Reactions of Arylglyoxals with Tetrasulfur Tetranitrides (S_4N_4): Formation of 2-Aroyl-5-arylimidazoles and 2-Aroyl-5-aryloxazoles

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Treatment of arylglyoxal monohydrates with tetrasulfur tetranitride in *p*-dioxane at reflux afforded 2-aroyl-5-arylimidizoles and 2-aroyl-5-aryloxazoles in 10 to 31% and 17 to 32% yields, respectively. With non-hydrate of arylglyoxals, yields of the latter increase somewhat, whereas essentially no changes in yields of the former were observed. A mechanism is proposed for the formation of the products.

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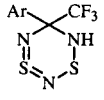
Recently we have shown that tetrasulfur tetranitride (S_4N_4) is a useful reagent for the synthesis of 3-aryl-4-halogeno-1,2,5-thiadiazoles **2** [1] in addition to 3-aryl-1,2,5-thiadiazoles **3** [2] and 5-aryl-5-trifluoromethyl-4*H*-1,3,2,4,6-dithiatriazines **4** [3]. The advantage of employing tetrasulfur tetranitride is to introduce sulfur and/or nitrogen atoms into a molecule in a single step.

Figure

2 X = F, Cl,Br
3 X = H



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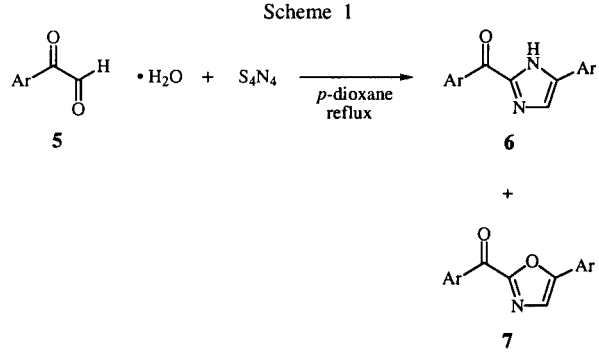
In a continuation of our study on the development of potential synthetic utility of tetrasulfur tetranitride, we became interested in studing the reactions of arylglyoxals **5**, which are 1,2-dicarbonyl compounds, with tetrasulfur tetranitride. Mataka and co-workers have extensively studied the reactions of tetrasulfur tetranitride with monoketones such as alkyl benzyl ketones [4], benzyl ketones having a substituent at *ortho* and *para* positions, respectively [4c], aryl methyl ketones [5] and cyclic ketones [4, 6]. The major products obtained from the reactions with these ketones were corresponding 3,4-disubstituted-1,2,5-thiadiazoles albeit in low yields. Acyclic amides [4c], *ortho*-substituted benzamides [4c], and 2,4,6-triaryltriazines [4c] were isolated as minor products, depending on the structures of the ketones. Of the cyclic ketones, the reaction of 1,2-indandione [4b, 6] in toluene for 24 hours at reflux afforded 2,3-dihydro-1*H*-indol-2-one in 38% yield, which appears to be the only report of the reaction of tetrasulfur tetranitride with 1,2-diketones.

Since nucleophilic attack on the terminal formyl group of **5** is preferable to that on the internal keto group from both the electronic and the steric point of view [7], it was anticipated that the α-iminoketones formed by the reaction of arylglyoxls with ammonia formed by decomposition of tetrasulfur tetranitride at high reaction temperature [8] might undergo a self-condensation reaction to give 2-aroyl-5-arylimidazoles, which had been seldom reported [9]. With this in mind, the reaction of tetrasulfur tetranitride with arylglyoxals in *p*-dioxane at reflux was studied. The results are described herein.

Results and Discussion.

Numerous arylglyoxal monohydrates **5** were prepared according to the documented procedures [10]. Heating a mixture of **5** and tetrasulfur tetranitride (*ca.* 0.2 equivalent) in *p*-dioxane at reflux for 6 to 9 hours caused a series of changes of color of the solution: orange → pale orange → dark red → dark black. Thin layer chromatography (Kiesel gel 60 F_{254}, ethyl acetate: *n*-hexane = 1:2) of the reaction mixture exhibited four groups of spot. The top group (R_f = 0.95) consisted of sulfur and unreacted tetrasulfur tetranitride. The second group (R_f = ~ 0.7) exhibited a major spot corresponding to 2-aroyl-5-aryloxazoles **7** with two satellite spots above and below the major spot. The third group (R_f = ~ 0.5) consisted of 2-aroyl-5-arylimidazoles **6** and a couple of weak spots. The last group (R_f = ~ 0.2) consisted of a trace amount of unknown mixtures. The reaction mixture was separated by column chromatography (silica gel, 230-400 mech, ASTM). Quantities of the reactants, reaction times, and yields of products **6** and **7** are summarized in Table 1 and the spectroscopic (^1H and ^{13}C nmr, ir, ms) and analytical data of **6** and **7** are summarized in Table 2.

Scheme 1



5 **6** + **7**

Table 1

Reaction Conditions and Yields and Melting Points of Compounds **6** and **7**

	Compounds **5**		S_4N_4	Time		Yields (%)	Mp		Yields (%)	Mp
	Ar	mmoles	mmole	hours		**6**	(°C)		**7**	(°C)
a	Ph	2.63	0.53	6	**a**	15, 12 [a]	192-193 [c] (lit 192-194 [9a])	**a**	19, 32 [a]	132-134 [e] (lit 134-136 [11])
b	4-$MeOC_6H_4$	2.20	0.44	6	**b**	10	215-216 [c] (lit 220-221 [9a])	**b**	32	153-155 [c]
c	4-MeC_6H_4	2.41	0.48	6	**c**	14, 13 [a]	209-211 [c] (lit 209-211 [9a])	**c**	17, 26 [a]	130-131 [c]
d	4-BrC_6H_4	2.07	0.41	6	**d**	31, 33 [a]	255-257 [d] (lit 257-258 [9a])			
e	4-ClC_6H_4	2.18	0.44	6	**e**	26	245-247 [d]			
		2.14	0.75	15	**e**	18 [b]				
f	4-NCC_6H_4	2.25	0.45	8	**f**	12	256-258 [c]	**d**	23	239-241 [c]
g	2-Thienyl	3.54	1.06	9	**g**	14	209-210 [c]			

[a] Yields of the products when freshly vacuum-distilled glyoxals (**5a**, b_{15} 90-95°; **5c**, b_{10} 104-110°; **5d**, b_{17} 135-142°) were used. [b] Yields when toluene was used as a solvent otherwise *p*-dioxane used. [c] From a mixture of dichloromethane and *n*-hexane. [d] From a mixture of chloroform and *n*-hexane. [e] From a mixture of benzene and *n*-hexane.

Table 2

^1H and ^{13}C NMR, IR, and MS Spectral and Analytical Data of **6** and **7**

Compounds	^1H NMR (dimethyl-d_6 sulfoxide) δ (ppm)	^{13}C NMR (dimethyl-d_6 sulfoxide) δ (ppm)	IR (potassium bromide) (cm^{-1})	MS (m/z, %)	Molecular Formula	Analyses % Calcd./Found C	H	N	S
6a	7.39-7.44 (m, 3H, ArH), 7.57-7.70 (m, 2H, ArH), 7.80 (d, 2H, J = 7.5 Hz, ArH), 8.08 (s, 1H, CH), 8.60 (d, 2H, J = 7.5 Hz, ArH), 13.6 (s, 1H, NH)	119.5, 125.7, 128.0, 129.2, 129.8, 131.5, 133.9, 134.5, 136.8, 143.8, 145.6, 181.6	3264, 3040, 1609,1561, 1443, 1276, 1161, 896, 758, 684	248 (M^+, 88), 220 (100), 105 (59), 77 (65)	$C_{16}H_{12}N_2O$	77.40 72.29	4.90 4.89	11.30 11.19	0.00 0.00
6b	3.78 (s, 3H, CH_3O), 3.87 (s, 3 H, CH_3O), 6.98 (d, 2H, J = 8.6 Hz, ArH), 7.14 (d, 2H, J = 8.9 Hz, ArH), 7.84 (d, 2H, J = 8.6 Hz, ArH), 7.90 (s, 1H, CH), 8.68 (d, 2H, J = 8.9 Hz, ArH), 13.4 (s, 1H, NH)	56.0, 56.4, 114.6, 114.9, 117.8, 127.0, 128.0, 129.5, 134.0, 143.5, 145.6, 159.4, 164.1, 179.8	3264, 2928, 1600, 1555, 1440, 1280, 1244, 1158, 1024, 902, 825, 771, 640	308 (M^+, 82), 280 (16), 207 (90), 135 (100), 77 (25)	$C_{18}H_{16}N_2O_3$	70.12 70.09	5.23 5.21	9.09 9.14	0.00 0.00
6c	2.32 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 7.23 (d, 2H, J = 7.6 Hz, ArH), 7.39 (d, 2H, J = 7.4 Hz, ArH), 7.81 (d, 2H, J = 7.6 Hz, ArH), 7.97 (s, 1H, CH), 8.51 (d, 2H, J = 7.7 Hz, ArH), 13.5 (s, 1H, NH)	21.7, 22.1, 118.7, 125.7, 129.3, 129.8, 131.6, 131.9, 134.3, 137.1, 143.8, 144.3, 145.5, 181.2	3264, 2896, 1606, 1555, 1443, 1276, 1164, 899, 812, 758, 640	276 (M^+, 99), 248 (100), 119 (65), 91 (58)	$C_{18}H_{16}N_2O$	78.24 78.20	5.84 5.81	10.14 10.09	0.00 0.00
6d	7.58 (d, 2H, J = 7.3 Hz, ArH), 7.78 (d, 2H, J = 7.6 Hz, ArH), 7.86 (d, 2H, J = 7.3 Hz, ArH), 8.12 (s, 1H, CH), 8.50 (d, 2H, J = 7.6 Hz, ArH), 13.7 (s, 1H, NH)	120.2, 127.7, 128.3, 132.3, 132.4, 132.7, 133.4, 133.7, 135.7, 142.7, 145.4, 180.5	3264, 3072, 1609, 1571, 1440, 1276, 1164, 1065, 896, 822 761, 640	404 (M^+, 48), 378 (50), 183 (93), 155 (65), 76 (34)	$C_{16}H_{10}Br_2N_2O$	47.30 47.18	2.50 2.39	6.90 6.75	0.00 0.00
6e	7.46 (d, 2H, J = 8.3 Hz, ArH), 7.64 (d, 2H, J = 8.3 Hz, ArH), 7.93 (d,	120.2, 127.4, 129.0, 129.2, 131.1, 132.5, 133.4, 135.3, 139.1,	3264, 3088, 1609, 1577, 1440, 1280,	316 (M^+, 79), 288 (84), 139 (100), 111	$C_{16}H_{10}Cl_2N_2O$	60.60 60.48	3.20 3.09	8.80 8.62	0.00 0.00

Table 2 (continued)

^1H and ^{13}C NMR, IR, and MS Spectral and Analytical Data of **6** and **7**

Compounds	^1H NMR (dimethyl-d_6 sulfoxide) δ (ppm)	^{13}C NMR (dimethyl-d_6 sulfoxide) δ (ppm)	IR (potassium bromide) (cm^{-1})	MS (m/z, %)	Molecular Formula	Analyses % Calcd./Found C	H	N	S
	2H, J = 8.3 Hz, ArH), 8.13 (s, 1H, CH), 8.60 (d, 2H, J = 8.3 Hz, ArH), 13.7 (s, 1H, NH)	142.7, 145.4, 180.2	1164, 1091, 1008, 899, 828, 764, 640	(70), 75 (24)					
6f	7.87 (d, 2H, J = 8.0 Hz, ArH), 8.05 (d, 2H, J = 8.5 Hz, ArH), 8.09 (d, 2H, J = 8.5 Hz, ArH), 8.33 (s, 1H, CH), 8.64 (d, 2H. J = 8.0 Hz, ArH), 13.9 (s, 1H, NH)	110.2, 115.9, 119.0, 109.8, 122.3, 126.3, 131.9, 133.1, 133.6, 138.8, 140.1, 142.2, 145.6, 180.5	3280, 2224, 1603, 1446, 1280, 1174, 902, 835, 764	298 (M^+, 73), 270 (100), 130 (63), 102 (69)	$C_{18}H_{10}N_4O$	72.48 72.53	3.38 3.45	18.78 18.90	0.00 0.00
6g	7.10 (d, 1H, J = 3.7 Hz, ArH), 7.34 (d, I H, J = 4.9 Hz, ArH), 7.45-7.49 (m, 2H, ArH), 7.95 (s, 1H, CH), 8.11 (d, 1H, J = 4.9 Hz, ArH), 8.68 (d, 1H, J = 3.7 Hz, ArH), 13.7 (s, 1H, NH)	118.9, 123.9, 125.5, 128.7, 129.4, 137.1, 137.4, 138.1, 139.2, 141.5, 144.4, 173.5	3224, 3072, 1593, 1507, 1465, 1404, 1385, 1270, 1110, 1046, 816, 771, 726, 688, 627	260 (M^+, 95), 176 (68), 111 (100), 83 (11)	$C_{12}H_8N_2OS_2$	55.36 55.19	3.10 3.02	10.76 10.58	24.63 24.82
7a [a]	7.46-7.53 (m, 3H, ArH), 7.55-758 (m. 3H, ArH), 7.63 (s, 1H, CH), 7.84 (d, 2H, J = 8.0 Hz, ArH), 8.49 (d, 2H, J= 8.2 Hz, ArH)		1644, 1584, 1468, 1436, 1350, 1164, 899, 758, 684, 633	249 (M^+, 63), 221 (77), 105 (10), 77 (47)	$C_{16}H_{11}NO_2$	77.10 76.98	4.40 4.19	5.60 5.48	0.00 0.00
7b [a]	3.81 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 6.86 (d, 2H, J = 8.4 Hz, ArH), 6.88 (d, 2H, J = 8.4 Hz, ArH), 7.41 (s, 1H, CH), 7.71 (d, 2H, J = 8.4 Hz, ArH), 8.53 (d, 2H, J = 8.4 Hz, ArH)		1635, 1593, 1558, 1472, 1414, 1299, 1248, 1152, 1017, 899, 819	309 (M+, 25), 135 (100), 107 (6), 77 (12)	$C_{18}H_{15}NO_4$	69.90 69.79	4.90 4.80	4.50 4.41	0.00 0.00
7c	2.42 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 7.30 (d, 2H, J = 8.4 Hz, ArH), 7.34 (d, 2H, J = 8.1 Hz, ArH), 7.57 (s, 1H, CH), 7.74 (d, 2H, J = 8.1 Hz, ArH), 8.40 (d, 2H, J = 8.4 Hz, ArH)		1635, 1596, 1465, 1350, 1276, 1164, 979, 899, 816, 694	277 (M^+, 22), 119 (100), 91 (33), 65 (11)	$C_{18}H_{15}NO_2$	77.96 78.12	5.45 5.60	5.05 5.21	0.00 0.00
7d	8.00 (s, 1H, CH), 8.07-8.12 (m, 6 H, ArH), 8.53 (d, 2H, J = 8.2 Hz, ArH)		1654, 1600, 1475, 1340, 1273, 1155, 905, 844 765	299 (M^+, 18), 130 (100), 102 (36)	$C_{16}H_9Br_2NO_2$	47.21 47.02	2.23 2.09	3.44 3.25	0.00 0.00

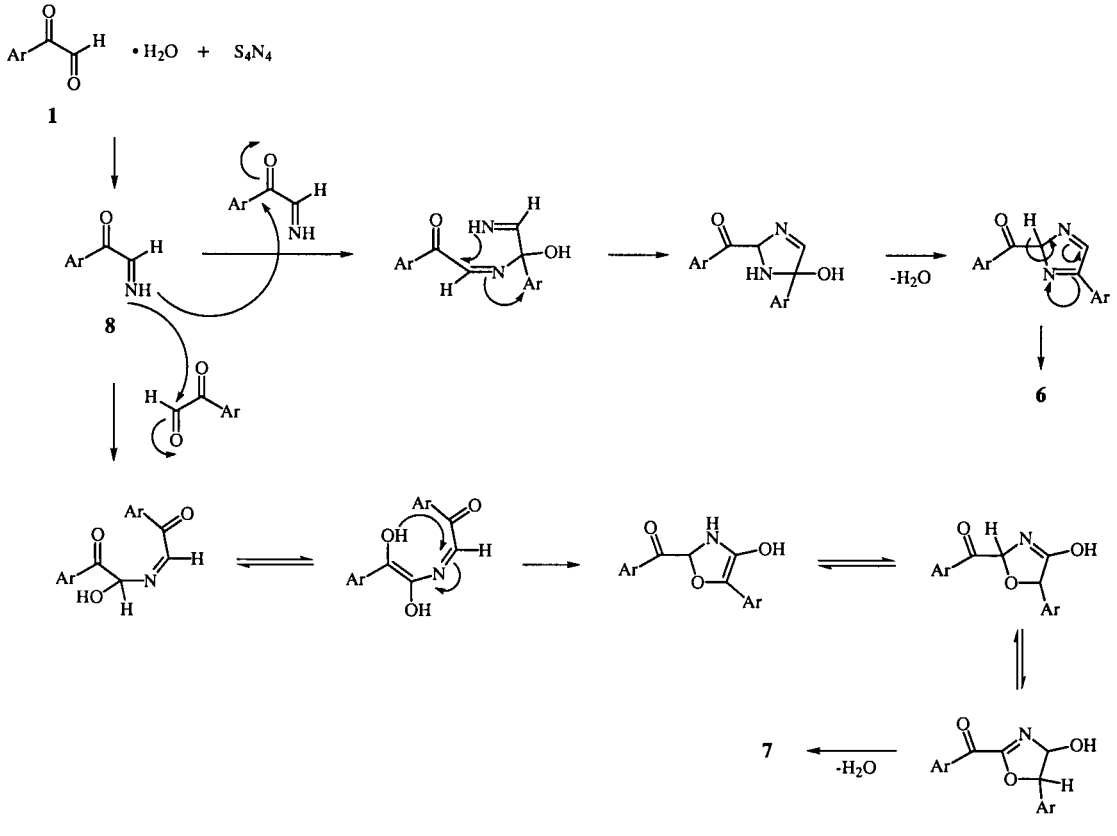
[a] Deuteriochloroform was used for ^1H nmr solvent.

The structures of compounds **6** were determined by comparing the melting point of each compound with that of the corresponding documented value [9a]. Interestingly, the melting point of 3-benzoyl-4-phenylpyrazole which is a structural isomer of **6a** was reported to be 193-194° [12] which is very close to that of **6a**. The infrared absorption of the carbonyl group recorded in potassium bromide pellets was reported to be 1650 cm^{-1}, which is different from the value 1609 cm^{-1} exhibited by **6a**. The infrared data eliminates clearly the possibility of a pyrazole derivative. In addition, the possible formation of 3-benzoyl-5-phenylpyrazole was ruled

out based on its melting point, 169.5-170.5°, which is different from that of **6a** by 22.5° and the infrared absorption of the carbonyl group at 1647 cm^{-1} recorded in dichloromethane [13]. The reported yields of **6a**, **6b**, and **6c** are 44, 26, and 24%, respectively [9a], which are slightly higher than those listed in Table 1, whereas the yield of **6d** was not described in the literature [9a]. Arylglyoxal employed for the reactions were monohydrate forms. In order to see the effect of non-hydrate arylglyoxals, selected arylglyoxals vacuum-distilled according to the literature [9a] prior to use were subjected to the same reaction conditions. Table 1 shows that yields of **6a**, **6c**, and **6d** seem to be essentially independent of the extent of hydration of arylglyoxals. When toluene which has a slightly higher boiling point than that of *p*-dioxane was used as a solvent, not only a longer reaction time and a greater amount of tetrasulfur tetranitride (0.3 equivalent) were needed to complete the reaction, but also the yield of **6e** decreased from 26% to 18%. The reason for the former may have been ready self-decomposition of tetrasulfur tetranitride at reflux temperature. The result suggests that *p*-dioxane is a better solvent than toluene, and *p*-dioxane was used as a solvent through the reactions.

Apart from the formation of 2-aroyl-5-arylimidazoles **6** and 3-hydroxy-2,5-diarylpyrazines by the reactions of **5** with ammonia in *p*-dioxane at reflux [9a], the reaction of **5** with tetrasulfur tetranitride in *p*-dioxane at reflux gave 2-aroyl-5-aryloxazoles **7** in addition to **6**. The formation of **7** appeared to be dependent on the substituents on the arylglyoxals because no formation of **7** was observed from the reaction of **5d**, **5e**, and **5g**. Interestingly, Table 1 shows that yields of **7** are not only higher than those of **6** in the cases where compounds **7** are formed, but also increase somewhat by employing freshly distilled arylglyoxals in which **7a** and **7c** were observed in 32% and 26% yields, respectively. The structure of **7** was determined based on comparison of the reported melting point and the spectroscopic data of **7a** with those of **7a** prepared. The melting point of **7a** prepared is in accord with the reported value but the carbonyl absorption of **7a** prepared appeared at 1644 cm^{-1}, which is 6 cm^{-1} lower than that of the reported value [11a-c]. Both were recorded in potassium bromide pellets. In spite of a small discrepancy in two carbonyl absorptions of the reported and prepared **7a**, more discrepancies in melting point and the infrared carbonyl absorption were observed by comparison with those of 2-benzoyl-4-phenyloxazole, which showed a melting point of 126.5-128° and a carbonyl absorption at 1660 cm^{-1} [15]. Furthermore, the proton nuclear magnetic resonance spectrum of 2-benzoyl-4-phenyloxazole exhibited singlets at 8.15 ppm, assignable to a proton bonded at C-5 [15], whereas **7a-c**, and **7d** prepared exhibited a singlet at 7.41-7.63 ppm and 8.00 ppm,

Scheme 2



respectively. Consequently it would be reasonable to eliminate the possibility of 2-aroyl-4-aryloxazoles for the structure of **7**. A literature survey shows that there are a few methods for the synthesis of 2-aroyl-5-phenyloxazoles. Treatment of 5-phenyloxazoles with *n*-butyllithium, followed by addition of *N*-methyl-*N*-(2-pyridinyl)carboxamides gave the desired acylated products [11d, 14]. However, this method suffers from the inconvenience of preparation of the activated oxazoles. Recently C-2 acylation of oxazoles derivatives was accomplished by reaction of oxazol-2-ylzinc chloride reagents with acid chlorides in the presence of cuprous iodide [11b]. Photolysis of 3-benzoyl-5-phenylisoxazole gave rise to 2-benzoyl-5-phenyloxazole (**7a**) albeit in low yield [11a].

The formation of **6** and **7** can be rationalized by assuming the formation of arylglyoxal monoimine **8** as an intermediate which is conceived to be formed by the reaction of arylglyoxals with ammonia formed by decomposition of tetrasulfur tetranitride. Similarly one might envisage the formation of **8** by the reaction of arylglyoxals with ammonium acetate [9a]. Condensation of two molecules of **8** can give rise to **6**. Alternatively, nucleophilic attack of imino nitrogen of **8** to the formyl carbon of **1**, followed by a series of proton transfers and elimination of a water molecule can afford **7** (Scheme 2). Therefore, it is expected that the formation of **7** would be more favorable in high concentrations of non-hydrated **1**, which is in good agreement with the increase in yields of **7** when a vacuum-distilled **1** was used.

EXPERIMENTAL

Arylglyoxal monohydrates were prepared by treatment of 1-arylethanones with selenium dioxide in aqueous *p*-dioxane [10]. Tetrasulfur tetranitride was prepared by the reaction of sulfur dichloride with ammonia gas according to the documental procedure [8]. *p*-Dioxane was obtained from Duksan Pharm. Co. Ltd., and freshly distilled prior to use. Thin layer chromatography was carried out on a Merck Chromatogram Sheet (Kiesel gel 60 F_{254}). The chromatogram was visualized with a mineral ultraviolet lamp. Column chromatography was performed using silica gel (Merck, 230-400 mesh). The ^1H nmr spectra were obtained with a Bruker AC-80 at 80 MHz and Bruker DPX 300 at 300 MHz, using tetramethylsilane as an internal standard. Infrared spectra were obtained using a Shimadzu Model JR-470 infrared spectrometer. Mass spectra were obtained using HP 6890 (GC) with a HP 5973 (MSD) mass spectrometer. Elemental analyses were determined by the Korean Basic Science Center. Melting points were determined on a Fisher-Johns melting point apparatus and were uncorrected.

General Procedure for the Reactions of Arylglyoxals with Tetrasulfur Tetranitride (S_4N_4).

A mixture of arylglyoxals (2.07-3.54 mmoles) and tetrasulfur tetranitride (0.41-1.06 mmoles) in *p*-dioxane (10-12 ml) was heated for an appropriate time at reflux. The orange-like color of the solution faded slowly at the beginning and then turned dark red. When the reaction was completed, the reaction mixture looked dark black. Thin layer chromatography (Kiesel gel 60 F_{254}, ethyl acetate:*n*-hexane = 1:2) showed four groups of spots: sulfur and unreacted tetrasulfur tetranitride (R_f = 0.95), oxazole derivatives (R_f = ~ 0.7), imidazole derivatives exhibiting weak fluorescence (R_f = ~ 0.5) by illumination with short wave, and unknown mixtures (R_f = ~ 0.2). Column chromatography (230-400 mesh, 3 x 12 cm) of the reaction mixture was performed. Elution with *n*-hexane gave sulfur. Elution with a mixture of ethyl acetate and *n*-hexane (1:5) gave unreacted tetrasulfur tetranitride and an unknown mixture. Subsequent elution with the solvent mixture (1:4) gave a mixture of 2-aroyl-5-aryloxazoles **7** and an unknown mixture, which was separated by repeated column chromatography using a mixture of ethyl acetate and *n*-hexane (1:3) as an eluent. Elution with the same solvent mixture (1:2) gave 2-aroyl-5-arylimidazoles **6**. Consult Table 1 for quantities of reactants, reaction conditions, yields, and melting points of **6** and **7** and Table 2 for the spectroscopic and analytical data of **6** and **7**.

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