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The Synthesis of 1,3,5-Thiadiazinylium Salts

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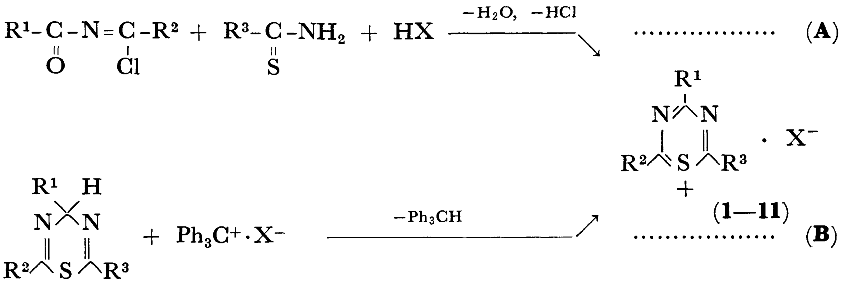
Synopsis. 1,3,5-Thiadiazinylium salts were synthesized in good yields by the reaction of *N*-acyl imidoyl chlorides with thioamides or the treatment of 4*H*-1,3,5-thiadiazines with trityl salts.

Heteroaromatic cation compounds, such as pyrylium, 1,3-oxazinylium salts, and their S-analogs, have been synthesized, and the reactions of these salts with various nucleophiles have been investigated to afford numerous derivatives. In these salts, the S-analog is stabler or less reactive than the corresponding O-analog. The present author has been studying the reaction of the 2,4,6-triphenyl-substituted compounds of these salts with active methylenes in order to ascertain the reactivity of these hetero rings.[1] 2,4,6-Triphenyl-1,3,5-oxadiazinylium salt has been known previously as the adduct of benzonitrile–benzoyl chloride–alminium chloride (2:1:1); since this salt is very hygroscopic, however, it is almost impossible to isolate as a pure salt.[2] On the other hand, the S-analog, 2,4,6-triphenyl-1,3,5-thiadiazinylium salt, has not yet been found, though this salt is supposed to be stabler than the corresponding O-analog. Therefore, it is expected that this salt may be obtained in a good purity if a synthetic route is found. 2-Amino-4,6-diphenyl-1,3,5-thiadiazinylium salts have been synthesized by Liebscher *et al.*[3] but his method is specific and almost impossible to apply to other 1,3,5-thiadiazinylium salts. In order to find the general synthetic method of 1,3,5-thiadiazinylium salts, several probable paths were offered by analogy with those of other known heteroaromatic cations, and their reaction conditions were checked. As a result, it was found that a number of 1,3,5-thiadiazinylium salts (**1**—**11**) were given by the paths, (**A**) and (**B**), shown in Scheme 1.

In Path **A**, *N*-acyl imidoyl chlorides reacted with thioamides in a strong acidic medium to produce cycloization products, **1**—**6**. In Path **B**, the starting



Scheme 1.

Table 1. 1,3,5-Thiadiazinylium salts (**1**—**11**)

Compd	R¹	R²	R³	X⁻	Yield/% Mp(dc)/°C	Found (Calcd) (%) C	H	N	S	IR(KBr)/cm⁻¹
1	C_6H_5-	C_6H_5-	C_6H_5-	ClO_4^-	87	58.93	3.55	6.56	7.26	1530, 1490, 1450,
					242	(59.09)	(3.54)	(6.56)	(7.51)	1390, 1340, 1080.
2	$(CH_3)_2N$-	$(CH_3)_2N$-	$(CH_3)_2N$-	ClO_4^-	81	32.92	5.53	21.44	9.78	1570, 1550, 1390,
					>300	(32.98)	(5.53)	(21, 36)	(9.78)	1370, 1080.
3	C_6H_5-	C_6H_5-	2-C_4H_3S-	ClO_4^-	78	52.57	3.04	6.47	14.85	1530, 1490, 1360,
					223	(52.72)	(3.03)	(6.47)	(14.81)	1330, 1080.
4	C_6H_5-	C_6H_5-	$C_6H_5CH_2S$-	ClO_4^-	60	55.58	3.71	5.81	13.74	1510, 1480, 1370,
					179	(55.87)	(3.67)	(5.92)	(13.56)	1330, 1080.
5	C_6H_5-	C_6H_5-	$(CH_3)_2N$-	ClO_4^-	46	51.90	4.11	10.70	8.07	1530, 1470, 1400,
					211	(51.84)	(4.10)	(10.67)	(8.14)	1340, 1080.
6	*p*-$CH_3C_6H_4$-	*p*-$CH_3C_6H_4$-	*p*-$CH_3C_6H_4$-	BF_4^-	63	62.88	4.64	6.14	7.04	1530, 1500, 1390,
					148	(63.17)	(4.64)	(6.14)	(7.03)	1330, 1170, 1050.
7	C_6H_5-	C_6H_5-	C_6H_5-	BF_4^-	81	60.73	3.70	6.85	7.95	1530, 1490, 1450,
					246	(60.89)	(3.65)	(6.76)	(7.74)	1390, 1350, 1050.
8	*p*-ClC_6H_4-	C_6H_5-	C_6H_5-	BF_4^-	56	56.60	3.44	5.98	7.02	1530, 1490, 1390,
					176	(56.22)	(3.14)	(6.24)	(7.15)	1350, 1050.
9	*p*-ClC_6H_4-	*p*-ClC_6H_4-	*p*-ClC_6H_4-	BF_4^-	40	48.81	2.59	5.40	6.21	1510, 1490, 1390,
					128	(48.73)	(2.34)	(5.41)	(6.19)	1340, 1220, 1050.
10	*p*-$CH_3OC_6H_4$-	C_6H_5-	$C_6H_5^-$	ClO_4^-	60	57.53	3.75	6.08	7.26	1510, 1480, 1450,
					148	(57.83)	(3.75)	(6.13)	(7.06)	1340, 1270, 1080.
11	*p*-$CH_3OC_6H_4$-	*p*-$CH_3OC_6H_4$-	*p*-$CH_3OC_6H_4$-	ClO_4^-	92	55.65	4.14	5.48	6.20	1530, 1500, 1440,
					261	(55.76)	(4.09)	(5.42)	(6.20)	1400, 1270, 1080.

materials, 4*H*-thiadiazines, were obtained by treating a mixture of aldehyde–nitrile–thioamide (1:1:1) with the BF_3–ether complex in chloroform[4] and then treated with trity salt to lead to **7**—**11**.

Satisfactory analytical data were obtained for all the compounds. Their IR spectra have four common characteristic absorptions at 1530–1330 cm^{-1} except for **2**. These salts are not so stable in a dilute solution, and consequently do not show exact UV spectra. The reaction of **1** or **7** with ammonia, hydrazine, or hydroxylamine gave 2,4,6-triphenyl-1,3,5-triazine, 3,5-dipenyl-1,2,4-triazole, or 3,5-diphenyl-1,2,4-oxadiazole respectively in good yields. These results show that the behavior of **1** or **7** toward these nucleophiles is in the same manner as the 2,4,6-triphenyl-1,3,5-oxadiazinylium salt.[5] It is thus confirmed that **1**—**11** are 1,3,5-thiadiazinylium salts.

Experimental

The Reaction of N-*Acyl Imidoyl Chloride with Thioamide.* Into a solution of *N*-acyl imidoyl chloride (0.011 mol) and thioamide (0.010 mol) in 15 ml of acetic anhydride, 1.2 ml of 70% perchloric acid or 2.4 ml of 40% tetrafluoroboric acid was stirred drop by drop, at room temperature for 10 min, the mixture was then allowed to stand at 0—5 °C for 2 d. The resulting precipitate was collected by filtration and then recrystallized from acetonitrile to give **1**—**6**. The data thus obtained are summarized in Table 1.

*The Reaction of 4*H*-Thiadiazine with Trityl Salt.* Into a stirred solution of 4*H*-thiadiazine (0.010 mol) in 20 ml of acetic anhydride, 0.012 mol of trityl perchlorate or tetrafluoroborate was added at room temperature for 15 min. The mixture was added to dry ether (10 ml), after which the mixture was allowed to stand 3 d at 0—5 °C. The resulting precipitate was collected by filtration and then washed with dry ether to give **7**—**11**. Their data are also given in Table 1.

*The Reaction of **1** or **7** with Ammonia, Hydrazine, or Hydroxylamine.* Into 10 ml of 28% ammonium hydroxide, 30% aqueous hydrazine, or a solution of $NH_2OH \cdot HCl$ (1.5 g) in 10 ml of 5 mol dm^{-3} NaOH, 1 mmol of **1** or **7** was stirred in small portions at 0—5 °C, after which the mixture allowed to stand at room temperature for 2 h. The resulting precipitate was filtered and recrystallized from acetic acid, ethanol, or methanol to give 2,4,6-triphenyl-1,3,5-triazine (87%, mp 233 °C), 3,5-diphenyl-1,2,4-triazole (78%, mp 192 °C), or 3,5-diphenyl-1,2,4-oxadiazole (71%, mp 108 °C) respectively. Their IR spectra were completely superimposed on those of the respective authentic samples.[2,6]

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