [c)]	〃	〃	〃	〃	3.9
10	3	〃	〃	155	〃	3	2.0
11	3	〃	〃	84	〃	1	2.0
12	3	〃	〃	45	〃	3	0.5
13	5	〃		200	〃	6	—
14	5	〃	EtOH	〃	〃	〃	—
15	5	$Ni(CO)_4$		330	〃	〃	—
16	5	$[Co(CO)_4]_2$	C_6H_6, H_2O 1 cc	185	〃	6	—
17	5	〃	C_6H_6, H_2O 0.5 cc	160	〃	〃	—
18	5	〃	C_6H_6	200 (0.01%O_2)	〃	〃	4.1
19	5	〃	〃	200 (0.15%O_2)	〃	〃	3.7
20	5	〃	〃	200	〃	5	trace

Concn. of Catalyst: 0.03 millimol./cc.

a) Benzaldehydeanil: 0.028 mol.

b) $[Co(CO)_4]_2$: 0.0015 mol.

c) $[Co(CO)_4]_2$: 0.0045 mol.

of the results are as follows:

a) No reaction without the catalyst (Expt. No. 1). b) Cobalt compound such as dicobalt octacarbonyl, iron pentacarbonyl (less active), metallic cobalt, and cobalt salt or complex and so on, which have the potentiality of forming metal carbonyl, would be effective in promoting the reaction (Expts. No. 2–5). c) Nickel carbonyl is ineffective (Expt. No. 7). d) As a solvent, aromatic hydrocarbons are appropriate and protonic solvents inhibit the reaction (Expts. No. 13–17). e) Temperature of about 200°C is necessary and appropriate temperature of reaction lies in the range of 220～230°C (Expts. No. 10–12). f) Since the change of carbon monoxide pressure in the range of 30～300 atm. did not show any appreciable effect on the reaction, the necessary pressure seems to be that which suffices to maintain the concentration of cobalt carbonyl at the reaction temperature (Expts. No. 10–12). g) Since cobalt carbonyl is decomposed by contact with oxygen, it was inevitably needed to exclude oxygen (Expts. No. 18–19). h) The effect of the inner wall of an autoclave generally was not noticed except at the beginning of its use, when sometimes an irregular behavior was observed.

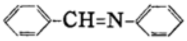
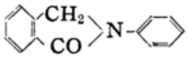
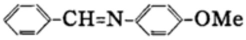
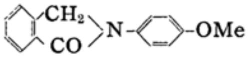
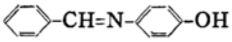
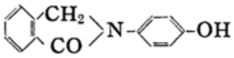
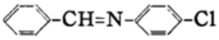
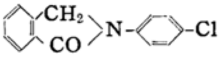
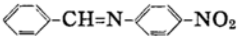
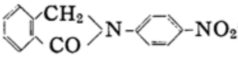
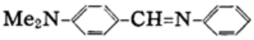
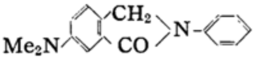
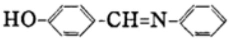
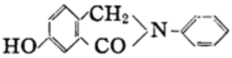
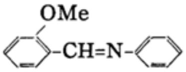
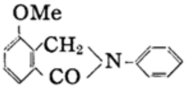
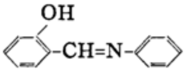
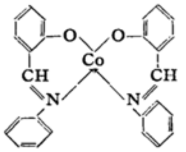
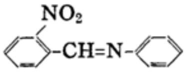
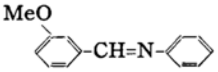
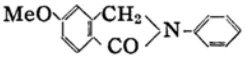
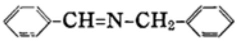
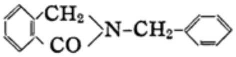
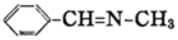
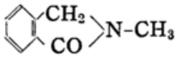
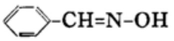
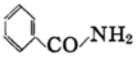
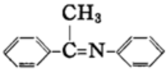
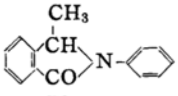
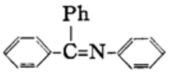
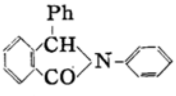
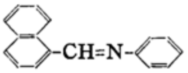
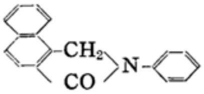
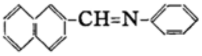
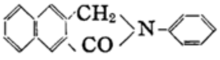
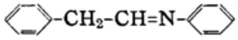
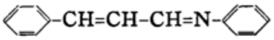
As this reaction is expected to give useful intermediates for dyestuffs and synthetic chemical reagents, the reactions between carbon monoxide and varieties of Schiff bases having various substituents were examined, as shown in Table II.

In both the cases of benzaldehydeanils with substituents (H, OMe, OH, Cl) in the *p*-position of aniline nucleus and those with substituents (OH, Me_2N) in the *p*-position of benzaldehyde side, all gave phthalimidines in good yields by the reaction with carbon monoxide, and no appreciable effect of the substituents was observed (Expts. No. 1–4 and 6–7). *o*-Methoxybenzaldehydeanil gave the expected phthalimidine though in a comparatively low yield. (Expt. No. 8).

In the case of salicylaldehydeanil, a stable red-colored complex containing cobalt was formed, and therefore, cobalt compound used as the catalyst did not promote the reaction but appeared only to have been converted to the stable complex compound II with salicylaldehydeanil (Expt. No. 9).

m-Methoxybenzaldehydeanil yielded a low yield of phthalimidine. The expected

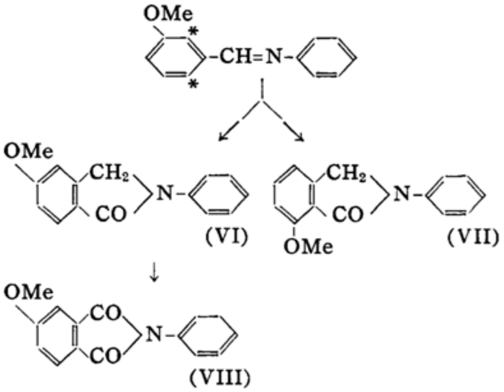
TABLE II. REACTION BETWEEN SCHIFF BASES AND CO

Expt. No.	Starting material		Product	Yield		m. p.	
	Schiff base	g.		g.	%	Author	Liter.
1		5		4.1	71.9	164	163
2		5		4.8	85.7	138	134
3		5		3.7	64.9	225	228
4		5		4.2	75.0	182	180
5		5	 *	—	—	—	—
6		5	 *	4.6	82.1	154	—
7		5	 *	4.4	77.2	216	—
8		5	 *	1.0	17.8	146	—
9		5		0.3	—	191	191
10		4	——	—	—	—	—
11		5	 *	0.3	5.3	146	—
12		5		4.7	82.4	91	91
13		5		3.0	48.6	115	120
14		5		1.3	26.0	128	128
15		5		3.5	61.4	82	80
16		3		3.2	96.9	196.5	—
17		2	 *	2.1	96.0	177	—
18		4	 *	1.5	80.0**	254	—
19		5	——	—	—	—	—
20		5	——	—	—	—	—

* New compounds.

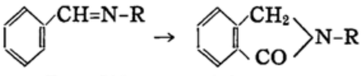
** Yield based on anil consumed.

products could be either VI or VII. Since the product was oxidized with sodium bichromate in acetic acid to yield 4-methoxyphthalic acid anilide (VIII), it was identified as a new compound, *N*-phenyl-5-methoxyphthalimidine (VI) (Expt. No. 11).



The ring closure is expected to take place at these asterisk positions.

Schiff base derived from aliphatic amine and benzaldehyde also gave the phthalimidine by the reaction with carbon monoxide (Expts. No. 12 and 13).

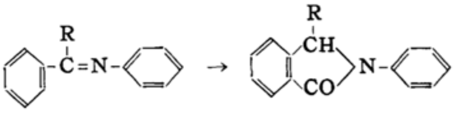


R: CH_3 and $PhCH_2$

Benzaldoxime did not give phthalimidine, but gave benzamide. This fact suggests that a part of cobalt carbonyl had been converted to cobalt hydrocarbonyl in the reaction condition and since this is a strong acid*** it might have promoted the Beckmann rearrangement.

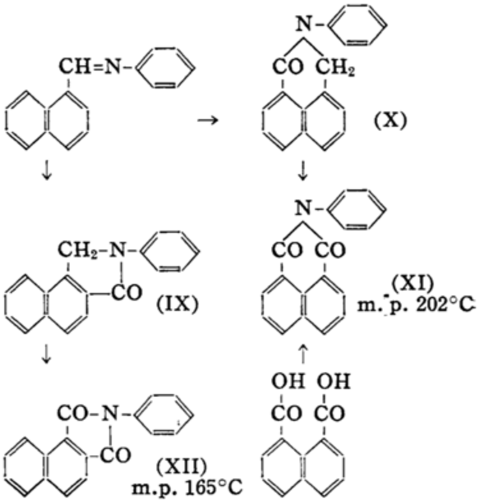
In the case of Schiff base having a nitro group, either on the side of aniline or on the benzaldehyde nucleus, the reaction became very complicated, yielding a deep violet infusible solid**** instead of the expected nitrophthalimidine (Expts. No. 5 and 10). As the model experiment on nitrobenzene (see *Experimental*) shows, the reaction was complicated owing to the presence of the nitro group, but the presence of phthalimidine grouping in the product was demonstrated by the occurrence of phthalic acid among the oxidation products.

Schiff bases, obtained from ketone such as acetophenone and benzophenone and aniline, reacted smoothly with carbon monoxide, yielding the expected phthalimidines (Expts. No. 15 and 16).



R: Me and Ph

Naphthaldehydeanils yielded the corresponding derivatives of phthalimidine in good yields. As 1-naphthaldehydeanil can be expected to ring-close with carbon monoxide at a 2- or 8-position, either one or a mixture of two (IX), (X) will be formed as the product. The product obtained, however, was not a mixture but a pure substance, and was converted to *N*-phenylnaphthalimide (m. p. 165°C) by oxidation with sodium bichromate in acetic acid. *N*-Phenyl-1, 8-naphthalimide (XI) synthesized from 1, 8-naphthalendicarboxylic acid and aniline, which has the melting point of 202°C, does not coincide with the oxidation product. Therefore, the phthalimidine obtained here would be IX and the oxidized product XII. Thus, the ring closure takes place at the 2-position to yield 2-phenylbenz [*e*] isoindolin-1-on (VI),



Although the chemical structure of compound IX has not yet been fully

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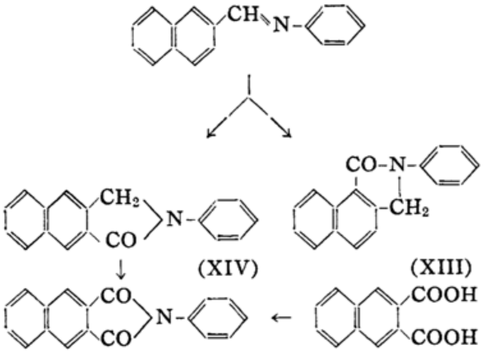
*** Since this rearrangement by cobalt carbonyl or more probably cobalt hydrocarbonyl was considered to be a new fact, the same method was attempted to apply to aliphatic oximes. However, aliphatic oximes were merely reduced and by cyclohexanone oxime, gave dicyclohexylurea besides an amino compouond.

**** It is apparent that the reducing power of carbon monoxide led to the formation of azo-linkage (G. D. Buckley, N. H. Ray; *J. Chem. Soc.*, **1949**, 1154) or of diphenylurea linkage (S. Horiie, unpublished) by the reduction of the nitro group. Reactions as these might be responsible for the reaction between carbon monoxide and the nitrocompound leading to the formation of an insoluble, infusible and deep violet substance.

ascertained by a direct comparison with the synthesized sample, its identity is considered to be well confirmed by the comparison with XV, and this will be described below.

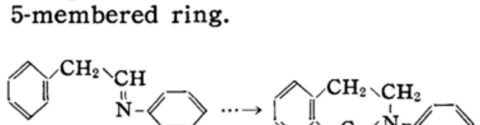
Since, in the case of 2-naphthaldehydeanil, the ring closure takes place at the 1- or 3-position of naphthalene nucleus, the expected product is either XIII of XIV. Only one kind of reaction product was also obtained here and, through the oxidation by sodium bichromate, it gave a *N*-phenylnaphthalimide, which coincided with *N*-phenyl-2, 3-naphthalimide (V), synthesized from 2, 3-naphthalene dicarboxylic acid and aniline. Therefore, the reaction product obtained with 2-naphthaldehydeanil was proved to be 2-phenylbenz[*f*]-isoindolin-1-on (XIV), which occurred as the result of the ring closure at the 3-position.

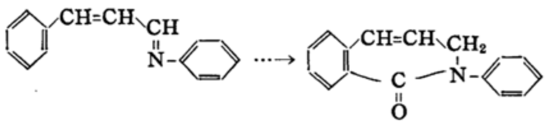

(XIV) (XIII)

(XV) mp. 278°C

This ring closure by carbon monoxide at the 3-position of the naphthalene derivatives is a very peculiar case and of interest in comparison with the fact that the ring closure usually occurs at the 1-position of 2-substituted naphthalene derivatives.

Starting from phenylacetaldehydeanil and cinnamaldehydeanil, the reaction should analogously be expected to lead to the formation of 6- and 7-membered rings, respectively, but the experiments were carried out in vain. This would suggest that the reaction with carbon monoxide seems to be characteristic of the azomethine group, conjugated with the aromatic ring and is limited to the formation of a 5-membered ring.





Experimental

1) Reaction between Benzaldehydeanil and Carbon Monoxide.—Five grams of benzaldehydeanil was dissolved in 50 ml. of benzene, and placed in an autoclave of 100 ml. content together with a catalytic amount of cobalt carbonyl solution (concn., 0.03 millimol./ml.) and carbon monoxide was pressed after replacement of air up to 100～200 atm., then the autoclave was heated at 220～230°C for 5～6 hr. with constant shaking. After cooling, the excess of carbon monoxide was purged and a greater part of *N*-phenylphthalimidine, which is produced, emitted as crystalline needles or scales and were collected on a filter and washed with a small amount of benzene, the crystal (4.1 g., 72% of theoretical) is almost pure, m. p. 163°C.

Anal. Found: C, 80.26; H, 5.47; N, 6.92. Calcd. for $C_{14}H_{11}ON$: C, 80.38; H, 5.26; N, 6.70%.

2) Hydrolysis of *N*-Phenylphthalimidine and Alkylation of the Hydrolyzed Product.—One gram of *N*-phenylphthalimidine was boiled with an alcoholic solution of potassium hydroxide (2 g. of potassium hydroxide in 20 ml. of alcohol-water (1 : 1) solu ion) and after 3 hr. the alcohol was distilled off and the remaining water solution was devided into two parts.

When one part of the solution had been made slightly acidic with dilute hydrochloric acid, the oil was separated out, which then crystallized after a while. This crystal (0.45 g.) was proved to be identical with *N*-phenylphthalimidine.

When the other portion of the solution was methylated with 0.6 g. of dimethylsulfate, an oil which gradually changed into crystalls, and which was identified as *N*-phenylphthalimidine, m. p. 162°C oozed out.

3) Oxidation of Phthalimidine with Bichromate.—The oxidation carried out referred to the work of Maxwell and Allen[1]. Thus, *N*-phenylphthalimidine (0.5 g.) was dissolved in anhydrous acetic (30 ml.) acid under stirring and warming at 90°C. Sodium bichromate in fine powder was charged slowly until no more color change was observed. After half an hour when the mixture was poured into water, a white crystalline precipitate, which was recrystallized from alcolol, in colorless needles (0.2 g.), m. p. 205°C separated out. The mixed melting point test with an authentic sample proved to be identical with *N*-phenylphthalimide.

4) *N*-Phenylphthalimidine. — *N*-Phenylphthalimide, which is obtained by fusion of aniline and phthalic anhydride was reduced with Zn-dust according to the method of Graebe[2] in an acetic acid solution at 80～90°C.

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[1] C. S. Maxwell and X. F. Allen, "Organic Syntheses", Vol. 24, John Wiley & Sons, Inc., New York (1944), p. 1.

[2] C. Graebe, *Ann.*, **247**, 288 (1888).

After reduction, the solution was poured into a large amount of water, and the white crystals separated. The crystals, after recrystallization from alcohol, were found to be identical with the sample obtained from benzaldehydeanil, m. p. 163°C.

5) **Synthesis of *N*-(*p*-Methoxyphenyl)phthalimidine.**—*N*-Benzyl-*p*-methoxyaniline (5 g.) was caused to react with carbon monoxide in the same manner as in the previous paper (Expt. Part 1) in Paper II). After being cooled, the reaction mixture was filtered to yield 4.8 g. of the colorless scaly crystals, m. p. 137~138°C (from methanol). A literature reported the m. p. of 135°C[3].

Anal. Found: N, 5.79. Calcd. for $C_{15}H_{13}O_2N$: N, 5.85%.

This crystals (1 g.) suspended in 50 ml. of 1 N sodium hydroxide and oxidized with potassium permanganate, yielded 0.2 g. of phthalic acid which was identified by the mixed melting point test with the authentic sample.

6) **Synthesis of *N*-(*p*-Hydroxyphenyl)phthalimidine.**—The colorless crystals (3.7 g.) were obtained in needles in a similar manner starting from benzal-*p*-hydroxyaniline (5 g.). The product was recrystallized from alcohol, m. p. 224~245°C.

Anal. Found: C, 74.65; H, 4.92; N, 6.22. Calcd. for $C_{14}H_{11}O_2N$: C, 74.56; H, 5.12; N, 6.42%.

The crystals (1 g.) were oxidized to phthalic acid (0.2 g.) by alkaline potassium permanganate.

7) **Synthesis of *N*-(*p*-Chlorophenyl)phthalimidine.**—Benzal-*p*-chloroaniline (5 g.) gave in a similar manner 4.2 g. of colorless scaly crystals, which was recrystallized from alcohol, m. p. 181~182°C.

Anal. Found: C, 69.14; H, 4.11; N, 5.19. Calcd. for $C_{14}H_{10}ONCl$: C, 69.40; N, 4.44; N, 5.99%.

The crystals (1 g.) were oxidized to phthalic acid (0.25 g.).

8) **Reaction of Carbon Monoxide with Benzal-*p*-nitroaniline.**—In a similar manner, there was obtained an amorphous deep purple substance, which was insoluble in organic and inorganic solvents and was infusible. The fact that oxidation of this substance by potassium permanganate yielded a minor amount of phthalic acid seems to show that the general reaction between benzal-*p*-nitroaniline and carbon monoxide has taken place to some extent.

9) **Synthesis of *N*-Phenyl-6-dimethylaminophthalimidine.**—*p*-Dimethylaminobenzaldehydeanil (5 g.) gave 4.6 g. of colorless needles, which were recrystallized from alcohol, m. p. 154°C.

Anal. Found: C, 76.00; H, 6.13; N, 11.30. Calcd. for $C_{16}H_{16}ON_2$: C, 76.16; H, 6.39; N, 11.10%.

10) **Synthesis of *N*-Phenyl-6-hydroxyphthalimidine.**—*p*-Hydroxybenzaldehydeanil (5 g.) also gave 4.4 g. of colorless needles, which were then recrystallized from alcohol, m. p. 215~216°C.

Anal. Found: C, 74.65; H, 4.88; N, 6.45. Calcd. for $C_{14}H_{11}O_2N$: C, 74.65; H, 4.92; N, 6.22%.

11) **Synthesis of *N*-Phenyl-4-methoxyphthalimidine.**—The reaction mixture from *o*-methoxybenzaldehydeanil (5 g.) and carbon monoxide, after distillation of benzene and after being kept for several days, gave 1 g. of brownish black crystals, which were then recrystallized from alcohol several times into colorless needles, m. p. 145~146°C.

Anal. Found: C, 75.70; H, 5.36; N, 5.96. Calcd. for $C_{15}H_{13}O_2N$: C, 75.30; H, 5.48; N, 5.86%.

12) **Formation of 3-Methoxyphthalic Acid Anil.**—Onto a boiling mixture of *N*-phenyl-4-methoxyphthalimidine (0.4 g.) and glacial acetic acid (10 ml.), sodium bichromate was added portionwise until the color of bichromate ion no longer disappeared, and then the whole mixture was poured onto water. White crystals were filtered off, washed with water and recrystallized from alcohol into colorless scaly crystals (0.2 g.), m. p. 188~189°C, which agreed well with m. p. of a literature[4].

Anal. Found: C, 71.00; H, 4.45; N, 5.75. Calcd. for $C_{15}H_{11}O_3N$: C, 71.14; H, 4.37; N, 5.53%.

13) **Formation of Salicylaldehydeanil-cobalt Complex.**—Salicylaldehydeanil (5 g.) gave in a similar manner, after removal of benzene and addition of a small amount of alcohol, 2.1 g. of red crystals, which were recrystallized from alcohol, m. p. 190~191°C. The existence of cobalt was ascertained qualitatively by the borax bead test.

Anal. Found: C, 68.55; H, 4.73. Calcd. for $(C_{13}H_{11}ON)_2Co$: C, 68.72; H, 4.84%.

Identification of this compound was carried out by the mixed melting point test with the sample, which was synthesized in the following way: a mixed solution of salicylaldehydeanil (1 g.) in benzene and cobalt carbonyl (1.5 g.), after being kept at room temperature for 3 days, was refluxed in a water bath to decompose the remaining carbonyl and then filtered. After removal of benzene from the filtrate, the remaining brown oil was kept standing with the addition of a small amount of alcohol to yield red crystals, m. p. 190~191°C. This compound showed the same melting point as the one which has been obtained from salicylaldehydeanil and cobalt acetate (m. p. 191°C)[5].

14) **Reaction between *o*-Nitrobenzaldehydeanil and Carbon Monoxide.**—*o*-Nitrobenzaldehydeanil yielded an amorphous deep purple substance just like the one of benzal-*p*-nitroaniline.

15) **Reaction between Nitrobenzene and Carbon Monoxide.**—The reaction mixture of nitrobenzene (40 g.) and cobalt carbonyl (0.5 g.) was subjected to steam distillation, yielding 15 g. of apparently amorphous and deep purple solid as residue, which was insoluble and infusible. An extraction of the solid with alcohol for a prolonged time gave 1.2 g. of diphenylurea.

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[3] A. T. Peters, G. T. Pringle and F. M. Rowe, *J. Chem. Soc.*, **1948**, 597.

[4] W. H. Benteley, R. Robinson and C. Weizmann, ibid., **1907**, 111.

[5] Endō, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **65**, 428 (1944).

16) Synthesis of *N*-Phenyl-5-methoxyphthalimidine.—The reaction mixture of *m*-methoxybenzaldehydeanil (5 g.) and carbon monoxide was refluxed to effect the decomposition of the catalyst, filtered, and evaporated to a brownish oil, which crystallized after standing in a vacuum dessicator (0.3 g.). Repeated recrystallizations from alcohol gave colorless needles, m. p. 145~146°C.

Anal. Found: C, 75.10; H, 5.68. Calcd. for $C_{15}H_{13}O_2N$: C, 75.30; H, 5.48; N, 5.86%.

m-Methoxybenzaldehydeanil (2.4 g.) was recovered by distillation of the mother liquor at a reduced pressure.

17) Formation of 4-Methoxyphthalic Acid Anilide.—*N*-Phenyl-5-methoxyphtalimidine (0.2 g.) in glacial acetic acid (4 ml.) was refluxed with sodium bichromate (2 g.), and the whole mixture was poured into-water, resulting in the formation of white crystals. After washing with water, the crystals were recrystallized from alcohol into colorless needles (0.1 g.), m. p. 177~178°C, which agreed well with the reported melting point of 4-methoxyphthalic acid anilide (179°C)[6]. The crystals showed a depression of melting point with 3-methoxyphthalic acid anilide, and so it was identified as 4-methoxyphthalic acid anilide.

Anal. Found: C, 71.32; H, 4.65. Calcd. for $C_{15}H_{11}O_3N$: C, 71.14; H, 4.37%.

18) Synthesis of *N*-Benzylphthalimidine. — Starting from benzalbenzylamine (5 g.), crystalline *N*-benzylphthalimidine (4.7 g.) was obtained in a similar manner, m. p. 90~91°C (from alcohol), which agreed well with Gabriel's value (m. p. 90~91°C)[7].

Anal. Found: C, 80.40; H, 5.49; N, 6.22. Calcd. for $C_{15}H_{13}ON$: C, 80.69; H, 5.87; N, 6.27%.

Oxidation of the crystals (0.5 g.) by potassium permanganate gave phthalic acid (0.2 g.), which was identified by the mixed melting point test with the known sample.

19) Synthesis of *N*-Methylphthalimidine. — Benzalmethylamine (5 g.) was reacted with carbon monoxide in a usual manner, giving *N*-methylphthalimidine (3.0 g.), which was recrystallized from alchohol in colorless cubic crystals, m. p. 114~115°C.

Anal. Found: C, 73.15; H, 6.36; N, 9.97. Calcd. for C_9H_9ON: C, 73.45; H, 6.16; N, 9.52%.

The crystals (0.5 g.) were oxidized by potassium permanganate to phthalic acid (0.1 g.), which was identified by the mixed melting point test with the known sample.

20) Reaction between Benzaldoxime and Carbon Monoxide.— Benzaldoxime (5 g.) gave 1.3 g. of colorless needles by the reaction with carbon monoxide, m. p. 127~128°C (from chloroform). The analytical data showed a good agreement with the composition of the original benzaldoxime, indicating that an additional reaction with carbon monoxide had not taken place. The crystal was considered as benzamide from the fact that its melting point does agree with that of benzamide and that it afforded benzoic acid by hydrolysis. Identification was carried out by the mixed melting point test with a known sample of benzamide.

Anal. Found: C, 69.07; H, 6.01; N, 14.01. Calcd. for C_7H_7ON: C, 69.40; H, 5.83; N, 11.56%.

21) Synthesis of *N*-Phenyl-3-methylphthalimidine.—Acetophenoneanil (5 g.) was reacted with carbon monoxide in a usual manner and, after removal of catalyst and benzene, the residue was extracted with hot petroleum ether. On cooling the extract, there were obtained crystals, which were recrystallized from petroleum ether into colorless needles (315 g.), m. p. 81~82°C.

Anal. Found: C, 81.10; H, 5.97; N, 6.21. Calcd. for $C_{15}H_{13}ON$: C, 80.69; H, 5.87; N, 6.27%.

A literature reported the same melting point (80°C)[8].

22) Synthesis of *N*-Phenyl-3-phenylphthalimidine.—Benzophenoneanil (5 g.) gave, after the treatment similar to Expt. 17, 2.2 g. of the product in colorless needles (from petroleum ether), m. p. 195~196.5°C.

Anal. Found: C, 84.20; H, 5.20; N, 4.98. Calcd. for $C_{20}H_{15}ON$: C, 84.18; H, 5.30; N, 4.91%.

23) Synthesis of 2-Phenylbenz[*e*]isoindolin-1-on.—1-Naphthaldehydeanil (2.0 g.) gave, in the usual way, a crystalline product (2.1 g.), m. p. 177°C (from alcohol).

Anal. Found: C, 83.68; H, 4.98; N, 5.65. Calcd. for $C_{18}H_{13}ON$: C, 83.38; H, 5.01; N, 5.40%.

24) Oxidation of 2-Phenylbenz[*e*]isoindolin-1-on. — The crystals (0.5 g.) were dissolved in 30 ml. of boiling glacial acetic acid and sodium bichromate was added gradually until the color of bichromate ion no longer disappeared. After cooling, the reaction mixture was poured into water, giving white crystals, which was then washed with water and recrystallized from alcohol into colorless needles (0.3 g.), m. p. 165°C.

Since these crystals showed a marked depression of the melting point when mixed with *N*-phenyl-1, 8-naphthalimide (m. p. 202°C), which was synthesized from the known sample of 1, 8-naphthalenedicaboxylic acid and aniline, the product was confirmed to be different from the latter compound.

25) Synthesis of 2-Phenylbenz[*f*]isoindolin-1-on. — From the reaction mixture of 2-naphthaldehydeanil (4.0 g.) and carbon monoxide there separated crystals which were recrystallized from alcohol into scaly crystals (1.5 g.), m. p. 254°C.

Anal. Found: C, 83.55; H, 5.05; N, 5.28. Calcd. for $C_{18}H_{13}ON$: C, 83.38; H, 5.01; N, 5.40%.

The unreacted 2-naphthaldehydeanil (2.2 g.) was recovered from the filtrate after removal of catalyst and benzene.

26) Oxidation of 2-Phenylbenz[*f*]isoindolin-1-on. — The crystal (0.5 g.) was dissolved in 30 ml. of boiling glacial acetic acid, and sodium bichromate added in portions until the color of bichromate ion no longer disappeared. After cooling the reaction mixture was poured into a large quantity of water, yielding white crystals, which

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[6] W. H. Bentley and C. Weizmann, *J. Chem. Soc.*, **91**, 104 (1907).

[7] S. Gabriel, *Ber.*, **45**, 724 (1912).

[8] A. Peters, F. M. Rowe and C. I. Brodrick, *J. Chem.* Soc., **1948**, 1259.

was then washed with water and recrystallized from alcohol into colorless needles (0.2 g.), m. p. 278°C. Identification was carried out by the mixed melting point test with a known sample of *N*-phenyl-2, 3-naphthalimide.

Anal. Found: C, 78.90; H, 4.29; N, 5.28. Calcd. for $C_{18}H_{11}O_2N$: C, 79.12; H, 4.03; N, 5.12%.

27) Synthesis of *N*-Phenyl-2, 3-naphthalimide.—Naphthalene-2, 3-dicarboxylic acid anhydride (0.5 g.), which was obtained by sublimation of naphthalene-2, 3-dicarboxylic acid at 240°C, was mixed with aniline (0.25 g.) and heated in a water bath[9]. The product was recrystallized from alcohol into colorless needles (0.6 g.), m. p. 278°C.

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[9] M. Freund and K. Fleischer, *Ann.*, **402**, 51 (1914).