Reaction of 1,3,5-Oxadiazinium Salts with Amines; Formation of *N*-(*N*-Benzoyliminobenzyl)-*N'*-substituted Benzamidines; a New Class of Compounds, Aza-vinylogues of *N*-Acylamidines[1]

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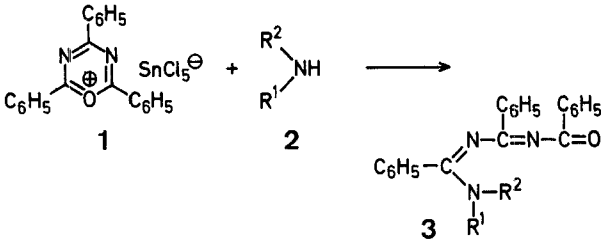
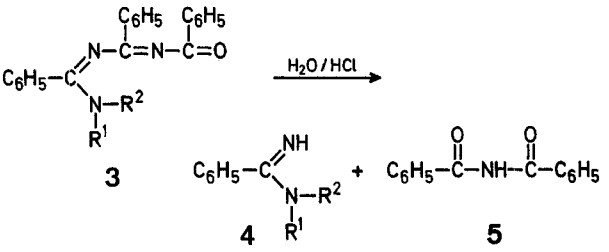
1,3,5-Oxadiazinium salts (e.g. **1**) are readily accessible from the reaction of a nitrile (1 mol) with an acyl chloride (1 mol) and a Lewis acid (1 mol)[2,3]. Various heterocyclic systems such as pyrimidine, *s*-triazine, triazole, and oxadiazole derivatives can be obtained from **1** by reaction with carbanions[4] (derived e.g. from malonitrile, methyl cyanoacetate, ethyl benzoylacetate, etc.), ammonia[5], hydrazines, hydroxylamines and urea[3], respectively. These reactions have been shown to take place via an initial nucleophilic attack at position 2 to open the ring and subsequent cyclisation with elimination of a small molecule such as water, methanol, ethanol, or benzamide[3,4,6].

In this communication we report the synthesis of *N*-(*N*-benzoyliminobenzyl)-*N'*-substituted benzamidines **3** by the reaction of 2,4,6-triphenyl-1,3,5-oxadiazinium pentachlorostannates **1** with primary and secondary aliphatic and/or aromatic amines **2**.

The products **3** are stable, in contrast to the corresponding, usually not isolated, intermediates in the ring transformation reactions mentioned above (compare also with the formation of *N*-substituted pyridinium salts by the reaction of primary amines with pyrylium salts[6,7,8]).



All new compounds **3** were characterised by microanalysis, I.R., U.V., ^{1}H-N.M.R., and mass spectral data (see Tables). They are stable in solid form or in aqueous base but are hydrolysed by aqueous acid to the benzamidine **4** and dibenzoylamine (**5**).



General Procedure for the Synthesis of *N*-(*N*-Benzoyliminobenzyl)-*N'*-substituted Benzamidines 3:

In a three necked flask fitted with a thermometer, a dropping funnel, and a gas inlet tube for nitrogen is placed 2,4,6-triphenyl-1,3,5-oxadiazinium pentachlorostannate[2] (**1**; 24.3 g, 0.04 mol) suspended in dry dichloromethane (100 ml). With magnetic stirring, the amine **2** (0.04 mol) in dichloromethane (40 ml) is added and the mixture is heated under gentle reflux for 3 h. The resultant

Table 1. Preparation of Benzamidines **3**

Product	R^1	R^2	Yield [%]	m.p. (recryst. from)	Molecular formula[a]	Mass spectra *m/e* M^+
3a	—$(CH_2)_5$—		71	173° (acetone)	$C_{26}H_{25}N_3O$ (395.5)	395
3b	C_6H_5	H	66	188° (ether)	$C_{27}H_{21}N_3O$ (403.5)	403
3c	4-Cl—C_6H_4	H	67	201° (ether)	$C_{27}H_{19}ClN_3O$ (437.5)	437
3d	*i*-C_3H_7	*i*-C_3H_7	19	129° (cyclohexane)	$C_{27}H_{29}N_3O$ (411.5)	411
3e	*cyclo*-C_6H_{11}	H	71	161° (CCl_4)	$C_{27}H_{27}N_3O$ (409.5)	409
3f	*n*-C_4H_9	H	50	143° (ethyl acetate)	$C_{25}H_{25}N_3O$ (383.5)	383
3g	4-H_3C—C_6H_4	H	78	182° (acetone)	$C_{28}H_{23}N_3O$ (417.5)	417
3h	4-H_3CO—C_6H_4	H	64	198° (ethyl acetate)	$C_{28}H_{23}N_3O_2$ (433.5)	—
3i	4-O_2N—C_6H_4	H	73	157° (CCl_4)	$C_{27}H_{20}N_4O_3$ (448.5)	448
3j	—$(CH_2)_2$—O—$(CH_2)_2$—		75	163° (cyclohexane)	$C_{25}H_{23}N_3O_2$ (397.5)	397

[a] All products gave satisfactory microanalyses (C ±0.4%, H ±0.3%, N ±0.4%).

Table 2. Spectral Data for Benzamidines **3**

Product	I.R. (KBr) ν [cm^{-1}][a] N—H	CH_{arom}	C=O	C=N	CH_2	C=C_{arom}	^{1}H-N.M.R. ($CDCl_3$) δ [ppm] H_{arom}	N—H	N—CH	>C—CH_2	>C—CH_3
3a	—	2930 (m)	1630 (s)	1550 (s)	1050 (m)	1590 (m)	7.5 (15H)	—	3.5 (4H)	1.7 (6H)	—
3b	3300 (s)	3050 (w)	1650 (s)	1540 (vs)	—	1585 (s)	7.5	5.8	—	—	—
3c	3230 (m)	3050 (w)	1650 (vs)	1530 (vs)	—	1580 (s)	7.5	—[b]	—	—	—
3d	—	2970 (w)	1650 (s)	1570 (vs)	1010 (m)	1600 (s)	7.5 (15H)	—	3.6 (2H)	—	1.4 (12H)
3e	3260 (m)	2990 (w)	1620 (s)	1550 (vs)	1040 (m)	1595 (s)	7.5 (15H)	5.1	3.8 (1H)	1.5 (10H)	—
3f	3270 (s)	2940 (m)	1620 (vs)	1515 (vs)	1025 (m)	1585 (s)	7.0–8.0 (15H)	5.4	3.3 (2H)	1.5–1.0 (7H)	
3g	3330 (m)	3010 (w)	1640 (vs)	1530 (vs)	1010 (s)	1590 (s)	7.0–8.0 (19H)	6.3	—	—	2.3 (3H)
3h	3210 (m)	3000 (w)	1625 (s)	1510 (vs)	1030 (s)	1600 (vs)	7.0–8.0 (19H)	—[b]	—	—	3.75 (3H)
3i	3250 (w)	3050 (w)	1630 (s)	1490 (vs)	1010 (s)	1600 (vs)	7.0–8.0 (15H)	5.1	4.1 (1H)	—	1.5 (6H)
3j	—	3050 (w)	1630 (s)	1550 (vs)	1015 (w)	1590 (s)	7.0–8.0 (15H)	—	3.5 (8H)		—

[a] vs = very strong; s = strong; m = medium; w = weak. [b] Not detected.

mixture is then cooled in ice/water and poured on to cold (0°) 1 molar aqueous sodium hydroxide solution (250 ml). The two phases are separated, the aqueous phase is reextracted with dichloromethane, the combined organic phases are dried ($MgSO_4$), and evaporated to dryness. The residue is recrystallised from a suitable solvent (see Table 1) to give the pure product **3**.

Hydrolysis of Products 3; Typical Procedure:

The benzamidine **3** ($R^1 = C_6H_5$, $R^2 = H$; 2 g, 0.005 mol) is dissolved in 6 normal hydrochloric acid (50 ml) and the solution is kept at room temperature for 72 h. It is then extracted with dichloromethane, the organic layer is dried and evaporated to give a crystalline residue. This is recrystallised from benzene to give pure dibenzoylamine (**5**); yield: 0.75 g (66%); m.p. and m.m.p. 147°; I.R. identical with an authentic sample[3].

The acidic layer is made alkaline with sodium hydroxide solution and extracted with dichloromethane. The organic layer is concentrated to give an oily residue. This is dissolved in 1 normal hydrochloric acid (150 ml), the solution is made alkaline with aqueous sodium hydroxide, and extracted with dichloromethane. The organic layer is dried and evaporated to an oily residue which is purified by column chromatography (silicagel 60/ethyl acetate). The product **4** is recrystallised twice from a little cyclohexane; yield: 0.2 g (20%); m.p. and m.m.p. 115°; I.R. identical with an authentic sample[10].

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