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Preparation and Conversion of Aminodiphenylcyclopropenium Salts to 1,2,3-Triazines

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Synopsis. Diphenylcyclopropenone gave aminodiphenylcyclopropenium fluorosulfate (**3**) by ethylation with ethyl fluorosulfate, followed by treating with secondary amine in one-pot operation. The salt **3** reacted with sodium azide to afford 1,2,3-triazine in a good yield.

In a continuation of our studies of the monoalkylthiocyclopropenium salts,[1)] we have become interested in the chemistry of monoaminocyclopropenium compounds.

Some aminodiphenylcyclopropenium salts have been prepared by the reaction of diphenylcyclopropenone with triethyloxonium tetrafluoroborate (Meerwein reagent), followed by treating with secondary amines.[2,3)]

In this communication we report an improved one-pot synthesis of 1-amino-2,3-diphenylcyclopropenium salts using commercially available ethyl fluorosulfate and its application to the synthesis of 5-amino-1,2,3-triazines.

Since the Meerwein reagent decomposes in atmospheric moisture, we used ethyl fluorosulfate (Aldrich Chem. Co.) which is easy to handle. The reagent reacted with diphenylcyclopropenone (**1**) in dry dichloromethane to yield the cyclopropenium salt **2**. The salt was *in situ* treated with equimolar amount of secondary amines to give 1-amino-2,3-diphenylcyclopropenium fluorosulfates (**3**) in moderate yields. The structure of **3** was elucidated on the basis of their IR (at around 1900 cm^{-1}) and ^{1}H-NMR data (Table 1).

It has been reported that cyclopropenium salts substituted with triamino[4)] or triaryl[5)] groups react with azide ion to yield 3-azidocyclopropenes which gave 1,2,3-triazines on heating. Although the reaction of 1-bis(1-methylethyl)amino-2,3-diphenylcyclopropenium perchlorate (**3b** analogue) and potassium azide has been reported[4)] to give 5-bis(1-methylethyl)amino-4,6-diphenyl-1,2,3-triazine (**4b**), the structure elucidation seems to be uncertain. The reaction of **3** with sodium azide gave 5-amino-1,2,3-triazines **4**

Table 1. Yields and physical properties of **3**

	Yield/%	Mp θ_m/°C	^{1}H-NMR($CDCl_3$)	Anal/% Found(Calcd) C	H	N	IR(KBr)/cm^{-1}
3a	74	164—165	1.41(6H, t, *J*=7 Hz, CH_3), 3.94(2H, q, CH_2), 7.5—8.1(10H, m, Ph)	63.06 (63.14)	5.47 (5.58)	3.91 (3.88)	1900
3b	16	197—202	1.65(12H, d, *J*=7 Hz, CH_3), 4.46(2H, sept, CH), 7.6—8.3(10H, m, Ph)	64.97 (64.76)	6.20 (6.21)	3.73 (3.60)	1890
3c	65	200—202	2.00(6H, bs, CH_2), 4.16(4H, bs, $(CH_2)_2N$), 7.6—8.3(10H, m, Ph)	64.20 (64.33)	5.39 (5.40)	3.67 (3.75)	1900
3d	57	217—218	4.18(8H, bs, $(CH_2CH_2)_2$), 7.1—8.2(10H, m, Ph)	60.62 (60.79)	4.69 (4.83)	3.70 (3.73)	1900
3e	43	188—190	3.75(6H, s, CH_3), 7.4—8.3(10H, m, Ph)	61.09 (61.25)	4.98 (4.84)	4.26 (4.20)	1900
3f	83	161—162	4.21(3H, s, CH_3), 7.4—8.5(15H, m, Ph)	66.66 (66.82)	4.50 (4.59)	3.49 (3.54)	1900

Table 2. Yields and physical properties of **4**

	Reaction time/h	Yield /%	Mp θ_m/°C	^{1}H-NMR($CDCl_3$)	MS (M^+)	Anal/% Found(Calcd) C	H	N
4a	16	89	216—217	0.90(6H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.68(4H, q, CH_2), 7.2—8.0(10H, m, Ph)	304	75.21 (74.97)	6.73 (6.62)	18.24 (18.41)
4b	20	73	200—201[a)]	0.82(12H, d, *J*=7 Hz, $\underline{Me_2}CH$), 3.26 (2H, sept, CH), 7.2—7.8(10H, m, Ph)	332	75.74 (75.87)	7.20 (7.28)	16.58 (16.85)
4c	19	81	256—272	1.35(6H, bs, $(CH_2)_3$), 2.65(4H, bs $N(CH_2)_2$), 7.59(10H, bs, Ph)	316	75.68 (75.92)	6.30 (6.37)	17.54 (17.71)
4d	82	82	250—252	2.70(4H, t, *J*=5 Hz, $N(CH_2)_2$), 3.45(4H, t, $O(CH_2)_2$), 7.4—7.9(1H, m, Ph)	318	71.21 (71.68)	5.69 (5.70)	17.00 (17.60)
4e	33	89	217—219	2.52(6H, s, Me), 7.4—8.0(10H, m, Ph)	276	74.01 (73.89)	5.81 (5.84)	20.39 (20.27)
4f	16	93	231—235	2.93(3H, s, Me), 6.4(15H, m, Ph)	338	77.78 (78.08)	7.21 (7.36)	16.44 (16.56)

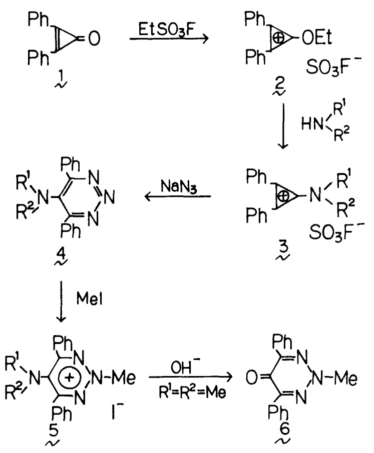
a) Lit,[4)] mp 186—188 °C.

Table 3. Preparation and physical properties of triazine derivatives

	Reaction conditions		Yield /%	Mp θ_m/°C	^{1}H-NMR($CDCl_3$)	Anal/% Found(Calcd)		
	Temp/°C	Time/h				C	H	N
5a	25	17	68	217—219	1.04(6H, t, J=7 Hz, CH_3), 3.44(4H, q, CH_2), 4.52(3H, s, NCH_3), 7.2—7.8(10H, m, Ph)	53.77 (53.82)	5.08 (5.19)	12.64 (12.55)
5e	25	9	76	100—101	2.95(6H, s, 5-NMe_2), 4.45(3H, s, 2-NMe), 7.1—7.8(10H, m, Ph)	51.47 (51.69)	4.36 (4.58)	13.25 (13.39)
5f	60	67	31	98—101	3.20(3H, s, PhN$\underline{Me}$), 4.61(3H, s, 2-NMe), 6.7—7.6(15H, m, Ph)	57.58 (57.51)	4.62 (4.41)	11.54 (11.66)
6			52	118	4.03(3H, s, Me), 6.7—8.1(10H, m, Ph)	73.22 (72.99)	5.05 (4.98)	15.91 (15.96)

Table 4. ^{13}C-NMR spectra of some triazine derivatives

4a	12.8(q, Me), 46.1(t, CH_2), 128.4(d), 128.7(d), 129.4(d), 137.0(s), 153.0(s)
4e	43.6(q, Me), 128.2(d), 128.5(d), 129.2(d), 136.4(s), 138.9(s), 150.0(s)
5a	10.8(q, $CH_2\underline{Me}$), 49.3(t, CH_2), 50.4(q, 2-NMe), 127.4(d), 128.7(d), 130.2(d), 132.4(s), 139.9(s), 142.0(s)
5e	49.0(q, 5-NMe_2), 50.5(q, 2-NMe), 127.9(d), 129.2(d), 130.5(d), 132.6(s), 139.6(s), 143.6(s)
6	50.7(q, Me), 128.0(d), 128.4(d), 130.1(d), 132.4(s), 151.7(s), 161.4(s)



3 4 5	R^1	R^2
a	Et	Et
b	i-Pr	i-Pr
c	$(CH_2)_5$	
d	$(CH_2)_2O(CH_2)_2$	
e	Me	Me
f	Me	Ph

whose structures were confirmed unambiguously by their ^{13}C-NMR spectra and chemical transformations. The ^{13}C-NMR spectra of **4a** and **4e** showed the symmetric structure for these compounds. Physical properties of **4** are shown in Table 2.

The reactions of **4a** and **4e** with methyl iodide took place easily to give 2-methyl derivatives **5a** and **5e**, respectively. Hydrolysis of **5e** with aqueous sodium hydroxide afforded 4,6-diphenyl-1,2,3-triazin-5(2*H*)-one (**6**). The structures of **5a**, **5e**, and **6** were confirmed on the basis of ^{1}H- and ^{13}C-NMR data (Tables 3 and 4).

Experimental

*Preparation of **3**: General Procedure.* A mixture of **1** (4.8 mmol) and ethyl fluorosulfate (5.3 mmol) in dry CH_2Cl_2 (10 cm^3) was stirred at room temperature for 1 h. To the resulting solution was added a dichloromethane solution of an amine (4.8 mmol in 5 cm^3) under nitrogen. After 30 min to the solution was added 25 cm^3 of ethanol and the mixture was condensed to 30 cm^3. The precipitated salt was recrystallized from CH_3CN (or $CHCl_3$) and ethanol to afford pure salt **3**.

*The Reaction of **3** with Sodium Azide: General Procedure.* A suspension of **3** (0.9 mmol) and sodium azide (2.7 mmol) in CH_2Cl_2 was stirred at room temperature for 16 h. The mixture was evaporated and benzene-soluble product was separated. Recrystallization from chloroform–ethanol gave pure triazine **4**.

*Reaction of **4a**, **e**, and **4f** with Methyl Iodide.* A mixture of **4a** (1 mmol) and MeI (10 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 12 h. Then the solution was evaporated and benzene-insoluble salt **5a** was separated. Similar treatment of **4e** and **4f** gave **5e** and **5f**.

*Hydrolysis of **5e**.* A mixture of **5e** (1 mmol) in benzene (10 cm^3) and 5 cm^3 of aq NaOH (10%) was stirred at room temp for 2 h, the organic layer was separated, and dried under reduced pressure. Recrystallization from ethanol afforded faint yellow needles **6** in 52% yield.

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