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Studies on Azole Compounds. V.[1] Reaction of 4-Phenyloxazole 3-Oxides with Arylisocyanates to give Imidazolino[4,5-*d*]-oxazolid-2-one Derivatives

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Reaction of 4-phenyloxazole 3-oxides (III) with arylisocyanates afforded imidazolin-[4,5-*d*]oxazolid-2-one derivatives (Vaa—Vbc). On pyrolysis of Vaa, Vab and Vba, a rearrangement of methyl group on the 5-position of imidazoline ring to yield imidazolinones (VIaa, VIab and VIba) was observed. When imidazolinones were treated with large excess of $NaBH_4$, reduction of ring amide group occurred.

Keywords——2,4-diaryl-5-methyloxazole 3-oxides; imidazolino[4,5-*d*]oxazolid-2-ones; 2-imidazolin-5-ones; rearrangement reaction of imidazolines; mass spectra; NMR

In the previous paper,[3] it has been reported that the reaction of 4-methyloxazole 3-oxides (I) with phenylisocyanate resulted in the formation of imidazole derivatives (II), as shown in Chart 1.

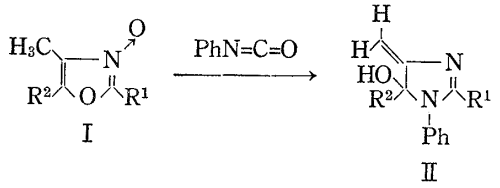
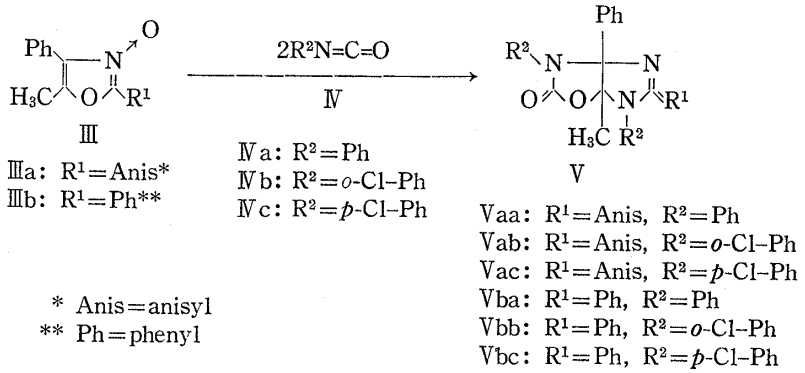


Chart 1

In an extension of the reaction to 4-phenyloxazole 3-oxides (III) with a variety of arylisocyanates (IV), we have encountered with formation of bicyclic compounds (V), totally different results from those with I and derivatives. We now wish to report the whole picture of the results and its reaction mechanism.



* Anis=anisyl
** Ph=phenyl

Chart 2

Addition of phenylisocyanate (IVa) into a chloroform solution of 2-anisyl-5-methyl-4-phenyloxazole 3-oxide (IIIa) at room temperature gave a crystalline substance $C_{30}H_{25}N_3O_3$ (Vaa). The compound is considerably stable to either acids or bases, and does not react with nucleophilic reagents such as aniline, morpholine, *etc.* Pyrolysis of the substance gave a compound of $C_{23}H_{20}N_2O_2$ (VIaa) with loss of phenylisocyanate, which was no longer convert-

1) Part IV: T. Matsuda, N. Honjo, M. Yamazaki, and Y. Goto, *Chem. Pharm. Bull.* (Tokyo), **25**, 3270 (1977).
2) Location: *Nanakuma, Nishi-ku, Fukuoka 814, Japan.*
3) Y. Goto, N. Honjo, and M. Yamazaki, *Chem. Pharm. Bull.* (Tokyo), **18**, 2000 (1970).

ed to starting material even on treatment with phenylisocyanate. VIaa was hydrolyzed with hydrochloric acid into *p*-methoxybenzoic acid and aniline. On hydrogenation of VIaa with large excess of sodium borohydride,[4] a crystalline substance $C_{23}H_{22}N_2O_2$ (VIIaa) was obtained,

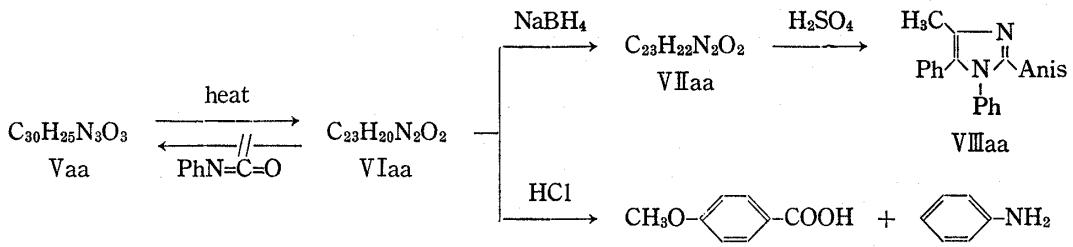


Chart 3

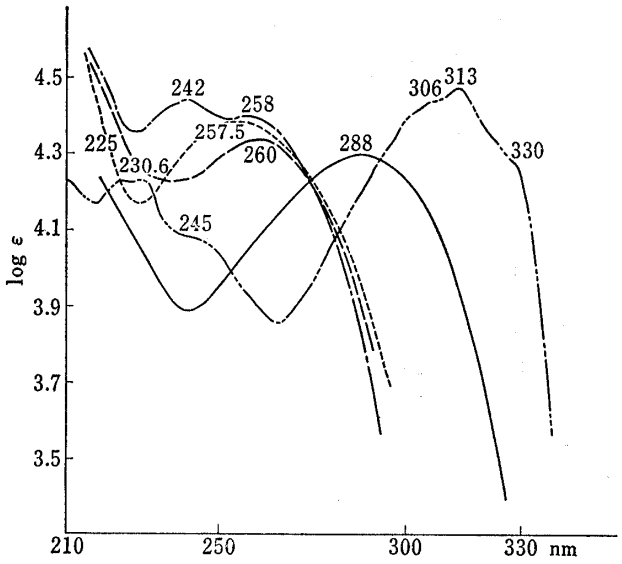


Fig. 1. UV Spectra of IIIa, Vaa, VIaa, VIIaa and VIIIaa in EtOH

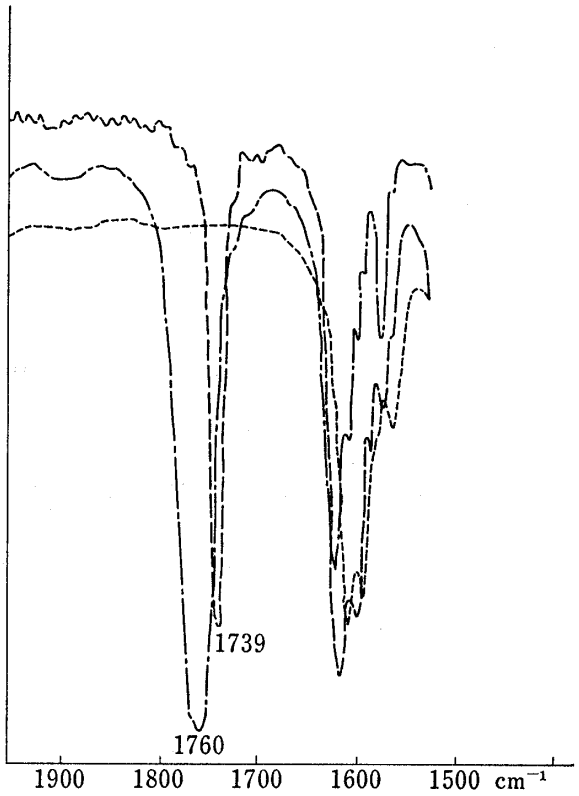
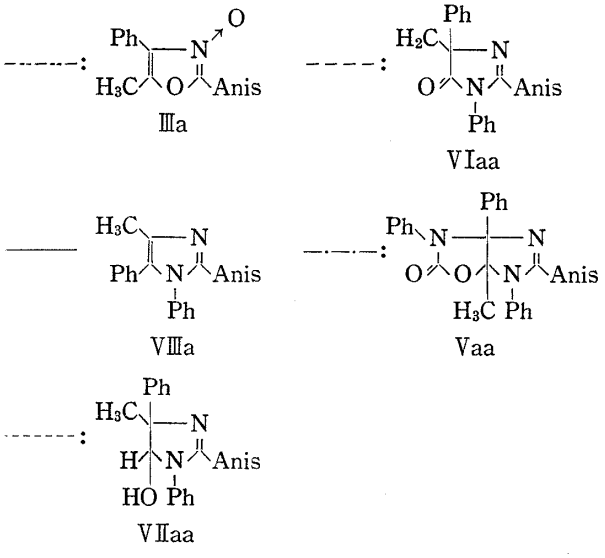
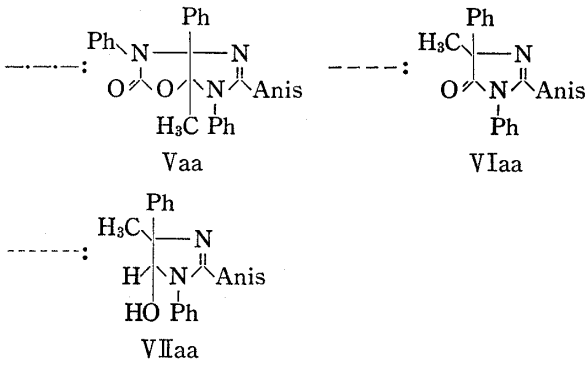


Fig. 2. IR Spectra of Vaa, VIaa, and VIIaa (KBr)





4) *a*) Z. Horii, C. Iwata, and Y. Tamura, *J. Org. Chem.*, **26**, 2273 (1961); *b*) S. Yamada, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 1083 (1970).

which on treatment with 50% sulfuric acid was converted easily into 2-anisyl-4-methyl-1, 5-diphenylimidazole (VIIIaa).[3]

As shown in Fig. 1, in the ultraviolet (UV) spectra of Vaa, VIaa, and VIIaa, the absorption due to a phenyloxazole ring disappears. The hydrogenated compound (VIIaa) consists of the mixture of two isomers due to the difference of the configuration of 4- and 5-positions. The ratio and the structures of these two isomers will be discussed later with the ^1H nuclear magnetic resonance (NMR) spectra of these compounds. The shape and the absorption maximum of the spectrum of VIIaa are very similar to those of 2-anisyl-5-hydroxy-4,5-dimethyl-1-phenyl-4,5-dihydroimidazole, which was already reported.[3]

In the infrared (IR) spectrum of Vaa (Fig. 2), the absorption due to the stretching vibration of a carbonyl group at 1760 cm^{-1} is observed, which is reasonable one of the carbonyl group of oxazolidone derivatives.[5] The absorption band at 1739 cm^{-1} of VIaa is considered

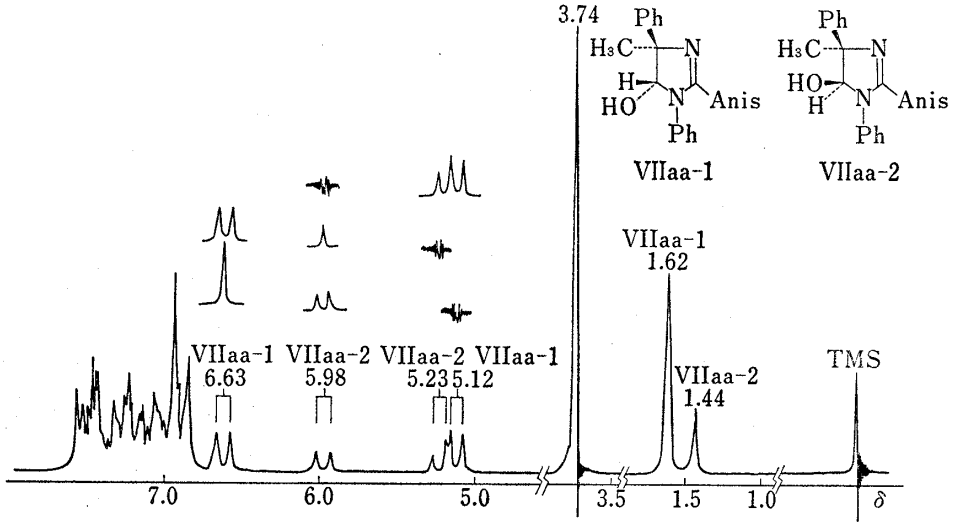


Fig. 3-A. ^1H NMR Spectrum of VIIaa at 35° in DMSO-d_6

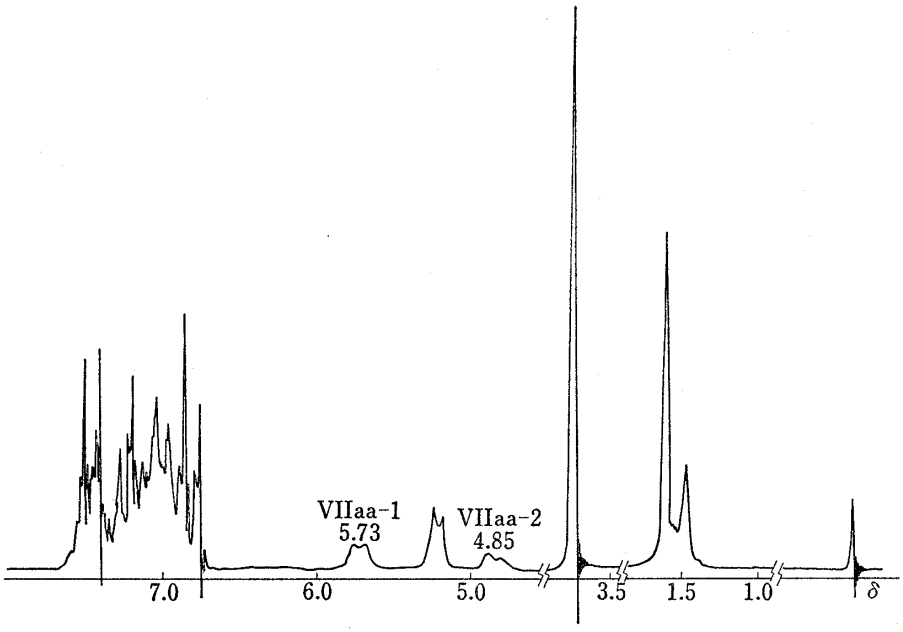


Fig. 3-B. ^1H NMR Spectrum of VIIaa at 180° in DMSO-d_6

5) S. Pinchas and D. Ben Ishai, *J. Am. Chem. Soc.*, **79**, 4099 (1957).

as the one arising from the carbonyl group of the amide of five membered ring, which disappears in the spectrum of VIIaa.

The ^1H NMR spectrum of VIIaa (the mixture of two isomers VIIaa-1 and VIIaa-2) in dimethyl-d_6-sulfoxide (DMSO-d_6) at 35° shows the characteristic signals, two doublets, arising from the secondary alcohol, *i.e.* δ 6.63 (3/4H, doublet, J=8 Hz, OH) and δ 5.98 (1/4H, doublet, J=8 Hz, OH) (Fig. 3-A). These signals and the signals at δ 5.12 and 5.23 are ascribed to the corresponding hydroxyl- and methine-protons of VIIaa-1 and VIIaa-2 by the method of double resonance respectively, which are shown in Fig. 3-A. The signal at δ 1.62 is attributable to the methyl protons of the structure of VIIaa-1 shown in Fig. 3-A, because it appears at lower field by the anisotropic effect of the hydroxyl group on the 5-position than that at δ 1.44 due to the methyl group of VIIaa-2. The signals due to the hydroxyl group of VIIaa shifted gradually to the higher field as temperature rises. When the spectrum was measured at 180°, it is observed in Fig. 3-B, that each signal due to the hydroxyl group shifted significantly to the higher field (OH of VIIaa-1: δ 5.73, OH of VIIaa-2: δ 4.85) and was broadened considerably. The ratio of VIIaa-1 and VIIaa-2 is 3:1 and the mixture of these compounds could not be separated.

The mass spectra of Vaa, VIaa, VIIaa and VIIIaa are shown in Fig. 4.[6] The mass spectrum of Vaa showed peaks at the following positions, *m/e* 475 (molecular ion), 431, 354,

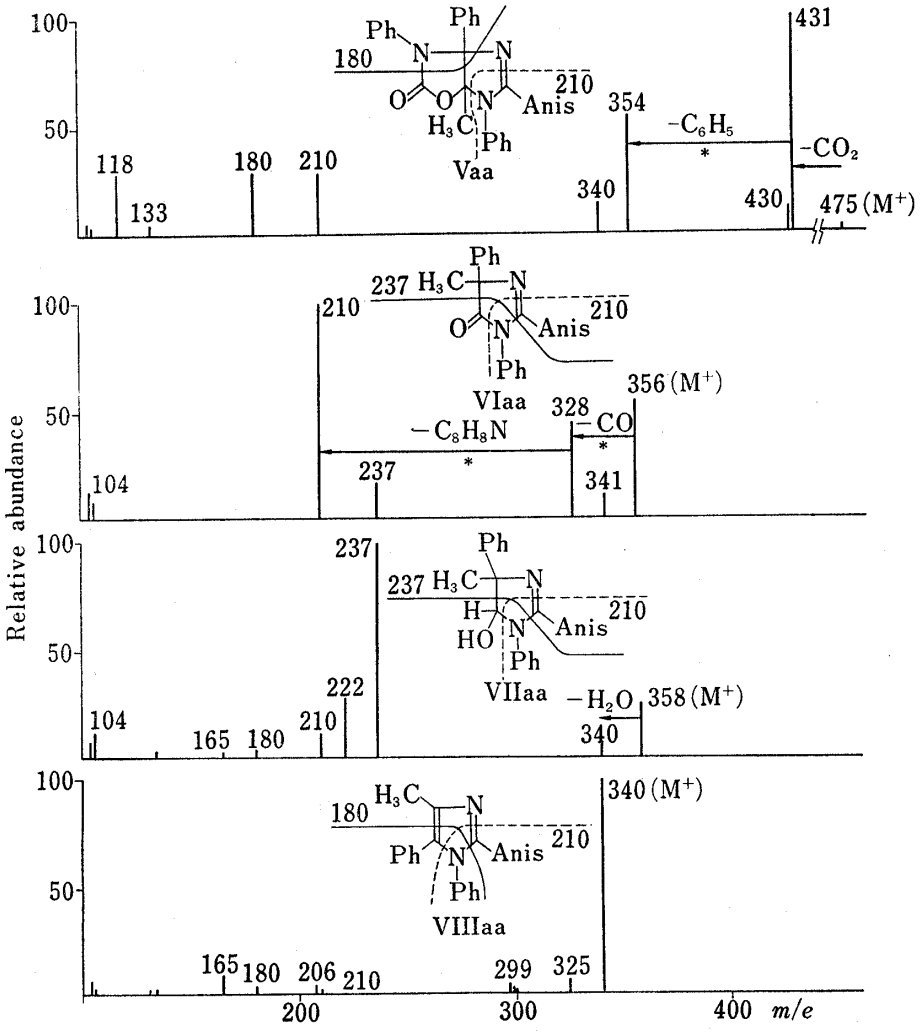


Fig. 4. Mass Spectra of Vaa, VIaa, VIIaa, and VIIIaa

6) All compositions of ions, being under discussion, were established by high resolution measurements.

340, 210, 180 and 118. The compound Vaa behaves as anticipated, in that elimination of carbon dioxide occurs from the molecular ion to furnish an ion of *m/e* 431, which dissociates further in two ways, firstly by loss of a phenyl radical to yield an ion of *m/e* 354 (metastable peak at *m/e* 290.8), and secondly by loss of C_6H_5N to give an ion *m/e* 340. The fragment

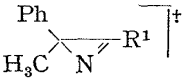
Table I. Mass Spectra of Vaa, Vab, Vac, Vba, Vbb, and Vbc

Compound No.		M	M-CO_2	M-CO_2-H	M-CO_2-C_6H_5	M-CO_2-H-ClC_6H_4	$R^2\overset{+}{N}\equiv CR^1$	$R^2\overset{+}{N}\equiv CPh$
Vaa	*m/e*	475	431	430	354		210	180
	Rel. Ab.[a]	2	100	12	54		28	30
Vab	*m/e*	544	500	499		388	244	214
	Rel. Ab.[a]	≪1	73	37		89	100	98
Vac	*m/e*	544	500	499		388	244	214
	Rel. Ab.[a]	≪1	34	100		46	90	98
Vba	*m/e*	445	401	400	324		180[b]	
	Rel. Ab.[a]	<1	100	20	52		77	
Vbb	*m/e*	514	470	469		358	214[b]	
	Rel. Ab.[a]	2	19	55		51	100	
Vbc	*m/e*	514	470	469		358	214[b]	
	Rel. Ab.[a]	≪1	45	100		4	27	

a) Rel. Ab.=relative abundance.

b) $R^2\overset{+}{N}\equiv CR^1$ can not be distinguished from $R^2\overset{+}{N}\equiv CPh$, because R^1 is phenyl group.

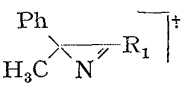
Table II. Mass Spectra of VIaa, VIab, VIba, and XII

Compound No.		M	M-CO		$R^2\overset{+}{N}\equiv CR^1$	$C_{13}H_9^{+}$[b]	$C_8H_8^{+}$
VIaa	*m/e*	356	328	237	210		104
	Rel. Ab.[a]	54	45	17	100		10
VIab	*m/e*	390	362	237	244	165	104
	Rel. Ab.[a]	66	55	24	100	7	50
VIba	*m/e*	326	298	207	180	165	104
	Rel. Ab.[a]	58	49	12	100	2	10
XII	*m/e*	398	360	269	180	165	
	Rel. Ab.[a]	28	37	12	100	22	

a) Rel. Ab.=relative abundance.

b) $C_{13}H_9^{+}$ is regarded as the fluorenyl ion. W.D. Crow, J.H. Hodgkin, and J.S. Shannon, *Aust. J. Chem.*, **18**, 1433 (1965).

Table III. Mass Spectra of VIIaa, VIIab, VIIba and XX

Compound No.		M	M-H_2O		$R_2\overset{+}{N}\equiv CR^1$	$C_{13}H_9^{+}$[b]	$C_8H_8^{+}$
VIIaa	*m/e*	358	340	237	210	165	104
	Rel. Ab.[a]	25	7	100	11	2	12
VIIab	*m/e*	392	374	237	244		104
	Rel. Ab.[a]	22	2	100	10		24
VIIba	*m/e*	328	310	207	180	165	104
	Rel. Ab.[a]	24	10	100	8	3	16
XX	*m/e*	390	372	269	180	165	
	Rel. Ab.[a]	12	14	100	4	49	

a) Rel.Ab.=relative abundance.

b) $C_{13}H_9^{+}$ is regarded as the fluorenyl ion.

Table IV. Mass Spectra of VIIIaa, VIIIab, and VIIIba

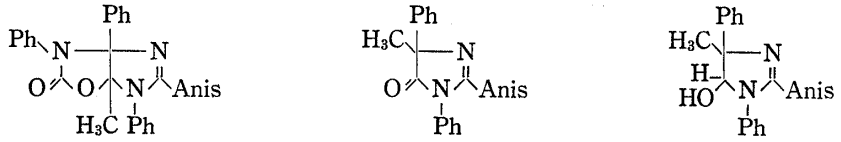
Compound No.		M	M-CH_3	M-CH_3CN	M-R^1CN-H	$R^2\overset{+}{N}\equiv CR^1$	$R^2\overset{+}{N}\equiv CPh$
VIIIaa	*m/e*	340	325	299	206	201	180
	Rel. Ab.[a]	100	10	2	5	1	3
VIIIab	*m/e*	374	359	333	240		214
	Rel. Ab.[a]	100	3	<1	3		4
VIIIba	*m/e*	310	295	269	206	180[b]	
	Rel. Ab.[a]	100	<1	3	6	3	

a) Rel.Ab.=relative abundance.

b) $R^2\overset{+}{N}\equiv CR^1$ can not be distinguished from $R^2\overset{+}{N}\equiv CPh$, because R^1 is phenyl group.

ion at *m/e* 210 is common in all four compounds and its structure is assumed as $C_6H_5\overset{+}{N}\equiv C-C_6H_4OCH_3$. The fragment ions at *m/e* 180, 133 and 118 are assumed as $C_6H_5\overset{+}{N}\equiv C-C_6H_5$, $CH_3OC_6H_4C\equiv N^+$ and $C_6H_5\overset{+}{N}\equiv C-CH_3$ respectively. In the mass spectrum of VIaa, no peaks at *m/e* 180 and 118 are observed. It is considered that the *m/e* 237 ion of VIaa is formed by loss of CO and C_6H_5N from the molecular ion, and the identical peak is also observed in the spectrum of VIIaa.

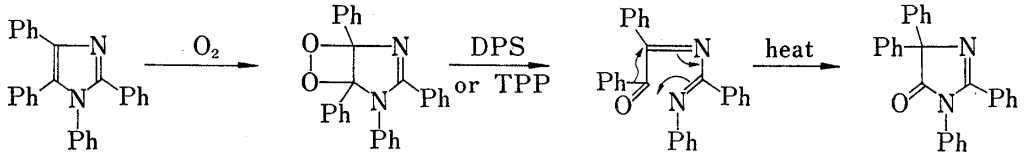
From these spectral data and the chemical behavior, it is concluded that the reasonable structures of compounds Vaa, VIaa and VIIaa are 5-anisyl-6a-methyl-3,3a,6-triphenyl-2′-imidazolino[4,5-*d*]oxazolid-2-one, 2-anisyl-4-methyl-1,4-diphenyl-2-imidazolin-5-one and 2-anisyl-5-hydroxy-4-methyl-1,4-diphenyl-2-imidazoline respectively (Chart 4).



Vaa VIaa VIIaa

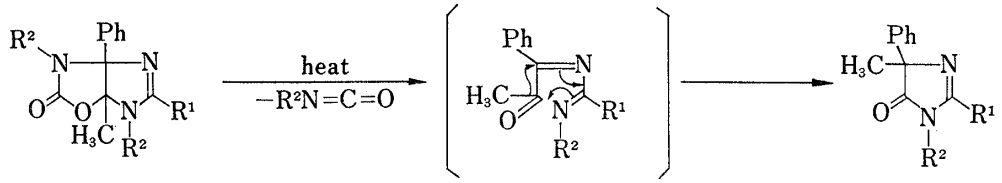
Chart 4

Recently Wasserman and Saito[7] have reported that 1,2,4,4-tetraphenyl-2-imidazolin-5-one (XII) was obtained by photooxidation of 1,2,4,5-tetraphenylimidazole (IX) in the presence of diphenyl sulfide (DPS). Later, the formation of XII *via* the intermediate (XI) from the



IX X XI XII

Chart 5



V XIII VI

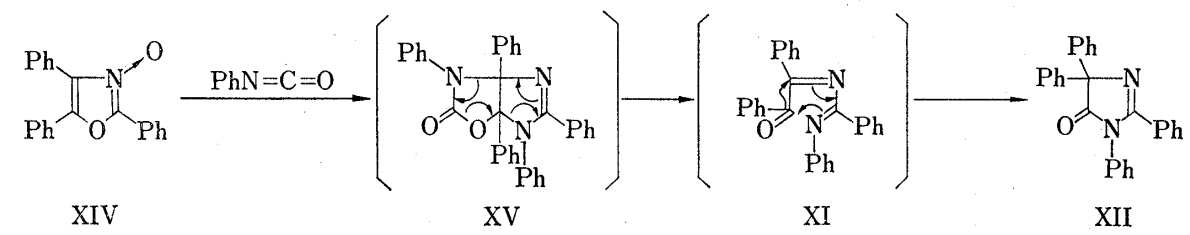
Chart 6

7) H.H. Wasserman and I. Saito, *J. Am. Chem. Soc.*, **97**, 905 (1975).

reaction of dioxetan (X) with triphenylphosphine (TPP) has been described by Rio and Serkiz.[8]

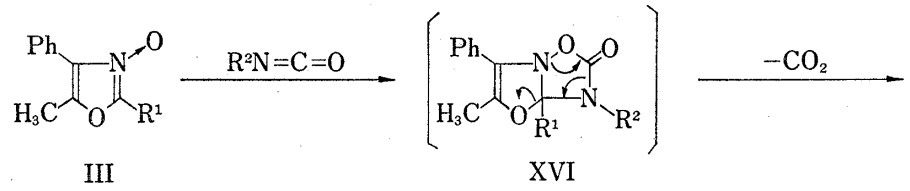
On pyrolysis of our compounds V, it seems that the reaction proceeds *via* the same intermediates (XIII) as XI to afford imidazolinones (VI) according to the following scheme (Chart 6).

As we would expect, the reaction of 2,4,5-triphenyloxazole 3-oxide (XIV) with phenylisocyanate resulted directly in the formation of 1,2,4,4-tetraphenyl-2-imidazolin-5-one (XII) without the isolation of the intermediates XV and XI because of their instability, which was identical in IR spectrum with an authentic sample[9] (Chart 7).

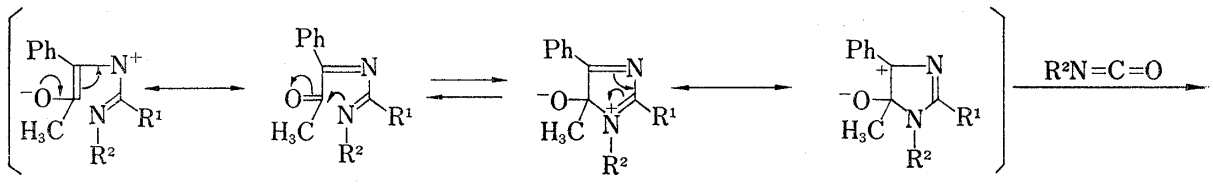


XIV XV XI XII

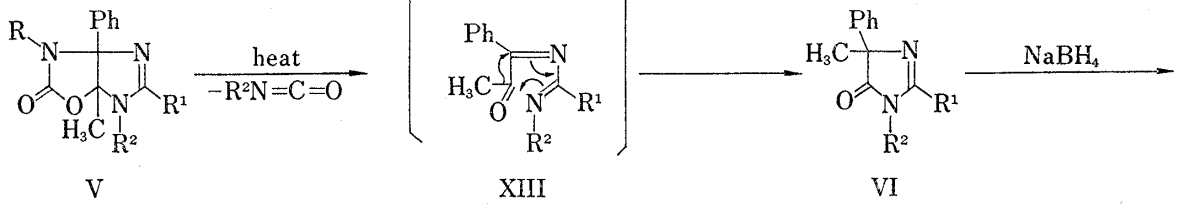
Chart 7



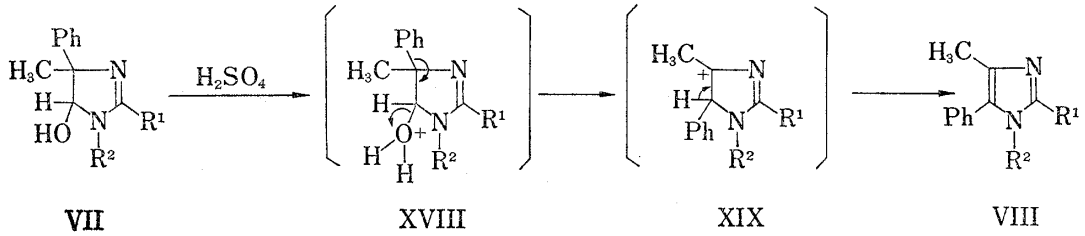
III XVI



XVII



V XIII VI



VII XVIII XIX VIII

Chart 8

8) G. Rio and B. Serkiz, *J. Chem. Soc., Chem. Commun.*, **1975**, 849.
9) The authentic sample was supplied by courtesy of Professor H.H. Wasserman.

From the results described above, it is concluded that all the reaction presented in this report proceeds according to the following scheme (Chart 8). At first, the addition of the first isocyanate to oxazole 3-oxide to give an intermediate XVI occurs, and carbon dioxide is easily eliminated from XVI, followed simultaneously by the attack of the second isocyanate to give the adduct, imidazolino[4,5-*d*]oxazolid-2-one (V). On pyrolysis of V, one mole of isocyanate is lost, followed by the rearrangement of methyl group to afford VI. On hydrogenation of VI with sodium borohydride, VII is obtained. VII transforms into VIII on treatment with sulfuric acid and the rearrangement of phenyl group is presumably catalyzed with acid shown in Chart 8.

Experimental[10]

Reaction of 4-Aryloxazole 3-Oxides (III) with Arylisocyanates (IV)——General Procedure: To a solution of 4-aryloxazole 3-oxide (III) (0.01 mol) in $CHCl_3$ (10 ml), arylisocyanate (IV) (0.022 mol) in $CHCl_3$ (10 ml) was added dropwise with stirring at room temperature. After the reaction mixture was further allowed to stand for 15 min at room temperature, the solvent was removed *in vacuo*. Ether was added to the residue and the oily residue was solidified gradually in a crystallized condition, filtered, washed with ether and recrystallized to give imidazolino[4,5-*d*]oxazolid-2-one derivative (V).

Imidazolino[4,5-*d*]oxazolid-2-one (Vaa): Colorless prisms (from acetone), mp 216—218°, 69% yield. *Anal.* Calcd. for $C_{30}H_{25}N_3O_3$: C, 75.77; H, 5.30; N, 8.84. Found: C, 75.98; H, 5.46; N, 8.62. UV λ_{max}^{EtOH} nm (log ε): 242 (4.44), 258 (4.40). IR ν_{max}^{KBr} cm^{-1}: 1760 (C=O), 1615 (C=N). NMR (in $CDCl_3$) δ: 1.08 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 6.80 (2H, d, J_{ortho}=9 Hz, anisyl 3, 5H), 7.58 (2H, d, J_{ortho}=9 Hz, anisyl 2, 6H), 7.08—8.10 (15H, m, C_6H_5).

Imidazolino[4,5-*d*]oxazolid-2-one (Vab): Colorless prisms (from ether), mp 190—191°, 79% yield. *Anal.* Calcd. for $C_{30}H_{23}Cl_2N_3O_3$: C, 66.18; H, 4.26; N, 7.72. Found: C, 66.01; H, 4.08; N, 7.67. UV λ_{max}^{EtOH} nm (log ε): 257.5 (4.28). IR ν_{max}^{KBr} cm^{-1}: 1773 (C=O), 1620 (C=N). NMR (in $CDCl_3$) δ: 1.18 (3H, s, CH_3), 3.96 (3H, s, OCH_3), 6.90—8.21 (17H, m, C_6H_5, $-C_6H_4-$).

Imidazolino[4,5-*d*]oxazolid-2-one (Vac): Colorless prisms (from acetone), mp 222—224°, 86% yield. *Anal.* Calcd. for $C_{30}H_{23}Cl_2N_3O_3$: C, 66.18; H, 4.26; N, 7.72. Found: C, 66.25; H, 4.30; N, 7.71. UV λ_{max}^{EtOH} nm (log ε): 247.5 (4.53), 275 (sh., 4.23). IR ν_{max}^{KBr} cm^{-1}: 1765 (C=O), 1625 (C=N). NMR (in $CDCl_3$) δ: 1.04 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 6.66—7.96 (17H, m, C_6H_5, $-C_6H_4-$).

Imidazolino[4,5-*d*]oxazolid-2-one (Vba): Colorless prisms (from acetone), mp 189—190°, 61% yield. *Anal.* Calcd. for $C_{29}H_{23}N_3O_2 \cdot 1/2H_2O$: C, 76.33; H, 5.32; N, 9.25. Found: C, 76.70; H, 5.05; N, 8.96. UV λ_{max}^{EtOH} nm (log ε): 236 (4.48). IR ν_{max}^{KBr} cm^{-1}: 1763 (C=O), 1620 (C=N). NMR (in $CDCl_3$) δ: 1.08 (3H, s, CH_3), 6.93—8.05 (20H, m, C_6H_5).

Imidazolino[4,5-*d*]oxazolid-2-one (Vbb): Colorless prisms (from acetone), mp 232—233°, 49% yield. *Anal.* Calcd. for $C_{29}H_{21}Cl_2N_3O_2$: C, 67.71; H, 4.12; N, 8.17. Found: C, 67.88; H, 4.08; N, 8.28. UV λ_{max}^{EtOH} nm (log ε): 236 (4.04), 256 (sh., 3.72). IR ν_{max}^{KBr} cm^{-1}: 1768 (C=O), 1620 (C=N). NMR (in $CDCl_3$) δ: 1.12 (3H, s, CH_3), 7.17—8.83 (18H, m, C_6H_5, $-C_6H_4-$).

Imidazolino[4,5-*d*]oxazolid-2-one (Vbc): Colorless prisms (from acetone), mp 205—206°, 72% yield. *Anal.* Calcd. for $C_{29}H_{21}Cl_2N_3O_2$: C, 67.71; H, 4.12; N, 8.17. Found: C, 67.79; H, 4.10; N, 8.26. UV λ_{max}^{EtOH} nm (log ε): 243 (4.55), 270 (sh., 3.97). IR ν_{max}^{KBr} cm^{-1}: 1767 (C=O), 1620 (C=N). NMR (in $CDCl_3$) δ: 1.08 (3H, s, CH_3), 6.90—7.92 (18H, m, C_6H_5, $-C_6H_4-$).

Reaction of 2,4,5-Triphenyloxazole 3-Oxide (XIV) with Phenylisocyanate——To a solution of XIV (3.13 g, 0.01 mol) in $CHCl_3$ (10 ml), phenylisocyanate (2.62 g, 0.022 mol) was added dropwise with stirring at room temperature. The reaction mixture was treated in the same way as that of the reaction described above. The residue was further heated on a steam bath for 30 min, and was chromatographed on silica gel (Merck Kieselgel 60, 70—230 mesh) with benzene–$CHCl_3$ (3: 1) in order to remove an impurity. The eluate was recrystallized from acetone to yield 1,2,4,4-tetraphenyl-2-imidazolin-5-one (XII), colorless prisms, mp 157°, in a 58% yield. *Anal.* Calcd. for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21. Found: C, 83.48; H, 5.23; N, 7.51. UV λ_{max}^{EtOH} nm (log ε): 227 (4.42), 260 (sh., 3.83), 267 (sh., 3.75). IR ν_{max}^{KBr} cm^{-1}: 1743 (C=O), 1613 (C=N).

Pyrolysis of Imidazolino[4,5-*d*]oxazolid-2-one Derivatives (V)——General Procedure: Until evolution of gas was complete, 0.5 g, of V was pyrolyzed for 30 min in an oil bath at the temperature, which is 50—60° higher than that of the corresponding melting point. After cooling to room temperature, the residue was

10) All melting points are uncorrected. UV spectra were measured on a Hitachi 556 double wavelength Spectrophotometer, IR spectra on a Hitachi 295 Infrared Spectrophotometer, ^1H NMR spectra on a Hitachi R22 Spectrometer at 90 MHz with tetramethylsilane as an internal standard, mass spectra on a JEOL Model JMS-01SG Spectrometer.

chromatographed on alumina with $CHCl_3$, and the eluate was recrystallized from acetone–petr. ether to yield 2-imidazolin-5-one derivative (VI).

2-Anisyl-4-methyl-1,4-diphenyl-2-imidazolin-5-one (VIaa): Colorless prisms (from acetone), mp 157°, 59% yield. *Anal.* Calcd. for $C_{23}H_{20}N_2O_2$: C, 77.50; H, 5.66; N, 7.86. Found: C, 77.49; H, 5.68; N, 7.91. UV λ_{max}^{EtOH} nm (log ε): 260 (4.34). IR ν_{max}^{KBr} cm^{-1}: 1739 (C=O), 1620 (C=N). NMR (in $CDCl_3$) δ: 1.89 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 6.62—7.90 (14H, m, C_6H_5, $-C_6H_4-$).

2-Anisyl-1-(*o*-chlorophenyl)-4-methyl-4-phenyl-2-imidazolin-5-one (VIab): Colorless prisms (from acetone–petr. ether), mp 135—136°, 43% yield. *Anal.* Calcd. for $C_{23}H_{19}ClN_2O_2$: C, 70.67; H, 4.90; N, 7.17. Found: C, 70.81; H, 4.79; N, 7.06. UV λ_{max}^{EtOH} nm (log ε): 265 (4.18). IR ν_{max}^{KBr} cm^{-1}: 1736 (C=O), 1606 (C=N). NMR (in $CDCl_3$) δ: 1.90 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 6.72—7.86 (13H, m, C_6H_5, $-C_6H_4-$).

4-Methyl-1,2,4-triphenyl-2-imidazolin-5-one (VIba): Colorless prisms (from acetone–petr. ether), mp 128—130°, 66% yield. *Anal.* Calcd. for $C_{22}H_{18}N_2O$: C, 80.95; H, 5.56; N, 8.58. Found: C, 80.55; H, 5.43; N, 8.61. UV λ_{max}^{EtOH} nm (log ε): 227.5 (4.41). IR ν_{max}^{KBr} cm^{-1}: 1740 (C=O), 1607 (C=N). NMR (in $CDCl_3$) δ: 1.89 (3H, s, CH_3), 7.02—7.92 (15H, m, C_6H_5).

Reduction of VIaa, VIab, VIba and XII with $NaBH_4$——General Procedure: To a solution of 2-imidazolin-5-one derivative (0.001 mol) in MeOH (20 ml), $NaBH_4$ (0.03 mol) in limited amounts was added carefully with stirring at room temperature. After evolution of gas was complete, the reaction mixture was refluxed for 1 hr. The solvent was removed *in vacuo*, and the residue was made basic to litmus with 5% NaOH solution, extracted with $CHCl_3$, the $CHCl_3$ layer was dried over Na_2SO_4. The solvent was removed. The residue was recrystallized from acetone–petr. ether to yield 5-hydroxy-2-imidazoline derivative.

2-Anisyl-5-hydroxy-4-methyl-1,4-diphenyl-2-imidazoline (VIIaa): Colorless prisms, mp 190—191°, 69% yield. *Anal.* Calcd. for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.19; N, 7.82. Found: C, 76.92; H, 6.10; N, 7.78. UV λ_{max}^{EtOH} nm (log ε): 257.5 (4.38). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1608 (C=N). NMR (in DMSO-d_6) δ: 1.44 (3/4H, s, CH_3), 1.62 (9/4H, s, CH_3), 3.74 (3H, s, OCH_3), 5.12 (3/4H, d, J=8 Hz, >C<u>H</u>OH), 5.23 (1/4H, d, J=8 Hz, >C<u>H</u>OH), 5.98 (1/4H, d, J=8 Hz, OH), 6.63 (3/4H, d, J=8 Hz, OH), 6.80—7.62 (14H, m, C_6H_5, $-C_6H_4-$).

2-Anisyl-1-(*o*-chlorophenyl)-5-hydroxy-4-methyl-4-phenyl-2-imidazoline (VIIab): Colorless needles, mp 215—218°, 28% yield. *Anal.* Calcd. for $C_{23}H_{21}ClN_2O_2$: C, 70.31; H, 5.39; N, 7.13. Found: C, 70.12; H, 5.42; N, 7.09. UV λ_{max}^{EtOH} nm (log ε): 253 (4.26). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1615 (C=N). NMR (in DMSO-d_6) δ: 1.57 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 5.31 (1H, d, J=7.6 Hz, >C<u>H</u>OH), 5.91 (1/4H, d, J=7.6 Hz, OH), 6.52 (3/4H, d, J=6.6 Hz, OH), 6.88 (2H, d, J=10 Hz, $-C_6H_4-$), 7.18—7.73 (11H, m, C_6H_5, $-C_6H_4-$).

5-Hydroxy-4-methyl-1,2,4-triphenyl-2-imidazoline (VIIba): Colorless prisms, mp 178—179°, 46% yield. *Anal.* Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.52; H, 6.13; N, 8.50. UV λ_{max}^{EtOH} nm (log ε): 230 (4.22), 265 (3.88). IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1610 (C=N). NMR (in DMSO-d_6) δ: 1.46 (3/5H, s, CH_3), 1.61 (12/5H, s, CH_3), 5.14 (4/5H, d, J=8 Hz, >C<u>H</u>OH), 5.23 (1/5H, d, J=8 Hz, >C<u>H</u>OH), 5.98 (1/5H, d, J=8 Hz, OH), 6.60 (4/5H, d, J=8 Hz, OH), 6.78—7.70 (15H, m, C_6H_5).

5-Hydroxy-1,2,4,4-tetraphenyl-2-imidazoline (XX): Colorless prisms, mp 184—186°, 35% yield. *Anal.* Calcd. for $C_{27}H_{22}N_2O$: C, 83.05; H, 5.68; N, 7.18. Found: C, 82.87; H, 5.70; N, 6.98. UV λ_{max}^{EtOH} nm (log ε): 240 (sh., 4.23), 266 (3.91), 273 (sh., 3.90). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1609 (C=N). NMR (in DMSO-d_6) δ: 5.92 (1H, d, J=8.4 Hz, >C<u>H</u>OH), 6.42 (1H, d, J=8.4 Hz, OH), 6.67—7.71 (20H, m, C_6H_5).

Dehydration of VIIaa, VIIab and VIIba with H_2SO_4——General Procedure: A solution of 0.5 g of 5-hydroxy-2-imidazoline derivative (VII) in 10 ml of 50% H_2SO_4 was heated at 90° for 90 min. The reaction mixture was neutralized with K_2CO_3, extracted with $CHCl_3$, the $CHCl_3$ layer was dried over Na_2SO_4. The solvent was removed. The residue was recrystallized to yield 5 phenylimidazole derivative (VIII).

2-Anisyl-4-methyl-1,5-diphenylimidazole (VIIIaa): Colorless needles (from acetone–petr. ether), mp 195—196°, 46% yield. *Anal.* Calcd. for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.10; H, 5.74; N, 8.16. UV λ_{max}^{EtOH} nm (log ε): 288 (4.30). IR ν_{max}^{KBr} cm^{-1}: 1604 (C=N). NMR (in $CDCl_3$) δ: 2.33 (3H, s, CH_3), 3.70 (3H, s, OCH_3), 6.63—7.32 (14H, m, C_6H_5, $-C_6H_4-$).

1-(*o*-Chlorophenyl)-4-methyl-2,5-diphenylimidazole (VIIIab): Colorless prisms (from ether), mp 134°, 69% yield. *Anal.* Calcd. for $C_{23}H_{19}ClN_2O$: C, 73.69; H, 5.11; N, 7.48. Found: C, 73.50; H, 5.04; N, 7.47. UV λ_{max}^{EtOH} nm (log ε): 285 (4.32). IR ν_{max}^{KBr} cm^{-1}: 1602 (C=N). NMR (in $CDCl_3$) δ: 2.34 (3H, s, CH_3), 3.70 (3H, s, OCH_3), 6.63—7.41 (14H, m, C_6H_5, $-C_6H_4-$).

4-Methyl-1,2,5-triphenylimidazole (VIIIba): Colorless prisms (from acetone), mp 203—204°, 54% yield. *Anal.* Calcd. for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.23; H, 5.77; N, 8.97. UV λ_{max}^{EtOH} nm (log ε): 287 (4.21). IR ν_{max}^{KBr} cm^{-1}: 1595 (C=N). NMR (in $CDCl_3$) δ: 2.35 (3H, s, CH_3), 6.86—7.48 (15H, m, C_6H_5).

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