*Studies on the High Pressure Reaction of Carbon Monoxide. III. Reaction between Azocompounds and Carbon Monoxide**

By Shigeki HORIIE** and Shunsuke MURAHASHI

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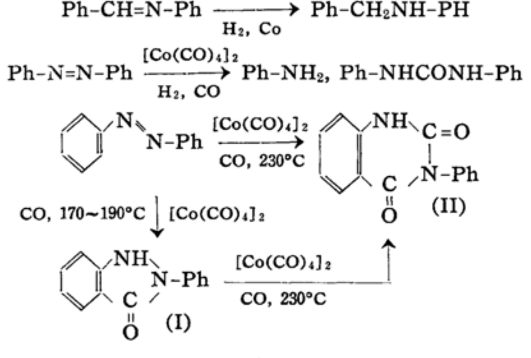
As was reported in Part I of this series, reaction of synthetic gas with Schiff base and with azobenzene principally results in reduction of " C=N " and " N=N " linkage. In the case of azobenzene, however, the principale product aniline was accompanied with a considerable amount of diphenylurea, indicating that azobenzene had reacted in some way with carbon monoxide in the presence of cobalt carbonyl[1]. During the study of the mechanism of diphenylurea-formation, the authors found another new reaction of carbon monoxide, that is, azobenzene gave indazolone and quinazolone by the reaction with carbon monoxide.



$$\text{Ph-CH=N-Ph} \xrightarrow[\text{H}_2,\ \text{Co}]{[\text{Co(CO)}_4]_2} \text{Ph-CH}_2\text{NH-PH}$$

$$\text{Ph-N=N-Ph} \xrightarrow[\text{H}_2,\ \text{CO}]{[\text{Co(CO)}_4]_2} \text{Ph-NH}_2,\ \text{Ph-NHCONH-Ph}$$

The authors wish to report in this paper on the formation of indazolone and quinazolone by the new reaction.

Azobenzene and 100~200 atmospheric pressures of carbon monoxide were heated at 220~230°C in the presence of cobalt carbonyl in aromatic hydrocarbon solvents such as benzene and xylene, resulting in the formation of 3-phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline (II) (69.2%) (for which, the authors later on will use an abridged expression, quinazolone or quinazolones in general). When the reaction was carried out at the temperature range of 170~190°C, 49.1% of 2-phenylindazolone (I) was obtained.

2-Phenylindazolone thus obtained was reacted again with carbon monoxide according to the condition used for the formation of quinazolone (230°C), yielding a high yield of quinazolone (II) (81.8%). Hence 2-phenylindazolone (I), is considered as an intermediate product in the formation of quinazolone (II) from azobenzene.

Since the formation of 2-phenylindazolone from azobenzene and carbon monoxide was expected from the analogy of formation of phthalimidine from benzaldehydeanil and carbon monoxide, product I was synthesized from another route that is, an azo compound was synthesized by the condensation of anthranilic acid amide and nitrosobenzene, hydrogenated to hydrazocompound, and then deaminated to 2-phenylindazolone and identified***.

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* Reported briefly in a previous communication: S. Murahashi and S. Horiie, *J. Am. Chem. Soc.*, **78**, 4416 (1956).

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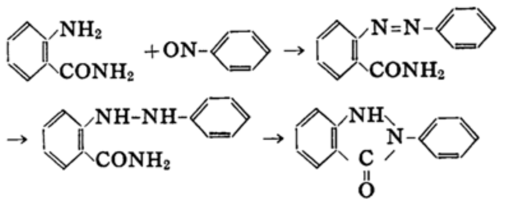
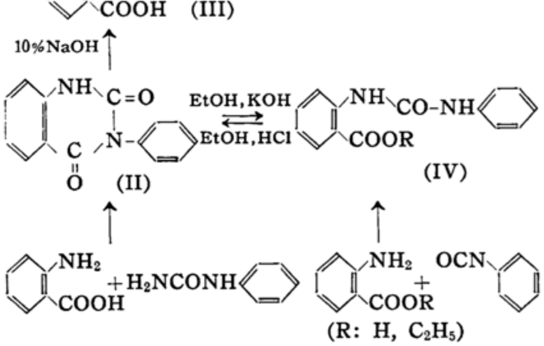
[1] S. Murahashi and S. Horiie, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 68 (1958).

*** The author synthesized 2-phenylindazolone starting from anthranilic acid amide according to the method of Auwers and Hüttenes[2].

[2] K. V. Auwers and K. Hüttenes, *Ber.*, **55**, 2680 (1922).



Identification of 3-phenyl-2, 4-dioxo-1, 2, 3,-4-tetrahydroquinazoline (II) was carried out in the series of reactions which follows: compound II was dissolved in 10% aqueous solution of sodium hydroxie, and was hydrolyzed by boiling the solution for 2∼3 hr. to yield anthranilic acid (III) almost quantitatively. Alcoholic potassium hydroxide decomposed compound II to *o*-carboxydiphenylurea (IV), which coincided with the known sample obtained from anthranilic acid and phenylisocyanate. Moreover, compound IV was converted to quinazolone (II) either by fusion of IV or by saturating the alcoholic solution of IV with dry hydrogen chloride.



Compound II was definitely identified as 3-phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline by comparing with the authentic sample that was synthesized from authranilic acid and phenylurea[3].

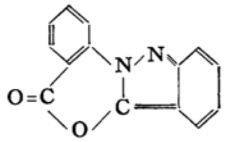
It was found that this new reaction was of value for the synthesis of large varieties of quinazolone derivatives to be elucidated later.

A survey of literatures reveals that the synthetic study of 2-phenylindazolone was meager and the yields were usualy rather low. Although at present our method does not allow high yield of indazolone selectively, being always accompanied with quinazolone and diphenylurea, the method is yet promising for the synthesis of indazolones.

Details of the scope of the reactions with varieties of azobenzene derivatives is described below. Generally, the reaction did not take place in the absence of catalysts. The effective catalysts are iron carbonyl, cobalt carbonyl, or cobalt compound, such as metallic cobalt, cobalt soap, and organic cobalt complex that can be converted into cobalt carbonyl under the reaction condition. Nickel carbonyl did not promote the reaction****. The solvents are preferably aromatic hydrocarbons, such as benzene, toluene, and xylene. The presence of polar substances such as water and alcohol inhibits the reaction[4]. The reaction temperature is preferably in the range of 220∼230°C. Below 200°C the proportion of indazolone, which is the intermediate to quinazolone, was pre dominant. Initial charge of carbon monoxide pressure of 100 atmospheric pressures is sufficient for the reaction. As oxygen decomposes the catalyst, it needs to be excluded from the system.

Since quinazolone(III)affords by hydrolysis anthranilic acids in a good yield, the reaction leads to a new and important preparative route of anthranilic acid.

As another by-product in this reaction besides diphenylurea, lactone of 2-(3-hydroxyindazol-2-yl)-benzoic acid (V)[5], and a neutral crystalline substance that has the melting point of 165°C, were obtained. The structure of the latter substance is now under study.



(V)

Next, the authors took up the problem of viewing the scope and the extent of this reaction. For this purpose azobenzenes and various kinds of compounds, which seem to be related, were subjected to the reaction. Table II shows the results on the formation of indazolones from substituted azobenzenes $RN=NR'$, and Table III shows the results of quinazolone-formation. As will be seen from the

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[3] F. Kunckell, *Ber.*, **43**, 1234 (1910).

**** The content of the study was presented at the Meeting of Yūkigōsei-kyokai, November, 1955. In the following year 1956, Prichard and others published a patent (U. S. Pat. 2,769,003), in which they claimed that the reaction of azobenzene with nickel carbonyl yielded mainly lactone of 2-(3-hydroxyindazole-2-yl) benzoic acid being accompanied with small amount of quinazolone and diphenylurea.

[4] The effects of various solvents on the reaction will be published in detail in the next paper.

[5] The lactone (V) was proved to be identical to the one that was obtained from azobenzene and nickel carbonyl according to the process of Prichard and others.

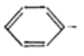
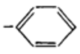
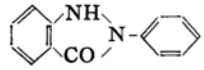
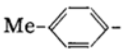
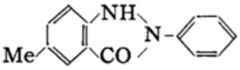
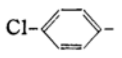
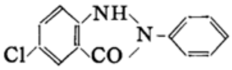
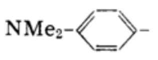
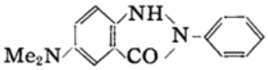
TABLE I. SYNTHESIS OF QUINAZOLONE*

Expt. No.	Catalyst	g.	Solvent	Initial atm.	Temp. °C	Time hr.	Quinazolone g.	Quinazolone %	Diphenylurea g.	Diphenylurea %
1	—	0	C_6H_6	150	230	3	0	0	0	0
2	$Ni(CO)_4$	3	C_6H_6	150	230	3	0	0	0	0
3	$Fe(CO)_5$	3	C_6H_6	180	240	4	0.8	12.3	0.1	1.7
4	$[Co(CO)_4]_2$	2	C_6H_6	150	230	0.5	4.5	69.2	0.7	12.1
5	$Co(II)(C_{18}H_{35}O_2)_2$**	2	C_6H_6	160	230	2.5	1.9	29.2	1.4	24.2
6	$Co(II)(C_5H_7O_2)_2$***	1	C_6H_6	150	240	2	1.5	23.1	0.8	13.8
7	$[Co(CO)_4]_2$	1	C_2H_5OH	150	230	3	0	0	0	0
8	$[Co(CO)_4]_2$	1	H_2O	160	230	3	0	0	0	0
9	$[Co(CO)_4]_2$	1	C_6H_6	150	190****	4	0.8	17.5	0.65	16.0
10	$[Co(CO)_4]_2$	1	C_6H_6	100	230	3	3.0	46.1	0.5	8.6

* Azobenzene, 5 g., Solvent, 50 ml., 18:8 Stainless autoclave of 100 ml. capacity.
** Co(II)-stearate.
*** Co(II)-acetylacetonate.
**** The main product was 2-phenylindazolone (2.8 g., 49.1%).

TABLE II. FORMATION OF INDAZOLONES FROM AZO-COMPOUND AND CO.

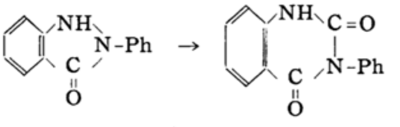
R-N=N-R′

R	R′	Indazolones	Yield g.	Yield %	m. p. °C
			2.8	49.1	204
			1.2	35.2	252
			1.3	23.8	233
			4.5	80.0	217

Azo-compound, 5 g.; $[Co(CO)_4]_2$, 0.05 m mol/cc.; CO 150 atm.; solvent, benzene; reaction temperature, 180∼190°C; reaction time, 2 hr.; reaction vessel, a 100 ml. rocking autoclave made of 18:8 stainless steel.

tables, the reaction can be applied to various derivatives of azobenzenes. It is interesting to note here that when one of the benzene ring has a substituent of electron-repelling character, the ring closure always occurs on the side of the nucleous having the substituent and where the substituent is electron-attracting the reaction does not take place. This fact suggests strongly that electronegativity of the nitrogen atom, which seems to be the site for the primary act of catalyst, is deeply influenced by these substituents.

The formation of 3-phenyl-2, 4-dioxo-1, 2-3, 4-tetrahydroquinazoline from indazolone is a new reaction, where a five membered ring was enlarged to a six-membered ring under the incorporation of a carbon monoxide molecule. This reaction appears to be formally quite similar to the formation of diphenylurea from hydrazobenzene.



To obtain a further information of the reaction the authors studied several ring compounds with a 5-membered ring under the same condition described as above. Indazol⁶⁾, indazolone⁶⁾, 2-phenyl-benzoxazol⁷⁾ and 2-phenyl-benzimidazole⁸⁾ were tested for this purpose. But none of them was found to be feasible for the ring enlargement.

A pyridine and a quinoline derivative, VI and VII⁹⁾, which are closely related to

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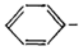
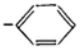
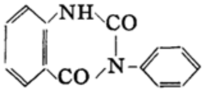
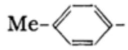
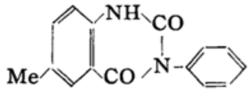
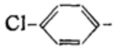
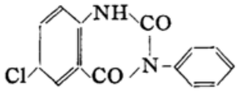
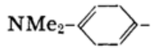
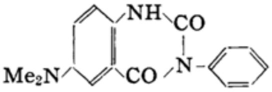
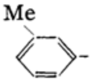
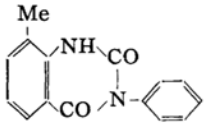
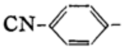
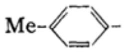
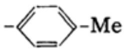
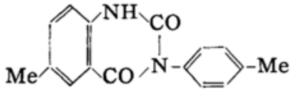
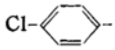
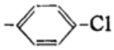
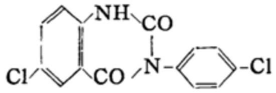
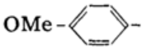
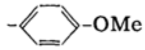
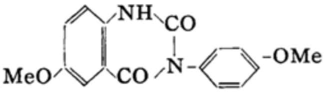
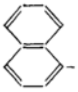
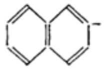
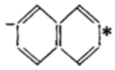
6) E. F. M. Stephenson, "Organic Syntheses", Vol. 29, John Wiley & Sons, Inc., New York (1949), p. 54.

7) L. C. Galatis, *J. Am. Chem. Soc.*, **70**, 1967 (1948).

8) D. Jerchel et al., *Ann.* **575**, 162 (1952).

9) H. K. S. Raw and T. S. Wheeler., *J. Chem. Soc.*, **1938**, 478; P. Ruggli et al., *Helv. Chim. Acta*, **27**, 649 (1944).

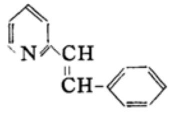
TABLE III. FORMATION OF QUINAZOLONES FROM AZO-COMPOUNDS AND CO.

R'-N=N-R		Quinazolone	Yield		m. p. °C
R'	R		g.	%	
			4.2	64.6	275
			2.3	35.9	296
			2.7	42.8	292
			1.1	18.0	231
			1.7	26.4	256
		?	trace	—	—
			2.5	40.0	285
			1.0	16.7	325
			1.6	27.7	279
	 *	—	—	—	—
	 *	—	—	—	—

Azo-compound, 5 g.; $[Co(CO)_4]_2$, 0.05 m mol./cc.; CO, 150 atm.; solvent, benzene; reaction temperature, 220～230°C; reaction time, 3 hr.; reaction vessel, a 100 ml. rocking autoclave made of 18:8 stainless steel.

* A small amount of dinaphthylurea was formed.

benzaldehydeanils were studied also under the similar condition.



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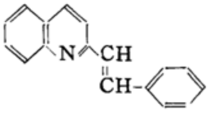


(VII)

In both cases, reactions took place with an uptake of carbon monoxide, but the reaction products thus obtained were colored deep violet-red and unstable solid and could not be crystallized into definite products.

In all cases quinazolone derivatives obtained gave, in good yield, anthranilic acid derivatives. (see *Experimental*)

On the By-product of the Reaction

As an example shows the following reaction products were obtained by the reaction where benzene was used as the reaction medium.

Quinazolone	64.1%
Diphenylurea	17.2%
Lactone	3.1%
Neutral substance	a small quanity
Aniline	〃

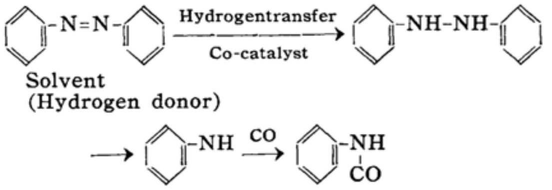
The formation of diphenylurea is significant, and so it would be necessary to learn the cause of its formation and to minimize its formation so as to obtain a complete information on the reaction and to improve the yield of quinazolone. From the result of the experiments it was shown that the formation of diphenylurea could not be observed in the decomposition reaction of quinazolone, and so was the quinazolone formation from diphenylurea and carbon monoxide. Hence it may be concluded that these two reaction products originate from different reaction courses.

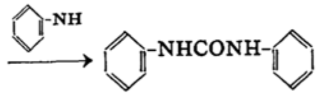
In order to account for the formation of diphenylurea from azobenzene, it is necessary for azobenzene to get one mole of hydrogen from somewhere, since the reactions are carried out with carbon monoxide alone in an anhydrous condition, none of the hydrogen atoms were available except from solvent molecules.

According to the gaschromatographic analysis of carbon monoxide used, the hydrogen in the gas was found to be 0.1% or less, and this quantity was proved to be too low to balance the urea-formation. Therefore, it was considered that solvent molecules are responsible for hydrogen supply. As an approach to this question various solvents were tested, including cyclohexane, *n*-hexane, dioxane, ether, acetonitrile, ethylalcohol, benzene, and naphthalene. Among these, cyclohexane found to produce diphenylurea in much abundance as campared to benzene and the same is also held in a comparison of *n*-hexane and benzene.

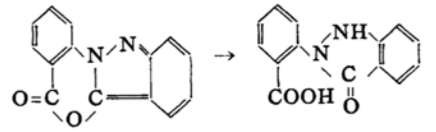
In both of the cases the quantity of urea and also the proportion of urea to quinazolone were increased. These seem to show that the solvent had contributed to the formation of urea by giving up its hydrogen necessary for the formation of urea.

As was described earlier in Part I of this series, the formation of urea was easier by hydrazobenzene than by azobenzene. From this and other facts in early parts of this paper, the authors tentatively propose the possible formation of urea derivatives as to proceed according to the following scheme:





The presence of this lactone [2-(3-hydrooxyindazol-2-yl) benzoic acid lactone] was easily confirmed through its hydrolysis and fomation of 2-(*o*-carboxyphenyl) indazolone. Prichard[10] obtained it by the reaction of azobenzene and carbon monoxide in the presence of nickel carbonyl catalyst and the authors' product was proved to be identical with this.



As was previously stated, the formation of quinazolone is strongly favored in the presence of cobalt catalyst in benzene solution, and the reaction proceeded via indazolone derivative as the intermediate. The same reaction failed when nickel carbonyl was used in a benzene solution.

Prichard has disclosed in his patent that he could observe the formation of this lactone as the main product and of small amount of quinazolone as a by-product, when nickel carbonyl was used as the catalyst in a cyclohexane solution. But, he did not observe anything about the intermediate formation of indazolone.

From the differences of reaction conditions including solvent and of the products which were formed, in quantity as well as in quality, it might be appropriate to conclude that the approach to quinazolone in the authors' experiments was not the same as that of Prichard.

It is well known that cobalt carbonyl is readily convertible to hydrocarbonyl, and so the very nature would be responsible for a hydrogen-transfer reaction. On the other hand, it is not known that nickel carbonyl possesses such a behavior of easy conversion to hydrocarbonyl and such a difference of the property between these two catalysts would be the main cause of differences observed in the authors' and Prichard's results. The authors will consider in detail this point later.

Experimental

1) Synthesis of 2-Phenylindazolone by the Reaction of Azobenzene with Carbon Monoxide. —A solution of azobenzene (5 g.) and cobalt

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[10] W. W. Prichard, U. S. Pat., 2,769,003 (1956).

carbonyl (1 g.) in benzene (25 ml.) was placed in an autoclave of 100 ml. capacity made of 18:8 stainless steel, and carbon monoxide was charged in up to 150 atmospheric pressures. The autoclave was heated at 180~190°C for 4 hr. under constant shaking. After being cooled, a crystalline substance in the reaction mixture was filtered (3.0 g.). From the filtrate, after removal of catalyst by refluxing on a water bath followed by filtration and removal of benzene, 1.5 g. of azobenzene was recovered. The crystalline substance was treated with 5% aqueous solution of sodium hydroxide, and filtered. The insoluble crystals were to be mainly of diphenylurea (0.65 g., 16%) containing, as contamination, some amount of yellow crystals, which were found to be lactone of 2-(3-hydroxyindazol-2-yl) benzoic acid, m. p. 296°C. Diphenylurea was recrystallized from alcohol (m. p. 240°C) and identified by the mixed melting point test with the sample prepared by an alternative way. The alkaline solution was acidified by either carbon dioxide, hydrochloric acid, or sulfuric acid, and a white crystalline substance separated. The crystalline substance, after filtration, was recrystallized from alcohol, yielding 0.8 g. of quinazolone (17.5%) as the insoluble part and 2.8 g. of 2-phenylindazolone (49.1%) as the soluble part. The latter were colorless needles, m. p. 204°C, and identified by the mixed melting point test with the sample synthesized as described below.

Anal. Found: C, 74.03; H, 4.82; N, 13.55. Calcd. for $C_{13}H_{10}N_2O$: C, 74.28; H, 4.76; N, 13.33%.

2) **Synthesis of 2-Phenylindazolone.**—Anthranilic acid was converted to isatoic anhydride[11], which was then treated with 20% aqueous ammonia, and converted to anthranilic acid amide[12] and was used as the starting material of this synthesis. Into a solution of anthranilic acid amide (8.0 g.) in 100 ml. of acetic anhydride, freshly distilled nitrosobenzene[13] (6.2 g.) was added in small portions. The mixture, after being kept at room temperature overnight, was diluted with equal volume of alcohol, and refluxed. Under vigorous stirring zinc powder (20 g.) was added portionwise. The red color of the solution faded out completely after about 1.5 hr. The solution was filtered and poured into a large quantity of water. The separated crystals were filtered off, and recrystallized from alcohol to yield pure 2-phenylindazolone (3.0 g.), m. p. 202~204°C.

3) **Synthesis of 3-Phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline by the Reaction of 2-Phenylindazolone with Carbon Monoxide.**—A mixture of 2-phenylindazolone (2 g.), cobalt carbonyl (1.0 g.) and benzene (50 ml.) was caused to react with 150 atmospheric pressures of carbon monoxide at 230°C for 2 hr. The crude crystals, that were obtained by filtering the reaction mixture after cooling, was recrystallized from alcohol to yield 1.8 g. of pure II (81.8%). Identification was carried out by the melting point test with a known sample.

Anal. Found: C, 70.29; H, 4.12; N, 11.66. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.20; N, 11.76%.

4) **Synthesis of 3-Phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline by the Reaction of Azobenzene with Carbon Monoxide.**—(i) A mixture of azobenzene (5.0 g.), cobalt carbonyl (2.0 g.) and benzene (45 ml.) was reacted with 150 atmospheric pressures of carbon monoxide at 220~230°C for 0.5 hr. After cooling, a crystalline mass (5.2 g.) in the reaction mixture was filtered off. The filtrate was refluxed on a water bath to effect the decomposition of the catalyst, and removed from inorganic substance by filtration. Yellow crystals, lactone of 2-(3-hydroxyindazol-2-yl) benzoic acid (0.1 g.) was obtained as a comparatively soluble part in benzene. The crystalline mass obtained above was treated with cold 5% aqueous solution of sodium hydroxide[14]. As the insoluble residue, diphenylurea (0.7 g., 12.1%) was obtained, and white crystals precipitated from the alkaline solution by acidifying (pH 4.0) with either carbon dioxide, hydrochloric acid, or sulfuric acid. The crystal was recrystalized from alcohol in colorless needles, m. p. 275°C, which was identified as 3-phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline by the mixed melting point test with the authentic sample.

Anal. Found: C, 70.63; H, 4.18; N, 11.90. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.20; N, 11.76%.

(ii) A mixture of azobenzene (5.0 g.), iron carbonyl (3.0 g.) and benzene (50 ml.) was heated with 180 atmospheric pressures of carbon monoxide at 240°C for 4 hr. to yield 3-phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline (0.8 g., 12.3%).

(iii) A mixture of azobenzene (5.0 g.), acetylacetone cobalt complex (1.0 g.), and benzene (50 ml.) was heated with 150 atmospheric pressures of carbon monoxide at 240°C for 5 hr. to yield 3-phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline (1.9 g., 29.2%).

(iv) A mixture of azobenzene (5.0 g.), cobalt stearate (2.0 g.) and benzene (50 ml.) was reacted with 160 atmospheric pressures of carbon monoxide at 230°C for 2.5 hr. to yield 1.9 g. of 3-phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline (29.2%).

5) **Hydrolysis of 3-Phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline by Sodium (or Potassium) Hydroxide.**—A solution of quinazolone (2.0 g.) in 10 ml. of 10% sodium (or potassium) hydroxide was refluxed. After 20 min. an oil began to separate, and the mixture was kept boiling for 2.5 hr. After cooling, aniline was removed by extraction with a small amount of ether. The aqueous solution was neutralized to pH 4.0 by diluted hydrochloric acid, and then a white solid precipitate was formed, which was filtered off, washed with water, and dried to yield 0.95 g. of gray crystalline anthranilic acid, m. p. 140°C (86.4%). Identification of the anthranilic was

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[11] E.C. Wagner and M.F. Fegley, "Organic Syntheses", Vol. 27, John Wiley & Sons, Inc., New York (1947), p. 45.

[12] Kolbe, *J. prakt. Chem.*, [2] 30, 475 (1884).

[13] G. H. Coleman, C. M. McCloskey and F. A. Stuart, "Organic Syntheses" Vol. 25, John Wiley & Sons, Inc., New York (1945), p. 80.

[14] Upon being warmed. quinazolne might be hydrolyzed to anthrailic acid.

carried out by the mixed melting point test with a known sample.

The filtrate gave by the addition of copper acetate 0.2 g. of copper anthranilate, which corresponds to 0.16 g. of anthranilic acid (10.1%).

6) **Hydrolysis of 3-Phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline by Alcoholic Potassium Hydroxide.**—A solution of quinazolone (2 g.), potassium hydroxide (8 g.) and 96% alcohol (40 ml.) was refluxed for 20 hr. After removal of alcohol, the residue was dissolved in water and acidified by concentrated hydrochloric acid, when a white solid precipitated. The solid was recrystallized from alcohol yielding as the insoluble part the recovered quinazolone (0.4 g.) and as the soluble part colorless needles, *o*-carboxydiphenylurea (0.8 g., 46.5%). The latter compound was identified by the mixed melting point test with a known sample prepared in the following manner.

Anal. Found: C, 65.28; H, 4.70; N, 10.86. Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.68; N, 10.93%.

7) **Synthesis of *o*-Carboxydiphenylurea.** — A solution of anthranilic acid (2 g.) in dry ether (10 ml.) and a solution of phenylisocyanate (1.8 g.) in dry ether (10 ml.) were combined under ice-cooling and stood at room temperature overnight. Crystals were filtered off and recrystallized from alcohol in colorless needles, *o*-carboxydiphenylurea (3.4 g., 90%), m. p. 187~188°C.

Anal. Found: C, 65.60; H, 4.72; N, 10.81. Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.68; N, 10.93%.

8) **Synthesis of *o*-Carboethoxydiphenylurea.**—Ethyl anthranilate (2 g.) was added gradually into phenylisocyanate (1.5 g.). The reaction was vigorously exothermic. The mixture was heated on a boiling water bath for about 0.5 hr. and the solid thus formed was recrystallized from alcohol in colorless needles, *o*-carboethoxydiphenylurea (3.3 g., 94.3%), m. p. 148°C.

Anal. Found: C, 67.30; H, 5.31; N, 10.15. Calcd. for $C_{16}H_{16}O_2N_3$: C, 67.60; H, 5.63; N, 9.86%.

9) **Synthesis of 3-Phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline (II).**—(i) *o*-Carboxydiphenylurea (1.0 g.) was heated for 30 min. at 190°C which is slightly above its melting point. The reaction mass was recrystallized from alcohol in colorless needles, II (0.05 g.), m. p. 273~275°.

(ii) When dry hydrogen chloride was introduced into a solution of *o*-carboxydiphenylurea (1.0 g.) in alcohol (30 ml.) at room temperature (20°C), the temperature of the content rose up to 30~40°C. Introduction of hydrogen chloride was continued for a while and the mixture was kept standing, and then colorless scaly crystals were formed. The crystals, after removal of alcohol and hydrogen chloride, were recrystallized from alcohol into colorless needles (0.9 g., 96.8%), m. p. 274~275°C.

TABLE IV. FORMATION OF ANTHRANILIC ACIDS FROM QUINAZOLONES

R	R′	g.	R	Yield g.	Yield %	m. p. °C
H	H	2.2	H	1.1	95.6	145
Me	H	2.0	Me	1.05	88.1	172
Cl	H	2.0	Cl	1.0	80.0	205
MeO	H	2.0	MeO	0.27	21.8	178
Me	Me	2.0	Me	1.1	97.3	172
Cl	Cl	2.0	Cl	1.05	94.5	205
MeO	MeO	2.0	MeO	0.35	28.2	178

(iii) *o*-Carboethoxydiphenylurea (0.2 g.) was heated at 200°C for 3 hr. in a sealed glass tube. After cooling, the reaction product was solidified at the bottom of the tube and the unreacted starting material was sublimed off on the upper wall of the tube. The product was recrystallized from alcohol into colorless needles (0.03 g., 18.1%), m. p. 273°C.

(iv) A mixture of anthranilic acid (5.0 g.) and phenylurea (5.0 g.) was heated at 200°C for 5 hr. in a sealed glass tube. The reaction product was treated with 100 ml. of 5% sodium hydroxide to remove the insoluble phenylurea. The alkaline solution was acidified by diluted hydrochloric acid, precipitating white crystalline acidic substance which was recrystallized from alcohol into colorless needles (2.5 g., 28.6%), m. p. 274°C.

10) **Reaction of *α*-Styrylpyridine and Carbon Monoxide.**—A solution of 3 g. of *α*-styrylpyridine and 1 g. of dicobalt octacarbonyl in 20 ml. of benzene was heated at 135~145°C under 130 atmospheric pressures of carbon monoxide for one hour to give 1 g. of amorphous product. This product was extracted with dimethylformamide and a reddish purple-colored amorphous substance melted at 200~250°C was obtained.

Anal. Found: C, 68.03; H, 5.24; N, 6.59; ash, 11.43%.

A similar experiment with *α*-styrylquinoline has failed to obtain any definite crystalline product, but resins.

11) **Effect of Solvents.**—For the purification of both naphthalene and *p*-dichlorobenzene, they were recrystallized from ethyl alcohol, and the crystals melting at 80 and 53°C respectively were collected.

Carbon tetrachloride and *n*-butylacetate were carefully fractionated and the fractions boiling at 76 and 126°C respectively were collected. Other solvents such as *n*-hexane, cyclohexane, benzene, toluene, tetraline, dioxane, ether, tetrahydrofuran, chlorobenzene, acetonitrile and ethylalcohol are, after drying over metallic sodium, fractionated. The fractions boiling at 69, 81, 80, 110, 207, 102, 34, 64, 122, 81 and 78°C respectively were collected.

12) **Reaction of Hydrazobenzene and Carbon Monoxide.**—A solution of 2 g. of hydrazobenzene and 1 g. of dicobalt octacarbonyl in 30 ml. of benzene was heated at 220~230°C under 120 atmospheric pressures of carbon monoxide for 4 hr. to give 0.95 g. of diphenylurea (41.3% yield) and 0.2 g. of 3-phenyl-2, 4-dioxo-1, 2, 3, 4-tetrahydroquinazoline (7.7% yield).

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