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MOLECULAR REARRANGEMENT IN POLYPHOSPHORIC ACID

I. FORMATION OF 1, 2-DIHYDRO-2-PHENYLIMINO-4H-3, 1-BENZOXAZIN-4-ONE AND REARRANGEMENT TO 3-phenyl-2, 4 (1H, 3H)-QUINAZOLINEDIONE IN POLYPHOSPHORIC ACID.*

Masaru Kurihara and Naoya Yoda
Basic Research Laboratories, Toyo Rayon Company, Ltd.
Kamakura, Japan

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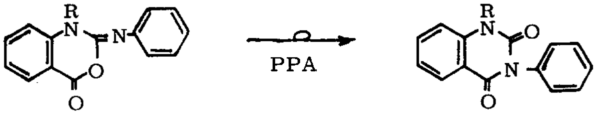
Although the area of molecular rearrangement in polyphosphoric acid has been extensively explored in recent years[1], to date no example of 1, 2-dihydro-2-phenylimino-4H-3, 1-benzoxazin-4-one (I) to 3-phenyl-2, 4 (1 H, 3 H)-quinazolinedione in polyphosphoric acid** has been reported.



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

II
(II a R = H)
(II b R = CH_3)

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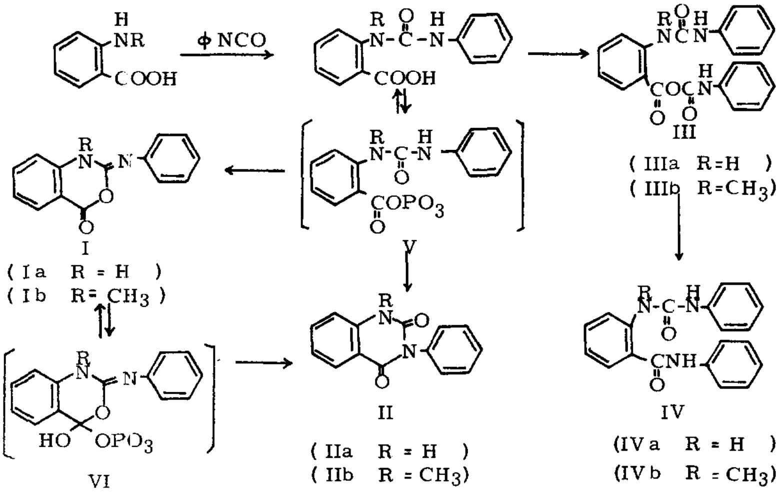
[*] N. Yoda and M. Kurihara , presented in part at the 13th Meeting of the High Polymer Symposium of Japan, Tokyo, November, 1964, and at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965 .

[**] A mixture of phosphoric acid and phosphorus pentoxide, hereinafter referred to as PPA. Chemically Pure Grade reagent PPA (P_2O_5 content ; 84%) of Nippon Kagaku Kogyo Ltd. was used.

This type of rearrangement in PPA would be especially notable because a possible mechanism for the cyclodehydration in PPA of N-(phenylcarbamoyl) anthranilic acid prepared by the reaction of equimolar amount of anthranilic acid with phenyl isocyanate involves phosphorylated reaction intermediates[2], and the reaction in PPA afforded the kinetically controlled product (I), exocyclic iminobenzoxazinone, which was originally isolated unknown material, and the thermodynamically controlled product (II), quinazolinedione depending on the reaction temperatures. Since the literature failed to disclose the compound (I), an investigation of the reaction in PPA was undertaken in connection with the solution polymerization in PPA of 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid with diisocyanate by cyclopolycondensation reactions[3].

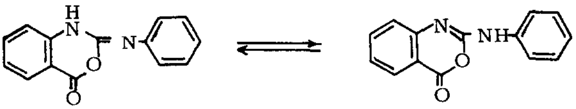
The method of synthesis of benzoxazinone (I), quinazolinedione (II) and related compounds is outlined in Scheme 1.



When N-(phenylcarbamoyl) anthranilic acid (m.p. 186°C ; from ethanol) is treated with PPA at 80 - 100°C. for 1 hr. cyclodehydration occurs to yield quantitatively 1, 2-dihydro-2-phenylimino-4H-3, 1-benzoxazin-4-one (I a) (m.p. 193°C ; from chloroform) through phosphorylated reaction intermediate (Va). The OPO_3 fragment represents the phosphoric acid moiety of indifinite composition. Molecular rearrangement is effected by the treatment of (Ia) with PPA at 150°C. for 1 hr., and it results in the formation of 3-phenyl-2, 4 (1H, 3H)-quinazolinedione (IIa) (m.p. 281 °C. from ethanol) in 80% yields. The reaction intermediate (VI$_a$) is formed by phosphorylation of carbonyl group of benzoxazinone (Ia) in PPA, followed by ring opening and recyclization to yield quinazolinedione (IIa) by losing the polyphosphoric acid species. The direct cyclodehydration of N-(phenylcarbamoyl) anthranilic acid is also effected by the treatment with PPA at 150°C. for 5 hr. to afford quinazolinedione (IIa). When anthranilic acid was treated with excess amount of phenyl isocyanate in bulk, 2-(phenylcarbamoyl) carbanilide (IVa) was obtained quantitatively.

The spectral and physical properties of the reaction products are summarized in Table I.

The structure of benzoxazinone (Ia) was identified as 1, 2-dihydro-2-phenylimino-4H, 3, 1-benzoxazin-4-one (Ia) based on the experimental



Ia Ia'

TABLE I

Spectral and Physical Properties of N-(Phenylcarbamoyl)-anthranilic Acid, Benzoxazinone (Ia), Quinazolinedione (IIa) and Related Compounds

Compounds	M.P. [lit.] (°C)	I.R. (cm^{-1})	Mol. Wt. [Calc.]	Elemental Analyses
N-(phenylcarbamoyl) anthranilic acid	186[183]6)	3320 1675 1663	255 [250][a]	C; C 65.62, H 4.72, N 10.93 F; C 65.72, H 4.72, N 10.89
1, 2-dihydro-2-phenylimino-4H-3, 1-benzoxazin-4-one (Ia)	193[192-3]4)	3300 1747 1644 1240 1060	237 [238][b]	C; C 70.58, H 4.23, N 11.48 F; C 70.28, H 4.25, N 11.25
3-phenyl-2, 4(1H, 3H)-quinazolinedion (II a)	284[280]6)	3200 1725 1650	241 [238][b]	C; C 70.58, H 4.23, N 11.48 F; C 70.33, H 4.38, N 11.76
2-phenyl-4H-3, 1-benzoxazin-4-one (VIII)	130[123]11)	1760 1612 1259 1060	230 [223][c]	C; C 75.32, H 4.06, N 6.28 F; C 75.15, H 4.03, N 6.21
2-methyl-4H-3, 1-benzoxazin-4-one (IX)	86 - 88 [80-81]12)	1757 1647 1268 1054	168 [161][c]	C ; C 67.05, H 4.38, N 8.69 F; C 67.15, H 4.45, N 8.70

a) methayl ethyl ketone

b) benzene

c) ethanol

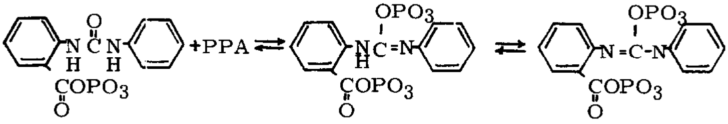
evidences obtained by comparison of infrared and ultraviolet spectra with model compounds and the chemical reactivity of the compound (I) towards phenyl isocyanate.

Infrared spectrum of (Ia) exhibits characteristic absorption bands of carbonyl group at $\nu_{C=O}$ 1747 cm^{-1} and C=N double bond at $\nu_{C=N}$ 1644 cm^{-1}. The ratio of extinction coefficients of C=O absorption (ε_1) and C=N absorption (ε_2) are compared in various systems.

This value in (Ia) is found to be $\varepsilon_2/\varepsilon_1 = 1.34$. In compounds such as 2-phenyl-4H-3,1-benzoxazin-4-one (VIII) and 2-methyl-4H-3,1-benzoxazin-4-one (IX), the C=N double bond is endocyclic and the ratio of ε values of C=O and C=N absorption are found to be $\varepsilon_2/\varepsilon_1 = 0.45$ and 0.82 respectively. It is clearly shown that the relative intensity of C=N stretching vibration of (Ia) at 1644 cm^{-1} is fairly strong as compared with the intensities of (VIII) and(IX), in which oxygen and nitrogen are attached to the double bond at carbon atom of C=N group. The endocyclic C=N double bond of structures (VIII) and IX) shows weaker absorption than carbonyl group, whereas in the exocyclic C=N double bond of structure (Ia), the intensity of the band at 1644 cm^{-1} is stonger than that of carbonyl absorption at 1747 cm^{-1}.

It was also found that the carbonyl absorption of (Ia) shows bathochromic shift of 13 cm^{-1} as compared with the carbonyl absorption of endocyclic C=N structure (IX), and it is presumed that the exocyclic C=N structure is resonance stabilized owing to the hybridization of π-electron orbitals of C=N double bond with phenyl group. The apparent stability of N-phenyl imino benzoxazinone (Ia) by resonance stabilization is supported by the fact that N-phenyl imino benzoxazinone (Ia) is isolated as a crystalline solid whereas N-methyl imino and N-ethyl imino derivatives are not stable enough to be isolated and only their presence are detected by thin layer chromatography4), 10).

Phosphorylated reaction intermediate (Va) exists in the following possible tautomeric forms.



Va Va' Va''

Since the structure of benzoxazinone exists as an exocyclic imino tautomer, a corresponding tautomer (I'a) is the stable tautomeric form based on the spectral and structural evidences for (Ia) and (I'a).

The absorption characteristics and intensities of ultraviolet spectra of benzoxazinone (Ia) and model compounds are summarized in Table II. The C=N double bond exhibits two characteristic absorption maxima in the range of 275 - 295 mμ. The endocyclic C=N double bond of structure (VIII) shows characteristic peaks at 285 and 298 mμ, and Schiff base (X) has two characteristic C=N- absorptions at 275 and 282 mμ. In the spectrum of benzoxazinone (Ia) characteristic maxima of C=N bond are found at 232 mμ (9, 200) and 292 mμ (8, 600). These peaks can be assigned to the exocyclic C=N double bond. They show bathochromic

TABLE II

Ultraviolet Absorption Characteristics of Benzoxazinone and Related Compounds

Compounds	U.V. λmax. (mμ) [lit.]	Ext. Coef. (ε)	log. ε
N-(phenylcarbamoyl) anthranilic acid	(1) $265^{8)}$[267]$^{c)}$	37,500	4.57 [4.4]$^{8)\,c)}$
	(2) $306^{8)}$[308]$^{c)}$	9,149	3.96 [3.75]$^{8)\,c)}$
1,2-dihydro-2-phenylimino-4H-3,1-benzoxazin-4-one (Ia)	(1) $244^{c)}$	8,160	3.91
	(2) 282	9,200	3.96
	(3) $292^{c)}$	8,600	3.93
	(4) 332	2,665	3.42
3-phenyl-2,4(1H,3H)-quinazolinedion (II a)	(1) $243^{8)}$[247]$^{c)}$	11,220	4.05[4.05]$^{8)c)}$
	(2) $312^{8)}$[313]$^{c)}$	3,490	3.53[3.52]$^{8)c)}$
2-(phenylcarbamoyl)carbanilide (IV a)	(1) $264^{9)}$[264]	34,100	4.53[4.55]$^{9)}$
	(2) $306^{9)}$[306]	9,800	3.99[4.00]$^{9)}$
2-phenyl-4H-3,1-benzoxazin-4-one (VIII)	(1) 241	22,220	4.35
	(2) 275 (sh)	16,400	4.21
	(3) 285	21,430	4.33
	(4) 298	19,740	4.29
	(5) 321	11,600	4.06
N-dibenzylmethylene-2-phenylenediamine (X)	(1) $244^{13)}$		$3.83^{13)}$
	(2) $275^{13)}$		$3.95^{13)}$
	(3) $282^{13)}$		$3.90^{13)}$

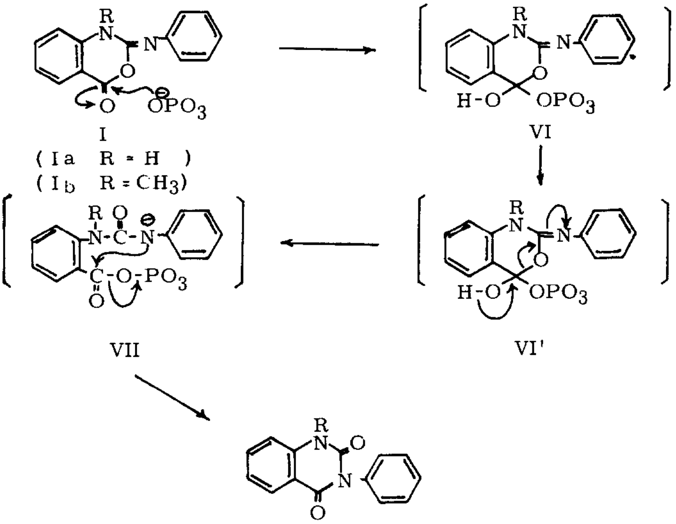
a) 99.5% ethanol, b) methanol, c) 95% ethanol effect in the following increasing order. As shown in Table II, the hyperchromic effect was also observed in the same order.

noncyclic $>C=N$ $<$ exocyclic $>C=N$ $<$ endocyclic $>C=N$

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

When N-methyl anthranilic acid is treated with equimolar amount of phenyl isocyanate, only exocyclic iminobenzoxazinone (I_b) is the possible product. It was found that it directly undergoes molecular rearrangement to form the thermodynamically controlled product, 1-methyl-3-phenyl-2, 4 (1H, 3H)-quinazolinedione (II_b) together with N-methyl-2-(phenylcarbamoyloxycarbonyl)-carbanilide (III_b) (m. p. 164 - 6°C. from chlororm and cyclohexane) and N-methyl-2-(phenylcarbamoyl) carbanilide (IV_b) (m. p. 252 - 3°C. from ethyl acetate). A possible mechanism for the molecular rearrangement of iminobenzoxazinone (I) to quinazolinedione (II) in PPA involves the phosphorylated intermediates (VI) and (VII) as shown in the following Scheme 2.

When (I) was treated with PPA at 150°C, carbonyl group of benzoxazinone (I) was phosphorylated to form the reaction intermediate (VI)



I

(Ia R = H)

(Ib R = CH_3)

VI

VI'

VII

II

(IIa R = H)

(IIb R = CH_3)

followed by ring opening to form mixed anhydride of carboxylic acid and phosphoric acid (VII). The anion of ureido nitrogen attacks carbonyl group of mixed anhydride to cleave phosphoric acid species. Recyclization is completed by quinazolinedione ring formation (II).

A detailed description of the experimental work, including the synthesis and infrared, ultraviolet and n.m.r. spectra of model compounds will appear in the complete article.

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