BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1942—1948 (1966)

Molecular Rearrangement in Polyphosphoric Acid. II. The Conversion of 1, 2-Dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one to 3-phenyl-2, 4(1*H*, 3*H*)-quinazolinedione[1,2]

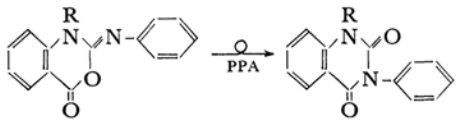
By Masaru KURIHARA and Naoya YODA

Basic Research Laboratories, Toyo Rayon Co., Ltd., Tebiro, Kamakura

(Received November 18, 1965)

The treatment in polyphosphoric acid of the *N*-(phenylcarbamoyl)-anthranilic acid prepared by the reaction of anthranilic acid with phenyl isocyanate has been shown to yield 1, 2-dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one or 3-phenyl-2, 4(1*H*, 3*H*)-quinazolinedione, depending on the reaction temperature. An intramolecular rearrangement has been found to occur by the treatment of exocyclic iminobenzoxazinone with polyphosphoric acid to afford quinazolinedione. The mechanisms of conversion in polyphosphoric acid have been proposed to account for the experimental results, and the structure of 2-phenylimino-4*H*-3, 1-benzoxazin-4-one has been presumed by means of infrared and ultraviolet spectroscopies and elemental analyses. The products of the reaction of *N*-methylanthranilic acid with phenyl isocyanate have been shown to be 1-methyl-3-phenyl-2, 4(1*H*, 3*H*)-quinazolinedione, 1-methyl isatoic anhydride and *N*-methyl-2-(phenylcarbamoyl)-carbanilide. Furthermore, the formation of the mixed anhydride of carboxylic acid and phosphoric acid as a reaction intermediate has been postulated.

The most frequently reported use of polyphosphoric acid is cyclodehydration, or more specifically, intramolecular acylation.[3,4] To our knowledge no studies have been carried out in polyphosphoric acid on the conversion of compound I to quinazolone derivatives II. In connection with the solution polymerization, in polyphosphoric acid, of 4, 4'-diamino-biphenyl-3, 3'-dicarboxylic acid with diisocyanate by cyclopolycondensation reactions,[5] the cyclodehydration of *N*-(phenylcarbamoyl)-anthranilic acid in polyphosphoric acid[6] was studied; two condensation products, 1, 2-dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one (Ia) and 3-phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (IIa) have been isolated, depending upon the reaction temperature. The authors also found that the intramolecular rearrangement in PPA of Ia to IIa occurs by heating Ia at 150°C through a phosphorylated reaction intermediate.



I II

(Ia R=H) (IIa R=H)
(Ib R=CH_3) (IIb R=CH_3)

In a previous paper[2] it has been shown that the reaction of anthranilic acid with aromatic isocyanate in the presence of PPA proceeded to the formation iminobenzoxazinone and quinazolinedione by way of phosphorylated intermediates. This type of rearrangement in PPA is especially notable because a possible mechanism for the cyclodehydration in PPA of *N*-(phenylcarbamoyl)-anthranilic acid involves phosphorylated reaction intermediates,[4] while the reaction in PPA afforded I and II, the former product arising from the presumed intermediate, V, via kinetic control, while the latter product was formed from V via thermodynamic control. The method of the synthesis of benzoxazinone (I), quinazolinedione (II) and related compounds is outlined in Scheme 1.

When *N*-(phenylcarbamoyl)-anthranilic acid (m. p. 186°C; from ethanol) is treated with PPA at 80—100°C for 1 hr., cyclodehydration occurs, thus yielding quantitatively 1, 2-dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one (Ia) (m. p. 193°C;

1) N. Yoda and M. Kurihara, presented in part at the 13th and 14th Meetings of the High Polymer Symposium of Japan, Tokyo, November, 1964, and Kyoto, October, 1965, and at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

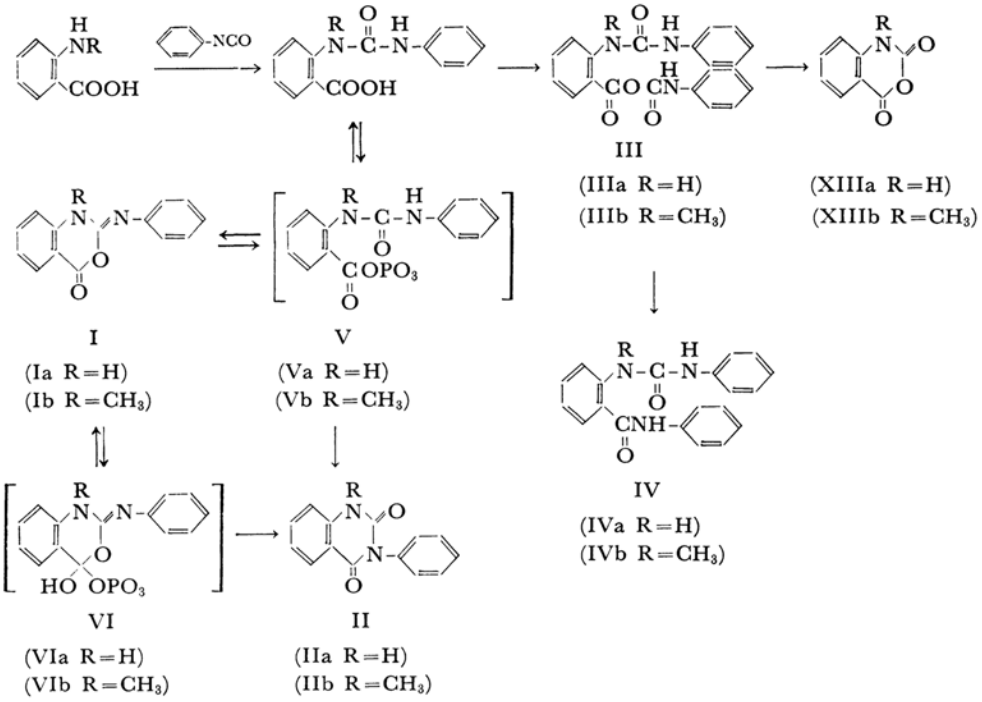
2) M. Kurihara and N. Yoda, *Tetrahedron Letters*, **1965**, 2597.

3) a) For a recent review with references, see J. P. Marthe and S. Munavalli, *Bull. soc. chim. France*, **1963**, 2679. b) F. Uhlig and H. R. Snyder, "Advances in Organic Chemistry," Vol. I, Ed. by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, New York, N. Y. (1960), p. 35.

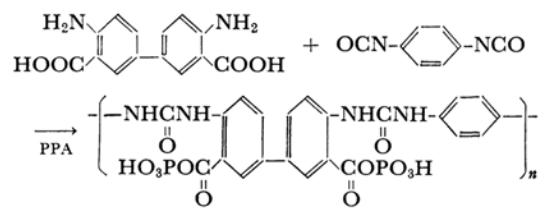
4) D. M. Brown, "Advances in Organic Chemistry," Vol. III, Ed. by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, New York, N. Y. (1963), p. 75.

5) N. Yoda, R. Nakanishi, M. Kurihara, Y. Bamba, S. Tohyama and K. Ikeda, *J. Polymer Sci.*, **B4**, 11 (1966).

6) A mixture of phosphoric acid and phosphorus pentoxide, hereinafter referred to as PPA. A chemically pure-grade reagent, PPA(P_2O_5 content; 84%), of Nippon Kagaku Kogyo, Ltd., was used.



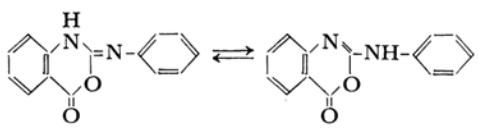
from chloroform), possibly through a phosphorylated reaction intermediate V. The OPO_3 fragment represents the phosphoric acid moiety, which is of an indefinite composition. A similar compound of phosphoric-carboxylic mixed anhydride was recently prepared by the reaction of silver dibenzyl phosphate with an alkyl chloroformate.[7] Conversion is effected by the treatment of Ia with PPA at 150°C for 1 hr.; this results in the formation of 3-phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (IIa) (m. p. 281°C from ethanol) in an 80% yield.[8] The presumed reaction intermediate VIa is formed by the phosphorylation of the carbonyl group of benzoxazinone (Ia) in PPA, followed by ring opening to Va and recyclization, thus yielding quinazolinedione (IIa) by losing the polyphosphoric acid species. The direct cyclodehydration of *N*-(phenylcarbamoyl)-anthranilic acid is also effected by treatment with PPA at 150°C for 5 hr., thus affording quinazolinedione (IIa). When anthranilic acid was treated with an excess amount of phenyl isocyanate in bulk, 2-(phenylcarbamoyl)-carbanilide (IVa) was obtained quantitatively.[2,8d] The phosphorylation mechanism is supported by the experimental evidence of the polymerization reaction of 4, 4'-diamino-biphenyl-3, 3'-dicarboxylic acid with phenyl diisocyanate in PPA and by the successful isolation of the corresponding *phosphoric-carboxylic anhydride of polyurea acid*. The structure was determined by analyses of the phosphorus content by means of both colorimetry and emission X-ray measurements.



(2)

For a detailed account of the polymerization mechanism and a characterization of the resulting polymer of phosphoric-carboxylic anhydride, see another article.[5]

The tautomeric structure of benzoxazinone (I) is expressed in the following equation:

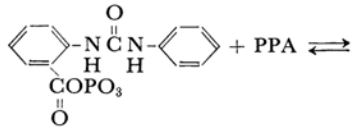


(3)

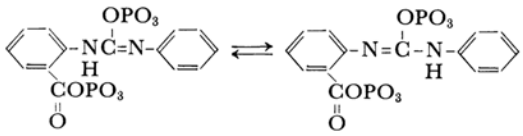
It is also possible that the phosphorylated reaction intermediate (Va) exists in the following tautomeric forms:

7) D. L. Griffith and M. Stiles, *J. Am. Chem. Soc.*, **87**, 3710 (1965).

8) During the progress of this investigation, similar results have been obtained in different systems, such as in an alkaline solution or in a 10% sulfuric acid solution. a) G. Doleschall and K. Lempert, *Tetrahedron Letters*, **1963**, 1195. b) K. Lempert and G. Doleschall, *Monatsh. Chem.*, **95**, 950 (1964). c) G. Doleschall and K. Lempert, *Monatsh. Chem.*, **95**, 1068 (1964). d) J. C. Sheehan and G. D. Daves, Jr., *J. Org. Chem.*, **29**, 3599 (1964). e) H. Herlinger, *Angew. Chem.*, **76**, 437 (1964).



Va



Va′ Va″

The infrared spectrum of I exhibits characteristic absorption bands of the carbonyl group at $\nu_{C=O}$ 1747 cm^{-1} and of the C=N double bond at $\nu_{C=N}$ 1644 cm^{-1} as is shown in Figs. 1 and 2. The ratios

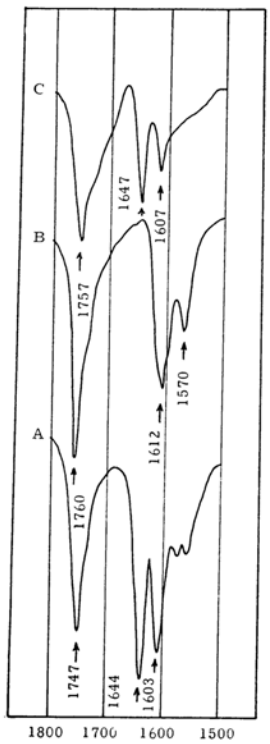


Fig. 1. Infrared spectra of benzoxazinone and related compounds (KBr).
(A) 1, 2-Dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one (Ia)
(B) 2-Phenyl-4*H*-3, 1-benzoxazin-4-one (VIII)
(C) 2-Methyl-4*H*-3, 1-benzoxazin-4-one (IX)[9]

of the extinction coefficients of the C=O absorption (ε_2) and C=N absorption (ε_1) are compared in various systems. The value in Ia is found to be $\varepsilon_2/\varepsilon_1=1.34$. In such compounds as 2-phenyl-4*H*-3, 1-benzoxazin-4-one (VII) and 2-methyl-4*H*-3, 1-benzoxazin-4-one (IX), the C=N double bond

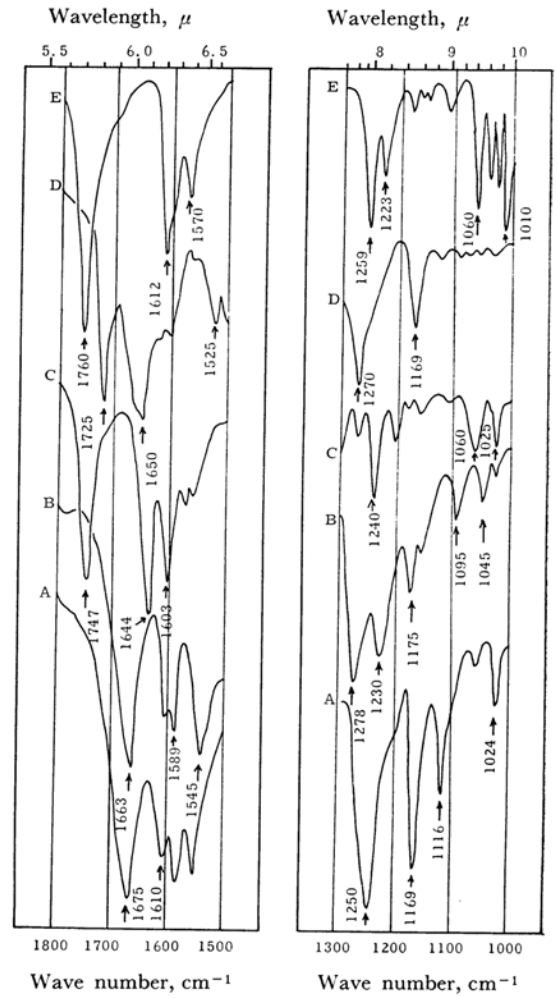


Fig. 2. Infrared spectra of quinazolinedione and related compounds (KBr).
(A) Anthranilic acid
(B) *N*-(Phenylcarbamoyl)-anthranilic acid[10]
(C) 1, 2-Dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one (Ia)
(D) 3-Phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (IIa)[10]
(E) 2-Phenyl-4*H*-3, 1-benzoxazin-4-one (VIII)[11]

is endocyclic and the ratio of the ε values of the C=O and C=N absorptions are found to be $\varepsilon_2/\varepsilon_1=0.45$ and 0.82 respectively. It is clearly shown that the relative intensity of the C=N stretching vibration of Ia at 1644 cm^{-1}, is fairly strong as compared with the intensities of VIII and IX.[12] It has also been found that the

9) M. T. Bogert and H. M. Seil, *J. Am. Chem. Soc.*, **29**, 517 (1907).
10) C. Paal, *Ber.*, **27**, 977 (1894).
11) a) R. Anschutz and O. Schmidt, ibid., **35**, 3483 (1902). b) R. Snyder and R. H. Levine, *J. Am. Chem. Soc.*, **60**, 2025 (1938).
12) J. Fabian and M. Legrand, *Bull. soc. chim. France*, **1956**, 1461.

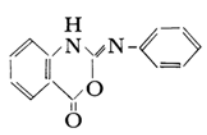
Table I. Ultraviolet absorption characteristics of benzoxazinone and related compounds

Compound	UV λ_{max} mμ [lit.]	Ext. coef. ε	log. ε
N-(Phenylcarbamoyl)-anthranilic acid	(1) 265[267][13,c]	37500	4.57[4.4][13,c]
	(2) 306[308][13,c]	9149	3.96[3.75][13,c]
1,2-Dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one (Ia)	(1) 244[c]	8160	3.91
	(2) 282	9200	3.96
	(3) 292[c]	8600	3.93
	(4) 332	2665	3.42
3-Phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (IIa)	(1) 243[13][247][c]	11220	4.05[4.05][13,c]
	(2) 312[13][313][c]	3490	3.53[3.52][13,c]
2-(Phenylcarbamoyl)-carbanilide (IVa)	(1) 264[14][264]	34100	4.53[4.55][14]
	(2) 306[14][306]	9800	3.99[4.00][14]
2-Phenyl-4*H*-3, 1-benzoxazin-4-one (VIII)	(1) 241	22220	4.35
	(2) 275(sh)	16400	4.21
	(3) 285	21430	4.33
	(4) 298	19740	4.29
	(5) 321	11600	4.06
N-Dibenzylmethylene-2-phenylenediamine (X)	(1) 244[15]		3.83[15]
	(2) 275[15]		3.95[15]
	(3) 282[15]		3.90[15]

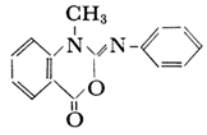
a) 99.5% ethanol, b) methanol, c) 95% ethanol

carbonyl absorption of Ia shows a bathochromic shift of 13 cm^{-1} as compared with the carbonyl absorption of the endocyclic C=N structure (IX); it is presumed that the exocyclic C=N structure is resonance stabilized because of the hybridization of π-electron orbitals of the C=N double bond with the phenyl group. The apparent stability of *N*-phenyliminobenzoxazinone (Ia) by resonance stabilization is supported by the fact that *N*-phenyliminobenzoxazinone (Ia) was isolated as a crystalline solid, whereas *N*-methyl imino and *N*-ethylimino derivatives are not stable enough to be isolated at 40—80°C; their presence was detected by thin-layer chromatography and by a study of the infrared spectrum at lower temperatures. The infrared data of these compounds will be compared elsewhere.

The absorption characteristics and the intensities of the ultraviolet spectra of benzoxazinone (Ia) and related compounds are summarized in Table I. The C=N double bond exhibits two characteristic absorption maxima in the 275—295 mμ range. The endocyclic C=N double bond of the VIII structure shows characteristic peaks at 285 and 298 mμ, and the Schiff base, *N*-benzylmethylene-2-phenylenediamine (X) has two characteristic C=N absorptions, at 275 and 282 mμ.[15] In the spectrum of benzoxazinone (Ia), characteristic maxima of the C=N bond are found at 282 mμ (9200) and 292 mμ (8600). Although the model compounds described in Table I, Fig. 1 and Fig. 2 may not represent exactly the fine structure of Ia, conclusive evidence was obtained by the direct comparison of the characteristic absorption bands of the infrared and ultraviolet spectra of Ia with those of Ib; these peaks of the C=N bond may be assigned to the exocyclic C=N bond on the basis of both the spectral comparison and the chemical reactivity of the compound Ia towards phenyl isocyanate.



(Ia)



(Ib)

They show a bathochromic effect in the following increasing order (as is shown in Table I, the hyperchromic effect was observed in the same order):

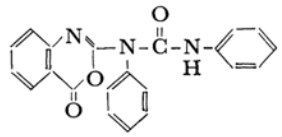
noncyclic C=N < exocyclic C=N < endocyclic C=N

These effects are in good agreement with the results on the infrared spectral characteristics, and a tautomeric structure Ia was assigned to iminobenzoxazinone. In the exocyclic iminobenzoxazinone (Ia), the C=N double bond is conjugated not only with the benzene ring but also with the benzoxazinone ring through unshared electrons of ester oxygen and the carbonyl group; this may explain the apparent stability of Ia relative to the other tautomeric structure Ia'.

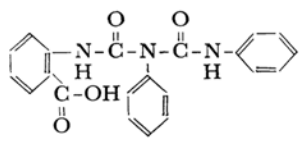
13) P. Grammaticakis, *Compt. rend.*, **247**, 2013 (1958).
14) P. Grammaticakis, *Bull. soc. chim. France*, **1962**, 487.
15) R. C. Elderfield and V. B. Meyer, *J. Am. Chem. Soc.*, **76**, 1887 (1954).

When *N*-methylanthranilic acid is treated with an equimolar amount of phenyl isocyanate, exocyclic iminobenzoxazinone (Ib) is the only possible product. It was found that it undergoes molecular rearrangement to form a thermodynamically-controlled product, 1-methyl-3-phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (IIb), together with 1-methylisatoic anhydride (XIIIb) (m. p. 164—166°C) and *N*-methyl-2(phenylcarbamoyl)-carbanilide (IVb) (m. p. 252—253°C).

The treatment of exocyclic iminobenzoxazinone (I) with phenyl isocyanate failed to produce either 2-(phenylcarbamoyl)-phenylamino-4*H*-3, 1-benzoxazin-4-one (XI) or the other possible product (XII).

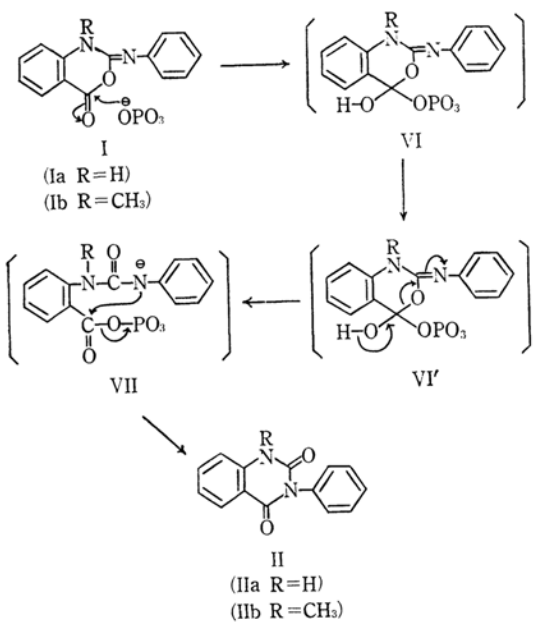


(XI)



(XII)

A possible mechanism for the molecular rearrangement of iminobenzoxazinone (I) to quinazolinedione (II) in PPA involves the phosphorylated intermediates VI and VII; it is shown in the following scheme (2), which is based on the experimental evidence of the phosphoric-carboxylic mixed anhydride of polyurea acid.[1,4]



I
(Ia R=H)
(Ib R=CH_3)

VI

VII

VI′

II
(IIa R=H)
(IIb R=CH_3)

When I is treated with PPA at 150°C, the carbonyl group of benzoxazinone I is phosphorylated to form the reaction intermediate VI, followed by ring opening to form the mixed anhydride of carboxylic acid and phosphoric acid VII. The anion of ureido nitrogen attacks the carbonyl group of the mixed anhydride to cleave the phosphoric acid species. Recyclization is completed by quinazolinedione ring fromation II. A similar mechanism has been suggested for the hydrolysis of salicylphosphate, which involves the formation of a cyclic transition state.[16]

Experimental[17]

The Preparation of *N*-(Phenylcarbamoyl)-anthranilic Acid.—A 3.5 g. portion (0.03 mol.) of phenyl isocyanate was dissolved in 20 ml. of benzene. The solution was then gradually added into 40 mol. of a benzene solution containing 2.74 g. (0.01 mol.) of anthranilic acid at 50°C. After the mixture had been heated under reflux at 80°C for 1 hr., the precipitate was filtered and washed several times with benzene. Recrystallization from ethanol yielded needles which melted at 185—186°C (lit.[10] m. p. 183°C). The yield was 4.97 g. (97%). The infrared spectrum (KBr) shows a band at 3320 cm^{-1} (N-H stretching). The carbonyl stretching bands fall at 1675 cm^{-1} (carboxyl) and at 1663 cm^{-1} (ureido carbonyl).

Ultraviolet spectrum: λ_{max} 265 mμ (ε, 37500); 306 mμ (ε, 9149).

Found: C, 65.70; H, 4.72; N, 10.93. Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.62; H, 4.72; N, 10.93%.

The Preparation of 3-Phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (IIa). — A mixture of 3.00 g. (0.0117 mol.) of *N*-(phenylcarbamoyl)-anthranilic acid and 200 g. of PPA was placed in a three-necked flask fitted with a mechanical stirrer. The mixture was heated at 150°C for 5 hr., and the resulting solution was poured into 300 ml. of distilled water. The precipitate was filtered off and washed twice with a dilute aqueous sodium carbonate solution. Then it was washed thoroughly with water and dried. The yield was 2.38 g. (100%). It was recrystallized from ethanol to obtain needles, m. p. 280°C (lit.[10] 280°C). The infrared spectrum (KBr) showed bands at 3200 cm^{-1} (bonded N–H), 1725 cm^{-1} (4-carbonyl), 1650 cm^{-1} (2-carbonyl) and 1600 cm^{-1} (phenyl). The ultraviolet spectrum exhibited absorption maxima at λ_{max} 243 mμ (ε, 11200) and 312 mμ (ε, 3490).

Found: C, 70.33; H, 4.38; N, 11.76; mol. wt.,

16) J. D. Chanley, E. M. Gindler and H. Sobotka, *J. Am. Chem. Soc.*, **74**, 4347 (1952).

17) All the melting points were taken on a Büchi Melting Point Apparatus and are uncorrected. The microanalyses were carried out by the Microanalytical Section of these laboratories. The infrared spectal were recorded with Perkin-Elmer (Model 125) and Hitachi (Model EPI-S) recording spectrophotometers, using a potassium bromide disk or Nujol. The ultraviolet spectra were recorded with a Cary Model 14 recording spectrophotometer in ethanol. The molecular weights were determined with a Mechrolab Model 310A vapor pressure osmometer in benzene and ethyl methyl ketone.

241. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.58; H, 4.23; N, 11.48%; mol. wt., 238.

The Preparation of 1, 2-Dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one (Ia).—A 0.300 g. portion (0.00117 mol.) of *N*-(phenylcarbamoyl)-anthranilic acid was added to 20 g. of PPA, and then the mixture was heated at 80—100°C for 1 hr., and after the reaction, poured into 100 ml. of distilled water. It was then filtered, and washed with a 10% aqueous sodium caraonate solution and distilled water successively. Several recrystallizations from chloroform yielded needles, m. p. 193°C (lit.[8a,d,e] 192—193°C), in a 95% yield. The infrared spectrum (Nujol) shows absorption bands at 3300 cm^{-1} (N–H), 1747 cm^{-1} (lactone carbonyl), 1650 cm^{-1} (>C=N–) and 1240 cm^{-1} and 1060 cm^{-1} (C–O–C). The ultraviolet spectrum had absorption maxima at λ_{max} 244 mμ (ε, 8160), 282 mμ (ε, 9200), 292 mμ (ε, 8600) and 332 mμ (ε, 2665).

Found: C, 70.28; H, 4.25; N, 11.25; mol. wt., 237. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.58; H, 4.28; N, 11.48%; mol. wt., 238.

The Intramolecular Rearrangement of 1, 2-Dihydro-2-phenylimino-4*H*-3, 1-benzoxazin-4-one (Ia) to 3-Phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (IIa).—A mixture of 0.200 g. (0.0084 mol.) of I and 20.0 g. of PPA was heated at 150°C for 5 hr. It was then poured into 100 ml. of distilled water, and the resulting precipitate was filtered and washed with a 10% aqueous sodium carbonate solution. It was then washed thoroughly with distilled water and dried. The yield was 0.140 g. (70%). It was recrystallized from ethanol to obtain colorless needles, m. p. 282°C. It was identified by a comparison of its infrared spectrum (KBr) with that of II prepared directly from *N*-(phenylcarbamoyl)-anthranilic acid in PPA. The infrared bands at 1240 cm^{-1} (-N=C–O–C-) and 1060 cm^{-1} (-C–O–C-) disappeared.

The Preparation of 2-Phenyl-4*H*-3, 1-benzoxazin-4-one (VIII).—A mixture of 3.40 g. (0.025 mol.) of anthranilic acid and 3.5 g. (0.025 mol.) of benzoyl chloride was dissolved into 115 g. of PPA; the solution was heated at 120 to 140°C for 12 hr., and then heated for 0.5 hr. It was then poured directly into 300 ml. of distilled water; the precipitate was filtered and washed thoroughly with distilled water to afford the product in a 99% yield. The product was recrystallized from ethanol to obtain colorless needles. It has a m. p. of 130.0—130.5°C. The infrared spectrum (KBr) shows carbonyl bands at 1760 cm^{-1} and 1060 cm^{-1} (C–O–C). The ultraviolet spectrum has bands at λ_{max} 241 mμ (ε, 22220), 275 mμ (ε, 16400) (shoulder), 285 mμ (ε, 21430), 298 mμ (ε, 19740) and 321 mμ (ε, 11600).

Found: C, 75.15; H, 4.03; N, 6.21; mol. wt., 230. Calcd. for $C_{14}H_9O_2N$: C, 75.32; H, 4.06; N, 6.28%; mol. wt., 223.

The Phosphorylated Intermediate of 4, 4'-Diamino-biphenyl-3, 3'-dicarboxylic Acid (BDC) with Phenyl Diisocyanate in PPA.—A 2.72 g. portion of purified BDC (0.01 mol.) and a 1.60 g. portion of phenyl diisocyanate (0.01 mol.) were dissolved in a 86 g. portion of PPA with vigorous mechanical stirring; the polymerization vessel was then heated at 90—100°C for 1 hr. After the completion of the reaction, the resulting polymer solution was poured into 300 g. of ice water and the precipitated polymer was filtered. It was washed several times with 50 ml. each of distilled water, and dried under a vacuum at 60°C. The phosphoric-carbonic anhydride of polyurea acid was obtained in 92% yield. The m. p. was above 350°C; the inherent viscosity measured in a 0.5% concentration at 25°C in concentrated sulfuric acid was found to be $\eta_{inh}=1.01$.

Found: C, 45.11; H, 2.82; N, 9.45; P*, 10.86. Calcd. for $(C_{22}H_{16}O_{12}N_4P_2)_n$: C, 44.79; H, 2.74; N, 9.50; P, 10.50%.

The Preparation of 2-Methyl-4*H*-3, 1-benzoxazin-4-one (IX).—A mixture of 2.74 g. (0.01 mol.) of anthranilic acid and 60 ml. of acetic anhydride was heated at 120°C under reflux for 5 hr. The solvent was then removed under reduced pressure, and the residue was recrystallized from petroleum ether to obtain colorless needles, m. p. 86—88°C (lit.[9] 80—81°C), in a 90% yield (3.45 g.).

The infrared spectrum (KBr) shows absorption band at 1757 cm^{-1} (carbonyl), 1647 (>C=N–), 1268 cm^{-1}, and 1054 cm^{-1} (=C–O–C).

The ultraviolet spectrum exhibits absorption maxima at λ_{max} 249 mμ (ε, 7160), 306 mμ (ε, 2900), and 315 mμ (ε, 2660).

Found: C, 67.15; H, 4.45; N, 8.70; mol. wt., 168. Calcd. for $C_9H_7O_2N$: C, 67.07; H, 4.38; N, 8.09%; mol. wt., 168.

The Reaction of *N*-Methylanthranilic Acid with Phenyl Isocyanate A).—A 3.02 g. (0.02 mol.) portion of *N*-methyl anthranilic acid (m. p. 186—187°C, recrystallized from aqueous ethanol) was dissolved into 100 ml. of benzene at 60°C for 20 min. To this solution there was they added a 2.38 g. (0.02 mol.) portion of phenyl isocyanate (b. p. 46—47°C/7 mmHg) in 10 ml. of benzene, and the mixture was refluxed at 80°C for 2.5 hr. After the mixture had been allowed to cool at room temperature, the precipitate was filtered, washed several times with distilled water, and dried. It was then recrystallized twice from ethyl acetate to obtain colorless needles in a 43% yield. M. p. 252—253°C. It was identified as *N*-methyl-2-(phenylcarbamoyl)carbanilide by a study of its infrared spectrum and by elemental analysis.

The infrared spectrum (KBr) shows absrotpion bands at 3300 cm^{-1} (N–H), and 1650 cm^{-1} (amide carbonyl). Ultraviolet spectrum: λ_{max} 210 mμ (ε, 29200), 257 mμ (ε, 33600).

Found: C, 73.49; H, 5.71; N, 12.60. Calcd. for $C_{21}H_{19}O_2N_3$: C, 73.02; H, 5.55; N, 12.17%.

The filtrate of the benzene solution was refluxed further at 80°C for 5 hr., and the benzene was removed under a vacuum to afford a cyclized reaction product. After recrystallization from a chloroform/cyclohexene (1 : 1) solution, colorless needles were obtained in 41% yield. M. p. 164—166°C. The product was found to be 1-methylisatoic anhydride by elemental analysis and by a study of its infrared spectrum. The infrared spectrum (KBr) shows absorption bands at 1770 cm^{-1} (carbonyl), 1720 cm^{-1} (carbonyl) and 1605 cm^{-1}.

The ultraviolet spectrum has bands at λ_{max} 223 mμ (ε, 49400), 248 mμ (ε, 17800), 252 mμ (ε, 17900), and 315 mμ (ε, 2730).

Found: C, 61.44; H, 4.40; N, 8.10; mol. wt., 177.

* The phosphorus was determined by colorimetry analysis with ammonium metavanadate and ammonium molybdate, and by emission X-ray analysis.

Calcd. for $C_9H_7O_3N$: C, 61.01; H. 3.98; N, 7.91%; mol. wt., 181.

B)—The reaction was carried out in tetrahydrofuran instead of benzene at −2°C for 1 hr., at 10°C for 1 hr., and at 20°C for 1 hr. successively. The solvent was then removed under a vacuum at 60°C, and the residue was extracted with 200 ml. of a 10% aqueous sodium carbonate solution. The product was precipitated by acidifying the solution with 12% hydrochloric acid. When the product was recrystallized from a chloroform/cyclohexane (1:1) solution, colorless needles were obtained in a 59.5% yield. M. p. 231—322°C. It was identified as 1-methyl-3-phenyl-2, 4(1*H*, 3*H*)-quinazolinedione (lit.[18] 229—230°C).

The infrared spectrum (KBr) shows characteristic carbonyl absorption bands of quinazoline-dione at 1706 cm^{-1}, 1680 cm^{-1}, 1658 cm^{-1} and 1610 cm^{-1}. The ultraviolet spectrum has absorption maxima at λ_{max} 245 mμ (ε, 5540) and 270 mμ (ε, 756).

Found: C, 71.08; H, 4.87; N, 10.80. Calcd. for $C_{15}H_{12}O_2N_2$: C, 71.41; H, 4.80; N, 11.11%.

The neutral fraction of the tetrahydrofuran solution was extracted with benzene, and a crystalline solid was obtained in a 14.5% yield; this was indentified as *N*-phenyl-2-(phenylcarbamoyl)carbanilide (m. p. 252—253°C) by a comparison of its infrared spectrum with that of an authentic sample and it was found to have no melting point depression on admixture.

The Attempted Cyclization of *N*-Phenyl-2-(phenylcarbamoyl)carbanilide with Polyphosphoric Acid.—A 1.0 g. portion of *N*-phenyl-2-(phenylcarbamoyl)carbanilide was added to 60 g. of polyphosphoric acid, and the mixture was heated at 140—150°C for 5 hr. After the reaction, the mixture was poured into 100 ml. of distilled water, washed with 50 ml. of 5% aqueous sodium carbonate, and filtered. The starting material was thus recovered almost quantitatively, m. p. 249—250°C.

Found: C, 73.44; H, 5.15; N, 12.50. Calcd. for $C_{21}H_{19}O_2N_3$: C, 73.02; H, 5.55; N, 12.17%.

The authors gratefully acknowledge the interest and encouragement of Drs. Toshio Hoshino and Ryoji Nakanishi of the Basic Research Laboratories, Toyo Rayon Company, Ltd. The authors are also indebted to Mr. Yasuyuki Ebata and his staff for their microanalyses, and Mr. Toshio Mizushima for his emission X-ray analysis.

18) C. M. Lee, *J. Heterocyclic Chem.*, **1**, 235 (1965).