A New Base Catalyzed Ring Contraction: 2,4,5-Triarylimidazoles from 2,4,6-Triaryl-4*H*-1,3,5-thiadiazines

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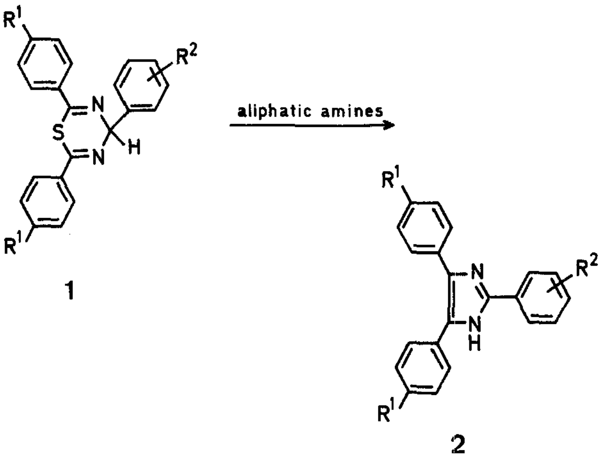
We wish to report that 2,4,5-triarylimidazoles can be easily obtained by reacting 2,4,6-triaryl-4*H*-1,3,5-thiadiazines with aliphatic amines at room temperature[1].



Imidazoles (**2**) are always obtained in high yields by using a catalytic amount of triethylamine in benzene (Table). The rate of formation of **2** is enhanced when R^1 or R^2 are electron-withdrawing substituents. Roughly the reaction rate increases with the basicity of the amines.

The most likely hypothesis on the reaction mechanism involves the formation of the anion **3**, a 8 π electron system, analogous to that obtained by treating 4*H*-1,3-oxazines with butyllithium[2], which then leads to the formation of **2** and sulphur.

Table. Preparation of 2,4,5-Triarylimidazoles[a]

Product[b] 2	R^1	R^2	Yield (%)[c]	m.p.[d]	Elemental Analyses					
a	H	H	88	277–278°	$C_{21}H_{16}N_2$	calc.	C 85.10	H 5.44	N 9.45	
				275–276° (methanol)[4]	(296.4)	found	85.05	5.51	9.43	
b	H	4-H_3C	87	239–240°	$C_{22}H_{18}N_2$	calc.	C 85.13	H 5.85	N 9.02	
				233–237° (methanol)[4]	(310.4)	found	85.05	5.75	9.15	
c	H	4-Cl	88	265–265.5°	$C_{21}H_{15}ClN_2$	calc.	C 76.24	H 4.57	N 8.47	Cl 10.72
				264–265.5° (ethanol)[4]	(330.8)	found	76.14	4.50	8.35	10.81
d	H	3-Br	99	309–310°	$C_{21}H_{15}BrN_2$	calc.	C 67.21	H 4.03	N 7.46	Br 21.29
				302–303° (benzene/THF)[5]	(375.3)	found	67.13	4.10	7.41	21.15
e	H	4-H_3CO	93	234–235°	$C_{22}H_{18}N_2O$	calc.	C 80.95	H 5.56	N 8.58	
				232–233° (ethanol)[4]	(326.4)	found	80.91	5.51	8.64	
f	H_3C	H	90	273–274°	$C_{23}H_{20}N_2$	calc.	C 85.15	H 6.21	N 8.64	
				269–271° (ethanol)[4]	(324.4)	found	85.07	6.15	8.70	
g	H_3CO[e]	H	88	199–200°	$C_{23}H_{20}N_2O_2$	calc.	C 77.50	H 5.66	N 7.86	
				197° (ethanol)[4]	(356.4)	found	77.40	5.72	7.91	
h	Cl	H	92	294–295°	$C_{21}H_{14}Cl_2N_2$	calc.	C 69.05	H 3.86	N 7.67	Cl 19.41
				294–295° (C_2H_5OAc)[4]	(365.2)	found	69.03	3.87	7.62	19.35

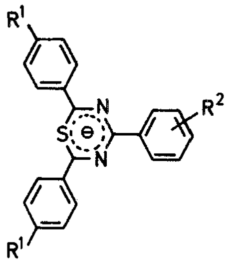
[a] The experimental procedure followed in carrying out the reaction of 2,4,6-triaryl-4*H*-1,3,5-thiadiazines with triethylamine is that described in the preparation of compound **2h**.

[b] The compounds are identified by I.R. and Mass spectra and are identical to authentic samples.

[c] Yields are calculated on the pure insoluble products filtered from the reaction mixture.

[d] Melting points are determined by the Kofler method and are not corrected. Ethanol is used as crystallization solvent.

[e] The reaction is carried out at 60°.



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Further work[3] is in progress to extend the scope of the reaction and to clarify the reaction mechanism.

2-Phenyl-4,5-bis[*p*-chlorophenyl]-imidazole (2h):

2,6-Bis[*p*-chlorophenyl]-4-phenyl-4*H*-1,3,5-thiadiazine (1.99 g, 5 mmol) and triethylamine (0.2 ml, d = 0.72, 1.4 mmol) are dissolved in benzene (80 ml). The solution is left to stand at room temperature for 76 h; during this time a white crystalline product is formed. The solid is isolated by filtration, washed with benzene, then with diethyl ether, and dried at 100°; yield 1.67 g (92%); m.p. 294–295° (95% ethanol) (294–295° from ethyl acetate)[4].

$C_{21}H_{14}Cl_2N_2$	calc.	C 69.05	H 3.86	N 7.67	Cl 19.41
(365.2)	found	69.03	3.87	7.62	19.35

Received: November 27, 1974

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[1] 2,4,6-Triaryl-4*H*-1,3,5-thiadiazines are prepared by treatment of aryl nitriles with an aryl thioamide and an aryl aldehyde at room temperature in the presence of boron trifluoride-etherate in chloroform. C. Giordano, *Italian Patent Appl.* 22.041, March 27, 1973; C. Giordano, A. Belli, in press.

[2] R. R. Schmidt, W. J. W. Mayer, and H.-U. Wagner, *Liebigs Ann. Chem.* **1973**, 2010.

[3] C. Giordano, L. Cassar, and A. Belli, to be published.

[4] H. Tanino, T. Kondo, K. Okada and T. Goto, *Bull. Chem. Soc. Japan* **45**, 1474 (1972).

[5] L. A. Cesconi, et al., *J. Org. Chem.* **36**, 2267 (1971).