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Reaction of γ-Bromoacetoacetyl Bromide with N-Phenylhydroxylamine Derivatives: Synthesis of 1,2-Oxazine Derivatives

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The reaction of γ-bromoacetoacetyl bromide (**1**) with N-arylhydroxylamines (**2**) afforded N-(γ-bromoacetoacetyl)-N-arylhydroxylamines (**3**), which were treated with sodium methoxide to give 2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione (**4**). Treatment of **3** with hydroxylamine directly afforded the 5-oxime derivatives of **4** (**7**), which could be transformed to **4** by mild hydrolysis with dilute mineral acid.

Keywords——2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione; γ-bromoacetoacetyl bromide; N-arylhydroxylamine; diketene; N-acetoacetylation; cyclization; hydrolysis of oxime

γ-Bromoacetoacetyl bromide (**1**), which can be readily prepared from diketene and bromine, seems to be a useful synthon, particularly in the synthesis of heterocyclic compounds. Early in 1910, Chick and Wilsmore obtained 4-bromomethylcarbostyril from **1** and aniline *via* γ-bromoacetoacetanilide, but they did not utilize the γ-bromine atom of **1**.[2] Recently we reported that **1** reacted with hydrazobenzene to afford 1,2-diphenylhexahydropyridazine-3,5-dione and 5-bromomethyl-1,2-diphenyl-3-pyrazolone.[3] In connection with this, King reported that the reaction of 1,3-dibromopropane and 1,4-dibromobutane with ethyl N-hydroxycarbamate in the presence of potassium hydroxide gave 1,2-isoxazolidine and 1,2-oxazine derivatives, respectively.[4]

In the present report, we describe a synthetic route to 1,2-oxazine derivatives by the reaction of **1** with N-phenylhydroxylamine derivatives.

When N-phenylhydroxylamine (**2a**, R=H) was allowed to react with **1** in the presence of triethylamine in chloroform, colorless needles of $C_{10}H_{10}BrNO_3$ (**3a**), mp 133°, were obtained in 64% yield. The chemical and spectroscopic properties showed this compound to be N-(γ-bromoacetoacetyl)-N-phenylhydroxylamine. Compound **3a** was soluble in alkali, and gave a positive ferric chloride test. The infrared (IR) spectrum, 1663 cm^{-1} (amide), and nuclear magnetic resonance (NMR) spectrum, 2.92 and 3.28 ppm (2H, AB-quartet, J=16

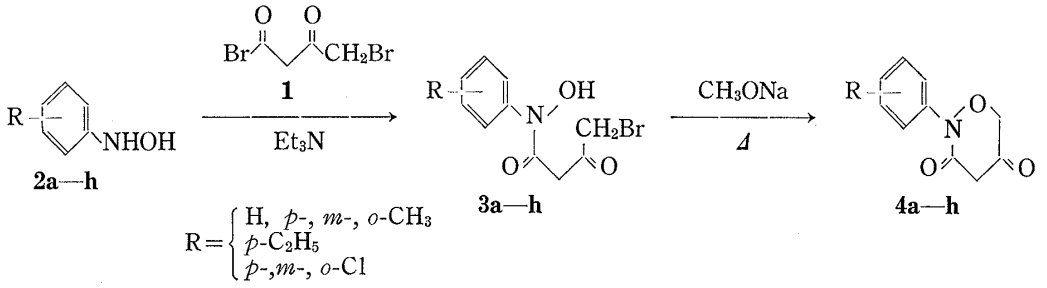

Chart 1

1) Location: *a) Horinouchi, 1432-1, Hachioji city, Tokyo, 192-03, Japan; b) Aobayama, Sendai, 980, Japan.*
2) F. Chick and N. Wilsmore, *J. Chem. Soc.*, **97**, 1978 (1910).
3) T. Kato, M. Sato, and K. Tabei, *J. Org. Chem.*, **39**, 3205 (1974).
4) H. King, *J. Chem. Soc.*, **1942**, 432.

Hz, active methylene) and 3.68 ppm (2H, singlet, $Br-CH_2-CO$), were consistent with the N-acyl structure (**3a**).

Similarly, seven kinds of N-arylhydroxylamine derivatives (**2b**—**h**) were allowed to react with **1** to give the corresponding N-(γ-bromoacetoacetyl)-N-arylhydroxylamine derivatives (**3b**—**g**) in 54—73% yields. In the case of *o*-chlorophenylhydroxylamine (**2h**), an attempt at purification by crystallization of the product (**3h**) was unsuccessful. The results are summarized in Table I.

Table I. N-(γ-Bromoacetoacetyl)-N-arylhydroxylamine Derivatives (3)

	R	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N	IR ν_{max}^{KBr} (cm^{-1}) Amide	NMR δ ($CDCl_3$) (ppm) α-H[a]	γ-H[b]
a	H	133	64	$C_{10}H_{10}BrNO_3$	44.14	3.70	5.14	44.28	3.74	5.03	1663	2.92, 3.28	3.68
b	*p*-CH_3	124	60	$C_{11}H_{12}BrNO_3$	46.17	4.23	4.90	46.18	4.26	5.02	1660	2.90, 3.28	3.65
c	*m*-CH_3	92	63	$C_{11}H_{12}BrNO_3$	46.17	4.23	4.90	46.20	4.18	5.16	1675	2.92, 3.27	3.63
d	*o*-CH_3	70.5	54	$C_{11}H_{12}BrNO_3$	46.17	4.23	4.90	46.17	4.19	5.07	1660	2.88, 3.28	3.58
e	*p*-C_2H_5	90	73	$C_{12}H_{14}BrNO_3$	48.02	4.70	4.67	48.11	4.70	4.72	1661	2.88, 3.28	3.60
f	*p*-Cl	118	57	$C_{10}H_9BrClNO_3$	39.18	2.96	4.57	39.16	2.88	4.63	1670	2.93, 3.28	3.68
g	*m*-Cl	132	59	$C_{10}H_9BrClNO_3$	39.18	2.96	4.57	39.01	2.86	4.86	1660	2.97, 3.28	3.70
h	*o*-Cl	—	—										

a) AB-quartet, J=14—16 Hz.
b) Singlet.

When a mixture of **3a** and equimolar of sodium methoxide in ethanol was heated under reflux, 2-phenyltetrahydro-2*H*-1,2-oxazine-3,5-dione (**4a**), $C_{10}H_9NO_3$, mp 87°, was obtained in 69% yield. Compound **4a** was soluble in alkali and gave a positive ferric chloride test. The IR spectrum of **4a** showed the presence of amide and keto carbonyl groups at 1670 cm^{-1} and 1750 cm^{-1}, respectively. The NMR spectrum of **4a** showed two singlet signals due to the methylene groups at 3.75 ppm ($-CO-CH_2-CO-$) and 4.50 ppm ($-CO-CH_2-O-$). The above

Table II. 2-Aryltetrahydro-2*H*-1,2-oxazine-3,5-dione Derivatives (4)

	R	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N	IR ν_{max}^{KBr} (cm^{-1}) Keto	Amide	NMR δ ($CDCl_3$) (ppm) 4-H[a]	6-H[a]
a	H	87	69	$C_{10}H_9NO_3$	62.82	4.75	7.33	62.54	4.68	7.47	1750	1670	3.75	4.50
b	*p*-CH_3	101	55	$C_{11}H_{11}NO_3$	64.38	5.40	6.83	64.35	5.40	6.68	1750	1670	3.72	4.51
c	*m*-CH_3	104	55	$C_{11}H_{11}NO_3$	64.38	5.40	6.83	64.59	5.31	6.88	1740	1675	3.73	4.50
d	*o*-CH_3	97	59	$C_{11}H_{11}NO_3$	64.38	5.40	6.83	64.61	5.50	6.97	1720	1687	3.74	4.50
e	*p*-C_2H_5	66	65	$C_{12}H_{13}NO_3$	65.74	5.98	6.39	65.92	6.00	6.13	1760	1675	3.73	4.52
f	*p*-Cl	110	68	$C_{10}H_8ClNO_3$	53.22	3.55	6.21	53.18	3.49	6.25	1760	1675	3.73	5.52
g	*m*-Cl	121	72	$C_{10}H_8ClNO_3$	53.22	3.55	6.21	53.37	3.81	6.35	1758	1672	3.73	4.51
h	*o*-Cl	133	35[b]	$C_{10}H_8ClNO_3$	53.22	3.55	6.21	53.26	3.52	6.29	1740	1685	3.74	4.62

a) Singlet.
b) The yield was calculated based on **2h**, since **3h** was not isolated.

data confirmed the structure of tetrahydro-2*H*-1,2-oxazine-3,5-dione. **4a** was also detected as a by-product in the acylation of **2a** with **1**.

In a fashion similar to that described for **4a**, six kinds of N-(γ-bromoacetoacetyl)-N-arylhydroxylamine derivatives (**3b**—**g**) were treated with sodium methoxide to afford the corresponding 2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione derivatives (**4b**—**g**) in 55—72% yields. The results are summarized in Table II.

An attempt to cleave the N–O bond of the 1,2-oxazine ring was made. The compound **4b** (R=*p*-CH_3) was reduced by catalytic hydrogenation on palladium to afford colorless needles of $C_{11}H_{13}NO_3$ (**5b**), mp 109°, in 62.5% yield, to which we assigned the ring-opened structure, N-(*p*-tolyl)-γ-hydroxyacetoacetamide. Compound **5b** was soluble in alkali and gave a positive ferric chloride test. The IR spectrum of **5b** indicated the presence of hydroxyl, keto, and amide groups (3200, 1720, and 1650 cm^{-1}, respectively). Moreover, the signals of the NMR spectrum in DMSO-d_6 appeared at 3.50 ppm (2H, singlet), 4.15 ppm (2H, doublet, J=8 Hz), and 5.28 ppm (1H, triplet, J=8 Hz, disappeared on addition of D_2O), and were consistent with the structure N–CO–CH_2–CO–CH_2–OH.

Following the procedure given for **5b**, **4e** (R=*p*-C_2H_5) was subjected to hydrogenolysis to afford N-(*p*-ethylphenyl)-γ-hydroxyacetoacetamide (**5e**), mp 104°, in 68.5% yield. The above results are also consistent with the designation of compound **4** as the 2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione structure.

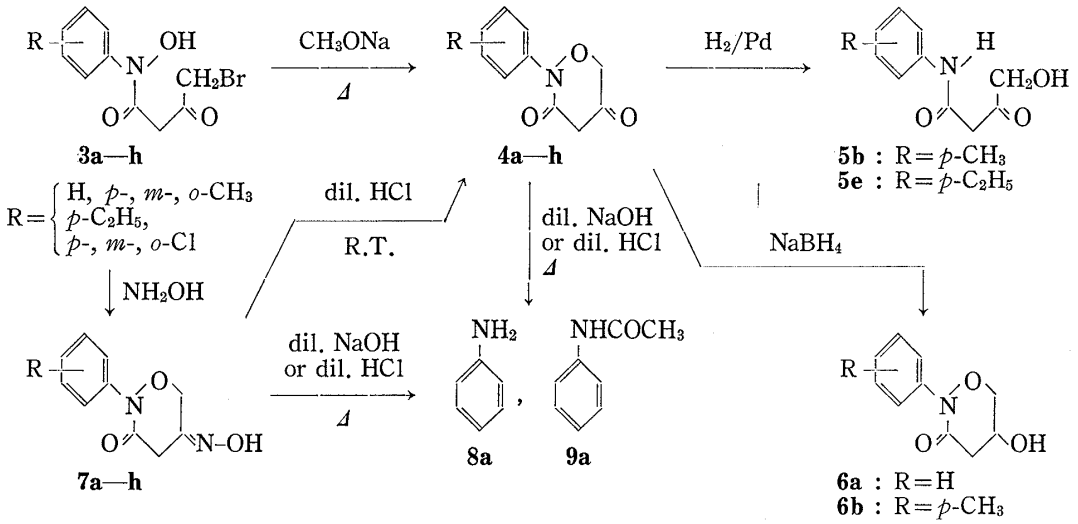

Chart 2

Reduction of **4a** with sodium borohydride in ethanol gave the product (**6a**), $C_{10}H_{11}NO_3$, mp 73°, in 79% yield. Compound **6a** was insoluble in alkali and gave a negative ferric chloride test. Its IR spectrum showed hydroxyl and amide stretching bands at 3400 and 1670 cm^{-1}, respectively. The NMR spectrum showed signals due to two methylene groups as an overlapping AB-quartet at 2.68—2.95 ppm (2H, J=16 Hz, 4-CH_2) and 4.02—4.42 ppm (2H, J=12 Hz, 6-CH_2), in addition to a methine proton at 4.65 ppm (1H, multiplet, 5-CH) and a hydroxyl proton at 3.65 ppm (1H, broad doublet, disappeared on addition of D_2O). On irradiation at 4.65 ppm, the overlapping AB-quartet signal of the 4-methylene group in the 2.68—2.95 ppm region changed to a simple AB-quartet at 2.71 and 2.91 ppm (J=16 Hz). These results were consistent with the 5-hydroxy-2-phenyltetrahydro-2*H*-1,2-oxazin-3-one structure (**6a**). A similar reaction of **4b** afforded 5-hydroxy-2-(*p*-tolyl)tetrahydro-2*H*-1,2-oxazin-3-one (**6b**), mp 95°, in 73% yield.

Treatment of **4a** with hydroxylamine in aqueous ethanol gave 2-phenyltetrahydro-2*H*-1,2-oxazine-3,5-dione 5-oxime (**7a**), $C_{10}H_{10}N_2O_3$, mp 134°, in 87% yield. Compound **7a** was

also obtained directly by the reaction of **3a** with hydroxylamine in 65% yield. Structural assignment was made on the bases of IR and NMR spectral data, as shown in Table III.

Hydrolysis of **7a** with 5% hydrochloric acid at room temperature afforded **4a** in 51% yield. Although the total yield of **4a** from **2a** was about 33%, the above reaction sequence, **2**→[**3**]→**7**→**4**, provides a facile method for the preparation of 1,2-oxazine derivatives.

Thus, seven kinds of 2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione 5-oximes (**7b**—**h**) were prepared from **2b**—**h** in 37—60% yields without isolation of the intermediates (**3b**—**h**). The 5-oximes (**7b**—**h**) were then treated with 5% hydrochloric acid at room temperature to give the corresponding 1,2-oxazine-3,5-dione derivatives (**4b**—**h**). The hydrolysis yields were over 70%, except in the cases of **7g** (R=*m*-Cl) and **7h** (R=*o*-Cl). Compound **7g** afforded **4g** in 23% yield on hydrolysis as described in the experimental section, and about 45% of the starting material (**7g**) was recovered. Compound **7h**, on the other hand, gave only a resinous substance even at low temperature. The results are summarized in Table III.

Hydrolysis of **4a** with mineral acid or alkali under reflux afforded a resinous substance, in addition to small amounts of aniline (**8a**) and acetanilide (**9a**).

Table III. 2-Aryltetrahydro-2*H*-1,2-oxazine-3,5-dione 5-Oximes (**7**)

	R	mp (°C)	Yield[a] (%)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N	IR ν_{max}^{KBr} (cm^{-1}) Amide	NMR δ ($CDCl_3$) (ppm) 4-H[b]	6-H[b]	Hydrolysis yield (%)
a	H	134	65	$C_{10}H_{10}N_2O_3$	58.25	4.89	13.58	58.06	4.91	13.62	1675	3.57	4.95	51
b	*p*-CH_3	132	60	$C_{11}H_{12}N_2O_3$	59.99	5.49	12.72	59.71	5.41	12.77	1670	3.55	4.97	78
c	*m*-CH_3	128	49	$C_{11}H_{12}N_2O_3$	59.99	5.49	12.72	60.29	5.41	12.55	1660	3.56	4.97	72
d	*o*-CH_3	123	47	$C_{11}H_{12}N_2O_3$	59.99	5.49	12.72	60.11	5.53	12.63	1655	3.60	4.95	58
e	*p*-C_2H_5	115	51	$C_{12}H_{14}N_2O_3$	61.52	6.02	11.96	61.42	6.09	12.03	1662	3.55	4.95	77
f	*p*-Cl	147	51	$C_{10}H_9ClN_2O_3$	49.90	3.74	11.64	50.01	3.64	11.50	1662	3.54	4.95	63
g	*m*-Cl	175	53	$C_{10}H_9ClN_2O_3$	49.90	3.74	11.64	49.91	3.49	11.91	1660	3.58	4.95	23[c]
h	*o*-Cl	138	37	$C_{10}H_9ClN_2O_3$	49.90	3.74	11.64	50.02	3.70	11.71	1660	3.59	5.05	—

a) The yields were calculated based on **2**.
b) Singlet.
c) About 45% of **7g** was recovered.

Experimental

All melting points are uncorrected. IR spectra were run on a Hitachi 215 spectrometer. NMR spectra were recorded at 100 MHz with a Hitachi Perkin-Elmer R-20 spectrometer using TMS as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad, with the coupling constant (*J* value) given in Hz. Mass spectra (MS) were obtained on a Hitachi RMU-7 mass spectrometer.

Reaction of N-Arylhydroxylamine (2) with γ-Bromoacetoacetyl Bromide (1)——General Procedure: Br_2 (1.6 g, 10 mmol) was added dropwise to a solution of diketene (0.84 g, 10 mmol) in CCl_4 (20 ml) at 0—5°. The mixture was added to a solution of **2** (10 mmol) and triethylamine (1.0 g, 10 mmol) in $CHCl_3$ (50 ml) under ice-cooling. After stirring for 10 min, the reaction mixture was washed with water, and dried over Na_2SO_4. Removal of the solvent by evaporation gave a brown residue, to which benzene (100 ml) was added; crystals that precipitated were collected. Recrystallization from $CHCl_3$ or $CHCl_3$–hexane mixture (2: 1) gave N-(γ-bromoacetoacetyl)-N-arylhydroxylamine (**3**) as needles. When the residue was difficult to crystallize from benzene, the oily residue was chromatographed on silica gel to give needles of **3**. The results are summarized in Table I.

2-Aryltetrahydro-2*H*-1,2-oxazine-3,5-dione (4)——General Procedure: A mixture of **3** (10 mmol) and sodium methoxide (0.54 g, 10 mmol) in EtOH (50 ml) was refluxed for 30 min. After removal of EtOH, the resulting residue was dissolved in $CHCl_3$, washed with water, and dried over Na_2SO_4. Removal of the solvent by evaporation gave a brown residue which was chromatographed on silica gel. The fraction eluted with $CHCl_3$ gave **4**, which was recrystallized from $CHCl_3$–hexane (2: 1). The results are summarized in Table II.

Hydrogenolysis of 4b——A solution of 2-(*p*-tolyl)tetrahydro-2*H*-1,2-oxazine-3,5-dione (**4b**) (0.51 g, 2.5 mmol) in EtOH (100 ml) was vigorously stirred with $PdCl_2$ (20 mg) in an H_2 atmosphere. After an equivalent

amount of H_2 (65 ml, 2.6 mmol) had been absorbed, the mixture was filtered. The filtrate was evaporated down, and the residue was chromatographed on silica gel. Elution with $CHCl_3$–AcOEt (10: 1) gave N-(*p*-tolyl)-γ-hydroxyacetoacetamide (**5b**), mp 109° (0.32 g, 62.5%), which was recrystallized from $CHCl_3$–hexane (2: 1). *Anal.* Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.83; H, 6.09; N, 6.73. IR ν_{max}^{KBr} cm^{-1}: 3200 (OH), 1720 (keto), 1650 (amide). NMR δ ppm (DMSO-d_6): 2.23 (3H, s, tolyl-CH_3), 3.50 (2H, s, α-CH_2), 4.15 (2H, d, $J=8$, γ-CH_2), 5.28 (1H, t, $J=8$, disappeared on addition of D_2O, OH), 7.10 and 7.45 (each 2H, AB_q, $J=12$, aromatic H), 9.95 (1H, br, disappeared on addition of D_2O, NH). MS *m/e*: 207 (M^+), 176, 149, 134, 133, 107.

Hydrogenolysis of 4e——Following the procedure described above, a solution of 2-(*p*-ethylphenyl)tetrahydro-2*H*-1,2-oxazine-3,5-dione (**4e**) (0.56 g, 2.5 mmol) in EtOH (100 ml) was subjected to catalytic hydrogenation to afford N-(*p*-ethylphenyl)-γ-hydroxyacetoacetamide (**5e**), mp 104° ($CHCl_3$–hexane, 2: 1), (0.38 g, 68.5%). *Anal.* Calcd. for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.01; H, 6.80; N, 6.29. IR ν_{max}^{KBr} cm^{-1}: 3200 (OH), 1720 (keto), 1655 (amide). NMR δ ppm ($CDCl_3$): 1.20 (3H, t, $J=11$, CH_2–$\underline{CH_3}$), 2.61 (2H, q, $J=11$, $\underline{CH_2}$–CH_3), 3.3 (1H, br, disappeared on addition of D_2O, OH), 3.57 (2H, s, α-CH_2), 4.37 (2H, br s, γ-CH_2), 7.12 and 7.38 (each 2H, AB_q, $J=9$, aromatic H), 8.5 (1H, br, disappeared on addition of D_2O, NH). MS *m/e*: 221 (M^+), 190, 163, 148, 147, 121.

Reduction of 4a with $NaBH_4$——$NaBH_4$ (0.2 g, about 0.5 mmol) was added to a solution of 2-phenyltetrahydro-2*H*-1,2-oxazine-3,5-dione (**4a**) (0.38 g, 2 mmol) in EtOH (50 ml) at room temperature. When the addition was complete, the mixture was stirred for 10 min. Removal of EtOH by evaporation gave a residue, which was extracted with AcOEt. The organic layer was washed with 5% NaOH and water. After drying over Na_2SO_4, the AcOEt solution was evaporated down to give a residue, which was crystallized from $CHCl_3$–hexane (2: 1) to give 5-hydroxy-2-phenyltetrahydro-2*H*-1,2-oxazin-3-one (**6a**), mp 73° (0.30 g, 79%). *Anal.* Calcd. for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.34; H, 5.76; N, 7.21. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1670 (amide). NMR δ ppm ($CDCl_3$): 2.68 and 2.86, 2.72 and 2.92 (each 1H, each AB_q, $J=16$, on irradiation at 4.65 ppm changed to AB_q at 2.71 and 2.91 ppm, 4-CH_2), 3.65 (1H, br, disappeared on addition of D_2O, OH), 4.02 and 4.40, 4.07 and 4.42 (each 1H, each AB_q, $J=12$, on irradiation at 4.65 ppm the high field signal of AB_q appeared at 3.92 and 4.03 ppm, 6-CH_2), 4.65 (1H, m, 5-CH), 7.1—7.7 (5H, m, aromatic H). MS *m/e* 193 (M^+), 175, 119, 107.

Reduction of 4b with $NaBH_4$——Following the procedure given for **6a**, 2-(*p*-tolyl)tetrahydro-2*H*-1,2-oxazine-3,5-dione (**4b**) (2.05 g, 10 mmol) was reduced with $NaBH_4$ (0.15 g) in EtOH (50 ml) to give 5-hydroxy-2-(*p*-tolyl)tetrahydro-2*H*-1,2-oxazin-3-one (**6b**), mp 95° ($CHCl_3$–hexane, 2: 1), (1.50 g, 73%). *Anal.* Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.84; H, 6.34; N, 6.77. IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1655 (amide), NMR δ ppm ($CDCl_3$): 2.30 (3H, s, tolyl-CH_3), 2.60 and 2.90, 2.73 and 2.97 (each 1H, each AB_q, $J=16$, on irradiation at 4.63 ppm AB_q signals appeared at 2.68 and 2.90 ppm, 4-CH_2), 3.80 (1H, br, disappeared on addition of D_2O, OH), 3.94 and 4.37, 4.04 and 4.41 (each 1H, each AB_q, $J=12$, on irradiation at 4.63 ppm the high field signals of AB_q appeared at 3.92 and 4.03 ppm, 6-CH_2), 4.63 (1H, br, 5-H), 7.13 and 7.47 (4H, AB_q, $J=8$, aromatic H). MS *m/e*: 207 (M^+), 133, 132, 121, 105.

2-Aryltetrahydro-2*H*-1,2-oxazine-3,5-dione 5-Oxime (7)——General Procedure: A mixture of **2** (10 mmol) and triethylamine (1.0 g, 10 mmol) in $CHCl_3$ (50 ml) was treated with an equivalent amount (10 mmol) of **1**. After stirring for 10 min, the solvent was evaporated off and the residue was dissolved in EtOH (50 ml). A mixture of NH_2OH·HCl (2.8 g, 40 mmol) and KOH (2.2 g, 40 mmol) in 50% EtOH (50 ml) (pH 7.5) was added at room temperature. After stirring for 10 min, the reaction mixture was evaporated down and the residue was extracted with AcOEt. The AcOEt solution was washed with water, and dried over Na_2SO_4. After removal of the solvent, the residue was recrystallized from EtOH giving 2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione 5-oxime (**7**). The results are summarized in Table III.

Hydrolysis of the Oxime (7)——General Procedure: A solution of 2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione 5-oxime (**7**) (2 mmol) in 5% HCl (50 ml) was stirred for 24 hr at room temperature. The reaction mixture was extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, and dried over Na_2SO_4. After removal of the solvent by evaporation, the residue was chromatographed on silica gel to afford needles of 2-aryltetrahydro-2*H*-1,2-oxazine-3,5-dione (**4**). The yields are listed in Table III.

Hydrolysis of 4a with Aqueous Alkali——A solution of 2-phenyltetrahydro-2*H*-1,2-oxazine-3,5-dione (**4a**) (0.1 g, 0.53 mmol) in 5% NaOH (30 ml) was refluxed for 30 min. The reaction mixture was neutralized with 5% HCl and extracted with AcOEt. The AcOEt solution was washed with water, and dried over Na_2SO_4. Removal of the solvent by evaporation gave a brown resinous substance, which was chromatographed on silica gel to give aniline (**8a**) (8 mg, 16%) and acetanilide (**9a**) (13 mg, 19%).

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