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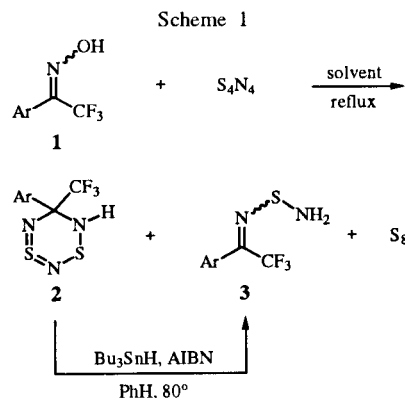
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The reactions of 1-aryl-2,2,2-trifluoroethanone oximes with tetrasulfur tetranitride (S_4N_4) in toluene at reflux gave 5-aryl-5-trifluoromethyl-4*H*-1,3,2,4,6-dithiatriazines **2**, 1-aryl-2,2,2-trifluoroethanonylidenedaminosulfenamides **3** and sulfur in 0-37%, 7-53%, and 2-41% yields, respectively. Treatment of **2** with tributyltin hydride in the presence of azobisisobutyronitrile in benzene at 80° afforded **3** in excellent yields.

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The utility of tetrasulfur tetranitride for synthesis of organoheterocyclic compounds with a high proportion of sulfur and nitrogen atoms has received much attention during the last three decades [1]. Among the compounds prepared are mainly confined to five-membered 1,2,5- and 1,2,4-thiadiazoles, six-membered 3,5-disubstituted 1,4,2,6-dithiatriazines and seven-membered 1,3,5,2,4-trithiadiazepines. Tetrasulfur tetranitride also reacts with olefines to give bisadducts formed by bonding between the olefinic carbons and sulfur atoms of tetrasulfur tetranitride. In addition, there are some five- and eight-membered organometallic compounds having nitrogen and sulfur atoms [1]. Recently we have studied the role of the halogen atom in the reactions of 1-aryl-2-haloethanones with tetrasulfur tetranitride. From the reactions with 1-aryl-2-haloethanones [2], and 1-arylethanone oximes [3] with at least two hydrogen atoms at α -carbon atom of the alkyl groups were obtained 3,5-diaroyl-1,2,4- and 3-aryl-1,2,5-thiadiazoles, respectively. By refluxing a mixture of tetrasulfur tetranitride and 1-aryl-2-chloroethanone oximes [4] in *p*-dioxane were able to be obtained 3-aryl-1,2,5-thiadiazoles in much better yields than the reported yields. Interestingly, 3-aryl-4-bromo-1,2,5-thiadiazoles as well as 3-aryl-1,2,5-thiadiazoles were obtained from the reactions of 1-aryl-2-bromoethanone oximes under the same conditions as with the chloro analogues [4].

As part of our studies on the reactions of 1-aryl-2-haloethanones and their oximes with tetrasulfur tetranitride, we have studied the reactions of 1-aryl-2,2,2-trifluoroethanones and their oximes with tetrasulfur tetranitride in toluene at reflux. Our results are described herein.



Results and Discussion.

The reactions with 1-aryl-2,2,2-trifluoroethanones such as 2,2,2-trifluoro-1-phenylethanone, 2,2,2-trifluoro-1-(4-methylphenyl)ethanone, and 2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone in toluene at reflux did not occur at all. However, the reaction of 2,2,2-trifluoro-1-

Table 1
Reactions of 2,2,2-Trifluoro-1-phenylethanone Oxime **1a** with Tetrasulfur Tetranitride in Various Solvents

Entry	1a (mmoles)	S_4N_4 [a] (mmoles)	Solvent	Time (hours)	2a	Yields (%) [b] 3a	S_8
1	2.99	3.00	benzene [c]	44	0	3	0.4
2	2.99	3.00	<i>p</i> -dioxane	130	24	8	12
3	3.99	4.00	toluene	25	34	13	22
4	2.99	3.00	chlorobenzene	25	11	22	23
5	2.99	3.00	<i>p</i> -xylene	21	18	9	5
6	2.99	3.00	anisole	6	6	17	51

[a] Tetrasulfur tetranitride. [b] Yield of isolated compounds. [c] Compound **1a** and tetrasulfur tetranitride were recovered in 38% and 43% yields, respectively.

Table 2
Reaction Conditions, Yields, and Analytical Data of 5-Aryl-5-trifluoromethyl-4*H*-1,3,2,4,6-dithiatriazines **2a-2i**

Substrate	Ar (mmoles)	S ₄ N ₄ [a] (mmoles)	Time (hours)	Product	Yield (%) [b]	mp (°C) [c]	Molecular Formula	Analyses, % Calcd./Found			
								C	H	N	S
1a	C ₆ H ₅ (3.99)	(4.00)	25	2a	34	80-81	C ₈ H ₆ N ₃ F ₃ S ₂ (265.27)	36.22	2.28	15.84	24.17
								36.41	2.28	15.69	23.98
1b	4-MeC ₆ H ₄ (3.08)	(3.02)	25	2b	37	liquid	C ₉ H ₈ N ₃ F ₃ S ₂ (279.30)	38.70	2.89	15.04	22.96
								38.86	2.89	14.92	22.86
1c	4-MeOC ₆ H ₄ (2.77)	(2.74)	23	2c	36	liquid	C ₉ H ₈ N ₃ OF ₃ S ₂ (295.30)	36.61	2.73	14.23	21.71
								36.75	2.76	14.16	21.65
1d	3-CF ₃ C ₆ H ₄ (4.78)	(4.78)	40	2d	17	liquid	C ₉ H ₅ N ₃ F ₆ S ₂ (333.27)	32.44	1.51	12.61	19.24
								32.61	1.58	12.45	19.15
1e	4-ClC ₆ H ₄ (2.15)	(2.07)	21	2e	19	liquid	C ₈ H ₅ N ₃ F ₃ S ₂ Cl (299.72)	32.06	1.68	14.02	21.39
								32.17	1.70	13.95	21.30
1f	4- <i>i</i> -PrC ₆ H ₄ (1.86)	(1.84)	11	2f	29	liquid	C ₁₁ H ₁₂ N ₃ F ₃ S ₂ (307.35)	42.99	3.94	13.67	20.86
								43.11	3.97	13.55	20.80
1g	3,4-Me ₂ C ₆ H ₃ (3.11)	(3.05)	7.5	2g	24	liquid	C ₁₀ H ₁₀ N ₃ F ₃ S ₂ (293.32)	40.95	3.44	14.33	21.86
								41.10	3.48	14.22	21.75
1h	[d] 3.00	(3.00)	30	2h	31	122-123	C ₁₄ H ₈ N ₃ OF ₃ S ₂ (355.35)	47.32	2.27	11.82	18.04
								47.49	2.30	11.70	17.99
1i	[e] 1.70	(1.69)	24	2i	24	164-166	C ₁₅ H ₁₀ N ₃ F ₃ S ₂ (353.38)	50.98	2.85	11.89	18.14
								51.11	2.89	11.75	18.05
1j	[f] 3.80	(3.80)	4	[g]							

[a] Tetrasulfur tetranitride. [b] Yield of isolated compounds. [c] Compounds **2a**, **2h**, and **2i** were recrystallized from *n*-hexane. Compounds **2b-2f** were yellowish green liquids. Compound **2g** was a green liquid. [d] Ar: Dibenzofuran-2-yl. [e] Ar: Fluoren-2-yl. [f] Ar: 1-Naphthalenyl. [g] From the reaction with **1j** was not obtained 5-trifluoromethyl-5-(1-naphthalenyl)-4*H*-1,3,2,4,6-dithiatriazine **2j**. Instead **3j** was obtained as a major product (Table 4).

phenylethanone oxime **1a** (Ar = C₆H₅) with tetrasulfur tetranitride in various solvents at reflux temperature gave 5-trifluoromethyl-5-phenyl-4*H*-1,3,2,4,6-dithiatriazine **2a** (Ar = C₆H₅), 2,2,2-trifluoro-1-phenylethanonylidenedaminosulfenamide **3a** (Ar = C₆H₅), sulfur, and unidentifiable complex

mixtures. Their yields were dependent on the solvent as shown in Table 1.

The reaction was monitored by the disappearance of the spot corresponding to **1a** on tlc (silica gel, carbon tetrachloride:chloroform = 1:1, v:v). It has been shown that the reaction

Table 3
Spectroscopic Data of **2a-2i**

Product	IR [a] ν (cm ⁻¹)	¹ H NMR (CDCl ₃) δ ppm, J (Hz)	MS m/z (%)
2a	3250, 1241, 1220-1110	3.68 (s, 1H, NH), 7.40-7.66 (m, 5H, ArH)	265 (M ⁺ , 22.4), 219 (81.0), 104 (100), 93 (22.5), 77 (51.6), 46 (33.8)
2b	3270, 1230-1130 (br, s)	2.38 (s, 3H, Me), 3.82 (s, 1H, NH), 7.37 (dd, 4H, J = 22, 6, ArH)	279 (M ⁺ , 16.7), 233 (52.2), 187 (23.0), 118 (100), 91 (23.5), 46 (6.6)
2c	3250, 1210-1130 (br, s)	3.86 (s, 4H, NH and MeO), 7.23 (dd, 4H, J = 48, 8, ArH)	295 (M ⁺ , 8.2), 279 (19.2), 249 (20.3), 233 (49.2), 203 (65.2), 187 (26.3), 134 (63.5), 118 (100), 91 (26.9)
2d	3250, 1230-1100	3.93 (s, 1H, NH), 7.48-7.90 (m, 4H, ArH)	333 (M ⁺ , 9.8), 287 (36.6), 222 (100), 172 (53.6), 145 (34.3), 93 (25.3), 75 (10.3), 46 (10.5)
2e	3270, 1230-1120	3.82 (s, 1H, NH), 7.40-7.60, (m, 4H, ArH)	299 (M ⁺ , 3.8), 253 (45.4), 207 (12.3), 140 (32.2), 138 (100), 111 (45.1), 93 (23.3), 75 (28.7), 46 (20.2)
2f	3280, 1211-1113	1.25 (d, 6H, J = 8, 2Me), 2.92 (hep, 1H, J = 6, CH), 3.81 (s, 1H, NH), 7.38 (dd, 4H, J = 20, 8, ArH)	307 (M ⁺ , 3.3), 261 (11.2), 215 (19.0), 214 (100), 200 (32.1), 146 (45.0), 130 (20.9), 103 (10.0)
2g	3280, 1220-1120	2.25 (s, 6H, 2Me), 3.80 (s, 1H, NH), 7.17-7.37 (m, 3H, ArH)	293 (M ⁺ , 10.2), 247 (20.0), 201 (40.7), 132 (80.2), 118 (18.5), 105 (13.2), 83 (100), 77 (18.5)
2h	3270, 1220-1120	3.88 (s, 1H, NH), 7.20-8.20 (m, 7H, ArH)	355 (M ⁺ , 6.4), 309 (15.7), 263 (78.3), 194 (100), 167 (14.9), 139 (47.0)
2i	3260, 1220-1120	3.83 (s, 3H, NH and CH ₂), 7.20-7.87 (m, 7H, ArH)	353 (M ⁺ , 20.0), 307 (8.2), 261 (100), 192 (65.3), 165 (48.9), 149 (58.9)

[a] The ir spectra of compounds **2a-2g** were taken in thin films of potassium bromide but those of compounds **2h** and **2i** were taken in potassium bromide discs.

was completed in a shorter time in aromatic solvents with a higher boiling point without regard to the yields of **2a** and **3a**. It appears that benzene is not an appropriate solvent because of its low boiling point (entry 1). The reaction in toluene at reflux gave **2a** in 34% yield (entry 3) which was better than the yields in other higher boiling solvents (entries 4-6) where the reactions proceeded to give undesired complex mixtures. *p*-Dioxane with a comparable boiling point to toluene was inferior to toluene with respect to both of the reaction time and yield (entry 2). Therefore, toluene was used as a solvent for the reactions of other 1-aryl-2,2,2-trifluoroethanone oximes **1** with tetrasulfur tetranitride. The yields and analytical data of the compounds **2** are summarized in Table 2 and their spectroscopic data in Table 3. The yields, spectroscopic, and analytical data of the compounds **3** are summarized in Table 4.

Compounds **2** and **3** are all new. The hydrogen atom of N-H group of **2** is exchangeable with deuterium oxide in deuteriochloroform. The ^{19}F nmr spectrum of **2a** exhibited

only a singlet at -23.63 ppm, which indicated no special interaction such as hydrogen bonding with a hydrogen on the nitrogen atom. ^{13}C nmr showed 6 peaks at 138.8, 130.0, 129.1, 128.2, 124.6, and 118.9 ppm. The molecular structure of **2a** is shown in Figure 1 together with the atom-numbering scheme. Atomic coordinates and anisotropic thermal parameters of nonhydrogen atoms are listed in Table 5 and 6, respectively. Bond distances and bond angles of **2a** are tabulated in Table 7 and 8, respectively. The crystal structure clearly shows the compound being a heterocyclic rather than an acyclic compound [5].

Compounds **2** have the same skeleton as that of eight π -electron antiaromatic 1,3,2,4,6-dithiazines which have been of interest in recent years [6-7]. In contrast, compounds **2** are neither aromatic nor planar due to the presence of a sp^3 hybrid carbon atom having two substituents at C-5.

Compound **2a** is inert toward acids such as concentrated hydrochloric acid and trifluoroacetic acid in

Table 4
Yields, Spectroscopic, and Analytical Data of 1-Aryl-2,2,2-trifluoroethanonylidenediaminosulfenamides **3a-3j**

Substrate	Ar	Yield (%) [a]	mp (°C) [b]	IR ν (cm^{-1})	^1H NMR (CDCl_3) δ ppm, J (Hz)	Molecular Formula	Analyses, % Calcd./Found			
							C	H	N	S
3a	C_6H_5	13 (91)	liquid	3400, 3300 (br, s), 1200-1100 (br, s)	3.80 (s, 2H, NH_2), 7.45 (s, 5H, ArH)	$\text{C}_8\text{H}_7\text{N}_2\text{F}_3\text{S}$ (220.21)	43.63	3.20	12.72	14.56
							43.74	3.25	12.56	14.66
3b	4-Me C_6H_4	22 (99)	liquid	3430, 3330, 1190, 1140	2.37 (s, 3H, Me), 3.75 (s, 2H, NH_2), 7.30 (s, 4H, ArH)	$\text{C}_9\text{H}_9\text{N}_2\text{F}_3\text{S}$ (234.24)	46.15	3.87	11.96	13.69
							46.22	3.90	11.85	13.57
3c	4-MeOC $_6\text{H}_4$	10 (88)	liquid	3400, 3300, 1220-1100	3.86 (s, 5H, NH_2 and MeO), 7.23 (dd, 4H, J = 40, 8, ArH)	$\text{C}_9\text{H}_9\text{N}_2\text{OF}_3\text{S}$ (250.24)	43.20	3.62	11.19	12.81
							43.28	3.64	11.11	12.78
3d	3-CF $_3\text{C}_6\text{H}_4$	8	liquid	3420, 3320, 1220-1100	3.85 (s, 2H, NH_2), 7.41-7.70 (m, 4H, ArH)	$\text{C}_9\text{H}_6\text{N}_2\text{F}_6\text{S}$ (288.21)	37.51	2.10	9.72	11.12
							37.62	2.11	9.60	11.03
3e	4-Cl C_6H_4	14 (94)	liquid	3425, 3325, 1220-1100	3.80 (s, 2H, NH_2), 7.40 (s, 4H, ArH)	$\text{C}_8\text{H}_6\text{N}_2\text{F}_3\text{SCl}$ (254.66)	37.73	2.37	11.00	12.59
							37.84	2.40	10.89	12.48
3f	4- <i>i</i> -Pr C_6H_4	11 (92)	liquid	3400, 3300, 1190, 1130	1.25 (d, 6H, J = 8, 2Me), 2.90 (hep, 1H, J = 8, CH), 3.77 (s, 2H, NH_2), 7.20-7.45 (m, 4H, ArH)	$\text{C}_{11}\text{H}_{13}\text{N}_2\text{F}_3\text{S}$ (262.29)	50.37	5.00	10.68	12.22
							50.45	4.95	10.60	12.15
3g	3,4-Me $_2\text{C}_6\text{H}_3$	9 (88)	liquid	3410, 3310, 1240, 1215, 1190, 1130	2.30 (s, 6H, 2Me), 3.74 (s, 2H, NH_2), 7.19 (s, 3H, ArH)	$\text{C}_{10}\text{H}_{11}\text{N}_2\text{F}_3\text{S}$ (248.27)	48.38	4.47	11.28	12.91
							48.45	4.49	11.19	12.88
3h	[c]	17 (84)	109-110.5	3425, 3325, 1200, 1165, 1125	3.82 (s, 2H, NH_2), 7.22-8.05 (m, 7H, ArH)	$\text{C}_{14}\text{H}_9\text{N}_2\text{OF}_3\text{S}$ (310.29)	54.19	2.92	9.03	10.33
							54.25	2.95	8.95	10.21
3i	[d]	6 (99)	106-108	3410, 3310, 1210, 1121	3.76 (s, 2H, NH_2), 3.90 (s, 2H, CH_2), 7.23-7.87 (m, 7H, ArH)	$\text{C}_{15}\text{H}_{11}\text{N}_2\text{F}_3\text{S}$ (308.32)	58.43	3.60	9.09	10.40
							58.50	3.61	9.01	10.30
3j	[e]	53	liquid	3410, 3300, 1240-1110	3.55 (s, 2H, NH_2), 7.35-8.00 (m, 7H, ArH)	$\text{C}_{12}\text{H}_9\text{N}_2\text{F}_3\text{S}$ (270.27)	53.33	3.36	10.36	11.86
							53.36	3.40	10.41	11.88

[a] Yield of isolated compounds. Numbers in the parenthesis represent the yield of **3** obtained from the reactions of **2** with tributyltin hydride in benzene at 80°. [b] Compounds **3h** and **3i** were white and yellow solids, respectively and recrystallized from *n*-hexane. Compounds **3a-3d**, **3f**, and **3g** were greenish liquids and compound **3e** was a colorless liquid. Compound **3j** was a reddish brown liquid. [c] Ar: Dibenzofuran-2-yl. [d] Ar: Fluoren-2-yl. [e] Ar: 1-Naphthalenyl.

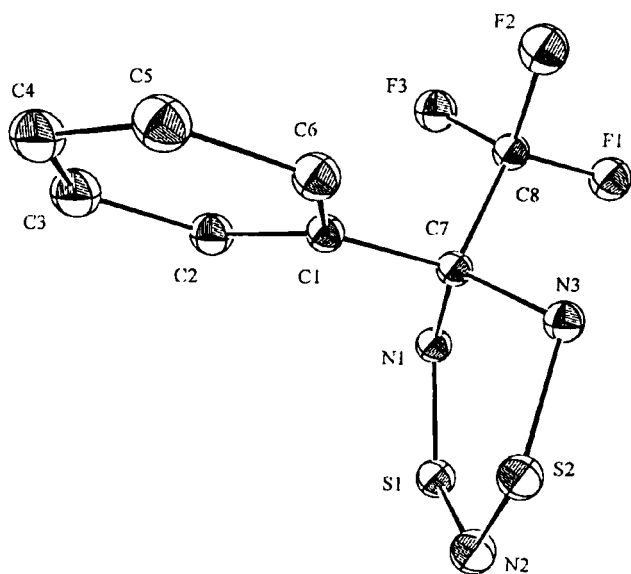


Figure 1. Drawing of 5-Trifluoromethyl-5-phenyl-4H-1,3,2,4,6-dithiazine (**2a**).

methylene chloride at room temperature and does not react with 4-biphenylcarbonyl chloride in the presence of triethylamine in methylene chloride either at room or

Table 5
Atomic Positional Parameters of Nonhydrogen Atoms for **2a**

Atom	X	Y	Z
S1	0.6954	-0.0958	0.0829
S2	0.9564	0.0529	0.2579
N1	0.6142	-0.1324	0.1490
N2	0.8658	-0.0047	0.1350
N3	0.7880	0.0235	0.3055
F1	0.4271	-0.0536	0.2895
F2	0.6081	-0.0644	0.3998
F3	0.4591	-0.1959	0.2605
C1	0.8422	-0.1401	0.2736
C2	0.8228	-0.2397	0.2077
C3	0.9462	-0.2881	0.2278
C4	1.0820	-0.2405	0.3137
C5	1.1008	-0.1424	0.3817
C6	0.9810	-0.0911	0.3635
C7	0.7060	-0.0878	0.2549
C8	0.5513	-0.1003	0.3020

reflux temperature.

However, compounds **2** are readily converted to the corresponding compounds **3** in excellent yields by treatment with tributyltin hydride (6 molar equivalents) in the presence of catalytic amount of azobisisobutyronitrile in benzene under nitrogen atmosphere at 80°. The reactions were completed in 1 hour. The yields of compounds **3** are listed in the parenthesis in Table 4.

Treatment of **2a** with a lesser amount of tributyltin hydride (2 molar equivalents) for even a longer reaction time (2.5 hours) under foregoing conditions gave **3a** in

Table 6
Anisotropic Thermal Parameters of **2a**

Atom	U (1,1)	U (2,2)	U (3,3)	U (1,2)	U (1,3)	U (2,3)
S1	0.06005	0.06815	0.06181	0.01708	0.02279	0.04070
S2	0.04426	0.04944	0.09120	0.00891	0.02209	0.04131
N1	0.03679	0.05434	0.05674	0.00426	0.01184	0.03050
N2	0.06103	0.06810	0.08642	0.01761	0.03800	0.04938
N3	0.04821	0.04143	0.06360	0.00854	0.01792	0.02999
F1	0.05389	0.08790	0.11513	0.03712	0.04381	0.07028
F2	0.07347	0.09020	0.06906	0.03129	0.03790	0.04563
F3	0.06535	0.06113	0.10149	0.01055	0.04078	0.04909
C1	0.04101	0.04023	0.05156	0.01181	0.02122	0.02654
C2	0.06929	0.04283	0.07074	0.01979	0.03521	0.03020
C3	0.07634	0.05576	0.09432	0.03148	0.04269	0.04392
C4	0.06228	0.06865	0.09571	0.02885	0.04214	0.05323
C5	0.05439	0.07193	0.08190	0.02827	0.02106	0.04940
C6	0.04896	0.06045	0.06182	0.01689	0.01502	0.03570
C7	0.03992	0.03817	0.05042	0.00714	0.01320	0.02528
C8	0.04956	0.05457	0.05654	0.01849	0.02208	0.03271

Table 7
Bond Distances in Angstroms for **2a**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	N1	1.557	C1	C7	1.504
S1	N2	1.545	C2	C3	1.391
S2	N2	1.657	C3	C4	1.348
S2	N3	1.700	C4	C5	1.370
N1	C7	1.455	C5	C6	1.395
N3	C7	1.503	C7	C8	1.534
C1	C2	1.379	F1	C8	1.399
C1	C6	1.399	F2	C8	1.323
			F3	C8	1.328

Table 8
Bond Angles in Degree for **2a**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	S1	N2	118.0	N1	C7	N3	113.0
N2	S2	N3	105.8	N1	C7	C1	112.7
S1	N1	C7	120.7	N1	C7	C8	104.1
S1	N2	S2	120.7	N3	C7	C1	111.9
S2	N3	C7	111.8	N3	C7	C8	104.9
C2	C1	C6	118.5	C1	C7	C8	109.6
C2	C1	C7	121.0	F1	C8	F2	105.8
C6	C1	C7	120.2	F1	C8	F3	105.3
C1	C2	C3	120.3	F1	C8	C7	112.5
C2	C3	C4	121.2	F2	C8	F3	107.5
C3	C4	C5	119.6	F2	C8	C7	113.5
C4	C5	C6	120.9	F3	C8	C7	111.7
C1	C6	C5	119.4				

decreased yield (64%). Compound **3a** was also formed in 76% yield under the foregoing conditions. The yield of **3a** was dependent on the concentration of tributyltin hydride in tetrahydrofuran as shown in Table 9.

In the presence of 2 molar equivalents of tributyltin hydride were obtained **3a** in 33% yield with recovery of **2a** in 45% yield (entry 1). The yield of **3a** increased to

Table 9

Reactions of 5-Trifluoromethyl-5-phenyl-4*H*-1,3,2,4,6-dithiaziazine (2a) with Tributyltin Hydride in Tetrahydrofuran at Reflux [a]

Entry	2a (mmoles)	Bu ₃ SnH [b] (mmoles)	Time (hours)	TF	Yield(%) [c]		HBDT
					2a	3a	
1	0.403	0.805	20		45	33	66
2	0.442	1.786	18		25	51	39
3	0.431	2.586	18	20	0	77	40
4	0.416	3.328	17	17	0	61	29
5	0.424	2.544	20	27	18	47	27

[a] Azobisisobutyronitrile (AIBN) (10 mg) was used for the reactions of entries 1-4 and no AIBN was used for the reaction of entry 5.

[b] Bu₃SnH: Tributyltin hydride. [c] Yield of isolated compounds by chromatography. TF: 2,2,2-Trifluoro-1-phenylethanone. HBDT: Hexabutyliditin.

77% with the increase of the concentration of tributyltin hydride to 6 molar equivalents (entry 3). Further increase (8 molar equivalents) of the concentration of tributyltin hydride, however, brought about decreased yield of 3a in 61% yield (entry 4). This propensity for the change in the yields of the compound 3a with the concentration of tributyltin hydride indicates that at least 6 molar equivalents of tributyltin hydride have to be used to obtain better yields of 3 from 2 in tetrahydrofuran. Noteworthy is the formation of 2,2,2-trifluoro-1-phenylethanone (TF) at the expense of the compound 2a when more than 6 molar equivalents of tributyltin hydride were used (entries 3, 4). In order to see if 2,2,2-

trifluoro-1-phenylethanone is formed *via* an intermediate produced by the reaction of compound 2a with tributyltin hydride, or formed from the continuous reaction of compound 3a in the presence of a large excess of tributyltin hydride, compound 3a (0.45 mmole) was treated with tributyltin hydride (2.70 mmoles) in the presence of azobisisobutyronitrile (10 mg) in tetrahydrofuran for 17 hours at reflux, which is a comparable condition with that for the reaction of entry 3 (Table 3). From the reaction was obtained 2,2,2-trifluoro-1-phenylethanone and 3a in 3% and 73% yield, respectively along with a mixture of compounds (466 mg) (*vide infra*). This result clearly indicates that the major pathway leading to 2,2,2-trifluoro-1-phenylethanone (entries 3-4) is not the secondary reaction of compound 3a associated with a large excessive amount of tributyltin hydride. Presumably it might be formed *via* hydrolysis of an intermediate of which structure has not been characterized. The yield of 3a decreased to 47% without azobisisobutyronitrile (entry 5), which is the same propensity for the reaction carried out in benzene (*vide supra*). The recovery of 2a in 18% yield in the absence of azobisisobutyronitrile (entry 5), whereas no recovery of the same compound in the presence of azobisisobutyronitrile (entry 3) suggests that a radical mechanism is involved for the formation of compounds 3 from compounds 2. Tlc of the reaction mixture obtained from the reaction of 2a with tributyltin hydride showed two spots corresponding to hexabutyliditin (R_f = 0.95, *n*-hexane) and aminosulfenamide

Table 10

Spectroscopic and Analytical Data of 1-Aryl-2,2,2-trifluoroethanone Oximes 1a-1j

Substrate	Ar	IR ν (cm ⁻¹)	¹ H NMR (CDCl ₃) δ ppm, J (Hz)	mp [°C] [d]	Molecular Formula or Lit mp (°C)	Analyses, % Calcd./Found		
						C	H	N
1a	C ₆ H ₅			85-86	83-84 [17]			
1b	4-MeC ₆ H ₄	3296, 1264, 1193, 1142	2.39 (s, 3H, Me), 7.35 (dd, 4H, J = 14, 8, ArH), 8.15 (s, 1H, OH)	89-90	C ₉ H ₈ NOF ₃ 62 [17]	53.21 53.26	3.97 3.99	6.89 6.85
1c	4-MeOC ₆ H ₄			104-106	105 [17]			
1d	3-CF ₃ C ₆ H ₄	3350, 1230-1120	7.42-7.95 (m, 4H, ArH), 9.29 (s, 1H, OH)	65-66	C ₉ H ₅ NOF ₆ (257.14)	42.04 42.02	1.96 1.97	5.45 5.48
1e	4-ClC ₆ H ₄	3300, 1210, 1140	7.45 (s, 4H, ArH), 8.80 (s, 1H, OH)	62-63	C ₈ H ₅ NOF ₃ Cl (223.58)	42.98 42.90	2.25 2.29	6.26 6.19
1f	4- <i>i</i> -PrC ₆ H ₄	3328, 1273, 1184, 1139	1.23 (d, 6H, J = 8.0, 2Me), 2.90 (hep, 1H, J = 8.0, -CH-), 7.37 (dd, 4H, J = 18, 8, ArH), 9.45 (s, 1H, OH)	liquid	C ₁₁ H ₁₂ NOF ₃ (231.22)	57.14 57.20	5.23 5.20	6.06 6.01
1g	3,4-Me ₂ C ₆ H ₃	3300, 1290, 1200, 1140	2.30 (s, 6H, 2Me), 7.22 (s, 3H, ArH), 8.87 (s, 1H, OH)	86-88	C ₁₀ H ₁₀ NOF ₃ (217.19)	55.30 55.40	4.64 4.68	6.45 6.50
1h	[a]	3300, 1250, 1190, 1170, 1155, 1139	7.26-8.10 (m, 7H, ArH), 8.55 (s, 1H, OH)	161-163	C ₁₄ H ₈ NO ₂ F ₃ (279.22)	60.22 60.15	2.89 2.91	5.02 5.09
1i	[b]	3300, 1245, 1210, 1150	3.95 (s, 2H, CH ₂), 7.29- 7.88 (m, 7H, ArH)	175-177	C ₁₅ H ₁₀ NOF ₃ (277.25)	64.98 65.11	3.64 3.66	5.05 4.96
1j	[c]	3300, 1233, 1210-1120	7.34-8.02 (m, 7H, ArH), 9.22 (s, 1H, OH)	62-64	C ₁₂ H ₈ NOF ₃ (239.20)	60.26 60.30	3.37 3.38	5.86 5.82

[a] Ar: Dibenzofuran-2-yl. [b] Ar: Fluoren-2-yl. [c] Ar: 1-Naphthalenyl. [d] All compounds 1a-1e and 1g-1j were recrystallized from ethanol.

Table 11

Reaction Conditions and Yields of **3** and Hexabutyliditin obtained from the Reactions of **2** with Tributyltin Hydride in the Presence of Azobisisobutyronitrile [a]

Substrate	Ar (mmole)	Bu ₃ SnH (mmole) [d]	Time (hours)	Product	Yield (%) [e]	(Bu ₃ Sn) ₂ % [f]
2a	C ₆ H ₅ (0.426)	2.53	1	3a	91	45
2a	C ₆ H ₅ (0.419)	0.818	2.5	3a	64 [g]	49
2b	4-MeC ₆ H ₄ (0.358)	2.12	1	3b	99	23
2c	4-MeOC ₆ H ₄ (0.339)	2.03	1	3c	88	59
2e	4-ClC ₆ H ₄ (0.167)	1.00	1	3e	94	45
2f	4- <i>i</i> -PrC ₆ H ₄ (0.358)	2.12	1	3f	92	34
2g	3,4-Me ₂ C ₆ H ₃ (0.410)	2.45	1	3g	88	62
2h	[b] (0.299)	2.16	1	3h	84	48
2i	[c] (0.289)	1.75	1	3i	99	52

[a] Benzene was used as a solvent and 0.061 mmole of azobisisobutyronitrile was used in each case. [b] Ar: Dibenzofuran-2-yl. [c] Ar: Fluoren-2-yl. [d] Bu₃SnH: Tributyltin hydride. [e] Yield of isolated compounds. [f] (Bu₃Sn)₂: Hexabutyliditin. [g] 2,2,2-Trifluoro-1-phenylethanone was isolated in 27% yield.

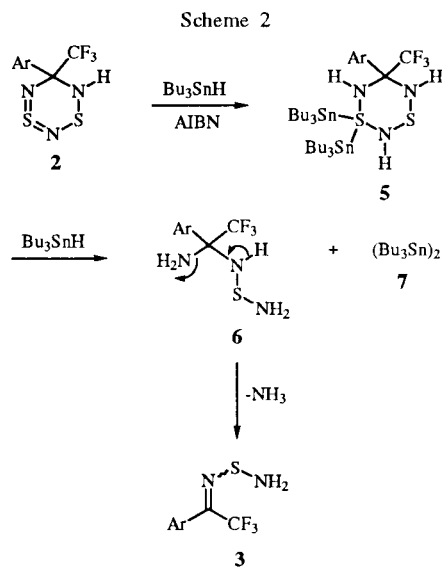
3a ($R_f = 0.09$, *n*-hexane) in addition to a spot at the origin. Since no spot corresponding to sulfur was observed on tlc, one might assume two possibilities on the fate of sulfur consisting of compound **2a**. That is, the original spot on tlc might be due to sulfur-containing compounds, or bis(tributyltin) sulfide which is expected to be formed as a byproduct show its R_f value close to that of hexabutyliditin so that it would be misjudged as a single spot on tlc. Consequently, bis(tributyltin) sulfide was synthesized according to the literature [8] and its ¹H nmr and ir spectra were compared with those of the mixture isolated from the reaction of **2a** with tributyltin hydride. The spectra were almost identical but the R_f value (0.86, *n*-hexane) of the authentic bis(tributyltin) sulfide was slightly smaller than that of the mixture ($R_f = 0.95$, *n*-hexane). When the authentic bis(tributyltin) sulfide was subjected to column chromatography to remove some impurities contaminated with it, it decomposed to give hexabutyliditin and sulfur, which could be identified by isolation of the two compounds.

In contrast, the reaction of **2a** with triphenyltin hydride under the same conditions as with tributyltin hydride gave bis(triphenyltin) sulfide isolable by chromatography. Chromatography of the reaction mixture using carbon tetrachloride as an eluent afforded a mixture, which showed two melting points at near 135° and 227-230°. In order to avoid possible decomposition of bis(triphenyltin) sulfide on silica gel, a direct recrystallization of the reaction mixture from a mixture of *n*-hexane and carbon tetrachloride was performed. The first crop was hexaphenyliditin. Removal of the solvent from the filtrate, followed by a repeated recrystallization of the residue from carbon tetrachloride gave bis(triphenyltin) sulfide of which structure was confirmed by its melting point [9] and spectroscopic (¹H nmr, ir) data. Therefore, it may be reasonable to assume the formation of bis(tributyltin) sulfide as one of the products and the formation of hexa-

butyliditin and sulfur by decomposition of bis(tributyltin) sulfide in the conversion of **2a** to **3a** by tributyltin hydride.

The compound having a *N*-(aminosulfonyl)imino functionality analogous to **3** is seldom reported. To the best of our knowledge, 9-fluorenylideneaminosulfenamide, which was prepared from the reactions of tetrasulfur tetranitride with 9-phenylthiofluorenyllithium [10], 9-fluororenimine, or 9-fluorenoxime [11] is the only example in the literature.

The mechanism for the formation of compounds **2** from the reaction of compounds **1** with tetrasulfur tetranitride is just speculative at this moment as in many other reactions with tetrasulfur tetranitride. Also more information is needed to delineate the mechanism of the formation of compounds **3** from compounds **2**. However, one might conceive a double tributylstannylation to two S=N bonds to give an intermediate **5**, which subsequently undergoes



decomposition to give an aminal **6** and bis(tributyltin) sulfide **7**. Ketoaminals without α -hydrogens are generally known to be stable for isolation [12]. Nevertheless, aminals from primary aromatic amines have seldom reported and primary aliphatic amines are reported not to give stable aminals [13].

Therefore, the aminal **6** is expected to be quite unstable and to lose ammonia molecule leading to compound **3** if it is involved as an intermediate.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded at 80 MHz in deuteriochloroform solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded in potassium bromide or thin films on potassium bromide plates. Mass spectra were obtained using HP 5890 A (GC) with HP 5970 (MSD) mass spectrometer. Microanalyses were performed by Perkin-Elmer 240 DS and Carlo Erbra 1106. Column Chromatography was performed using silica gel (230-400 mesh, Merck). X-Ray crystallographic analysis was determined by the Korea Air Force Academy. Melting points are uncorrected.

Tetrasulfur tetranitride (S_4N_4) was prepared by the reaction of sulfur monochloride with ammonia gas at room temperature [1]. 2,2,2-Trifluoro-1-phenylethanone and 2,2,2-trifluoro-1-(3-trifluoromethylphenyl)ethanone were purchased from Aldrich. 2,2,2-Trifluoro-1-(4-methylphenyl)ethanone [14], 2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone [14], 1-(dibenzofuran-2-yl)-2,2,2-trifluoroethanone [14], 2,2,2-trifluoro-1-(3,4-dimethylphenyl)ethanone [14], 1-(fluoren-2-yl)-2,2,2-trifluoroethanone [14], 1-(4-chlorophenyl)-2,2,2-trifluoroethanone [14], 2,2,2-trifluoro-1-(1-naphthalenyl)ethanone [15], 2,2,2-trifluoro-1-(4-isopropylphenyl)ethanone [14] were prepared by the literature methods. Various ketoximes were prepared by the standard method [16]. Spectroscopic and analytical data of ketoximes **1a-1j** are summarized in Table 10.

General Procedure for the Reactions of Tetrasulfur Tetranitride with **1**.

A mixture of **1** (2-4 mmole) and equimolar amount of tetrasulfur tetranitride in toluene (30 ml) was refluxed until no spot corresponding to **1** was observed on tlc (silica gel, carbon tetrachloride: chloroform = 1:1, v:v). After the reaction was completed, the solution became pale red. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (2.5 x 5.0 cm). Elution with *n*-hexane gave sulfur and unused tetrasulfur tetranitride. In addition, the reaction with **1c**, **1f**, and **1h** gave 2,2,2-trifluoro-1-(4-methoxyphenyl)ethanone (28%), 2,2,2-trifluoro-1-(4-isopropylphenyl)ethanone (20%), and 1-(dibenzofuran-2-yl)-2,2,2-trifluoroethanone (30%), respectively, which were eluted with *n*-hexane. Elution with carbon tetrachloride gave 5-aryl-5-trifluoromethyl-4*H*-1,3,2,4,6-dithiatriazines **2**. The reaction with **1i** gave 1-(fluoren-2-yl)-2,2,2-trifluoroethanone (41%) and 1-(fluoren-2-yl)-2,2,2-trifluoroethanonylidenediaminosulfenamide (**3i**), which were eluted with carbon tetrachloride. Elution next with chloroform gave 1-aryl-2,2,2-trifluoroethanonylidenediaminosulfenamides **3**. In each case, consult Table 2 and 3 for reaction conditions, yields, and

analytical data and spectroscopic data of compounds **2**, respectively. Yields, spectroscopic, and analytical data of compounds **3** are summarized in Table 4.

General Procedure for the Reactions of 5-Aryl-5-trifluoromethyl-4*H*-1,3,2,4,6-dithiatriazines **2** with Tributyltin Hydride in the Presence of Azobisisobutyronitrile.

To a solution of **2** in dried benzene (20 ml) were added tributyltin hydride (6 molar equivalents) and azobisisobutyronitrile (10 mg), which was heated at reflux under nitrogen atmosphere until no spot corresponding to **2** was observed on tlc. The reaction mixture was cooled to room temperature, followed by addition of water (20 ml), which was extracted with ether (50 ml x 2). The extract was dried over magnesium sulfate. After removal of the solvent, the residue was chromatographed on silica gel (230-400 mesh, 2 x 3 cm). Elution with *n*-hexane and chloroform gave hexabutylditin and 1-aryl-2,2,2-trifluoroethanonylidenediaminosulfenamides **3**, respectively. In each case, consult Table 11 for reaction conditions, yields of **3a-3i** and hexabutylditin.

General Procedure for the Reaction of **2a** with Tributyltin Hydride in Tetrahydrofuran in the Presence of Azobisisobutyronitrile.

To a solution of **2a** (0.4 mmole) in dried tetrahydrofuran (20 ml) were added tributyltin hydride (0.8-2.5 mmole) and azobisisobutyronitrile (10 mg), which was heated at reflux under nitrogen atmosphere until no spot corresponding to **2a** was observed on tlc. The reaction mixture was worked up as with the reaction carried out in benzene. In each case, consult Table 9 for reaction conditions, yields of **3a**, 2,2,2-trifluoro-1-phenylethanone, and hexabutylditin.

Attempted Synthesis of Bis(tributyltin) Sulfide.

To a cooled solution of tributyltin chloride (1.0 g, 3.1 mmole) in petroleum ether (bp 35-60°, 30 ml) in an ice-water bath was added a solution of sodium hydrosulfide hydrate (866 mg) in water (20 ml), which was stirred for 5 hours at 0°. The organic layer was separated and dried on anhydrous magnesium sulfate. The tlc of the mixture showed a major spot ($R_f = 0.86$, *n*-hexane) with a long tail. After removal of the solvent, the residue (0.8 g) was chromatographed on silica gel (230-400 mesh, 2.0 x 3.0 cm) during which time unpleasant smell was generated. Elution with *n*-hexane as an eluent gave an oily mixture of sulfur and hexabutylditin ($R_f = 0.95$, *n*-hexane) from which sulfur was solidified.

Reaction of **2a** with Triphenyltin Hydride in the Presence of Azobisisobutyronitrile.

From the reaction of **2a** (104 mg, 0.392 mmole) with triphenyltin hydride (820 mg, 2.34 mmole) and azobisisobutyronitrile (10 mg) in benzene for 2 hours were obtained a mixture which showed two major spots ($R_f = 0.77$ and 0.42) on tlc (silica gel, carbon tetrachloride:chloroform = 1:1, v:v). The mixture was chromatographed on silica gel (230-400 mesh, 2.0 x 3.0 cm). Elution with carbon tetrachloride (50 ml) gave a mixture (450 mg) which showed two melting points at 135° and 227-230°. Continued elution with methylene chloride (50 ml) gave **3a** (56 mg, 65%). The mixture showing two melting points was recrystallized from a mixture of *n*-hexane and carbon tetrachloride. White crystals ($R_f = 0.82$, carbon tetrachloride:chloroform = 1:1, v:v) formed first were filtered. The crystals melted at 229-231°,

identified to be hexaphenylditin (lit [18] mp 232°); ^1H nmr (deuteriochloroform, 80 MHz): δ 7.20-7.80 (m, 30 H, ArH); ir (potassium bromide): ν 3040, 1577, 1475, 1417, 1331, 1299, 1190, 1158, 1075, 1020, 995, 729, 694, and 400 cm^{-1} . The solvent from the filtrate was evaporated to give a residue, which was recrystallized from carbon tetrachloride to give another white solid, mp 135-137°. Repeated recrystallization from the same solvent afforded a pure compound ($R_f = 0.77$, carbon tetrachloride:chloroform = 1:1, v:v), mp 138-140°, identified as bis(triphenyltin) sulfide (lit [11] mp 141.5-143°); ^1H nmr (deuteriochloroform, 80 MHz): δ 7.00-7.50 (m, 30H, ArH); ir (potassium bromide): ν 3056, 1574, 1478, 1427, 1331, 1299, 1260, 1187, 1158, 1072, 1024, 998, 915, 857, 729, 697, and 441 cm^{-1} .

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