Reactions of Trimethylsilylmethyl Azide with Aromatic Acid Derivatives Catalyzed by Fluoride Ion

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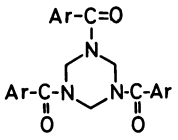
Synopsis. The treatment of an aromatic acid halide with trimethylsilylmethyl azide (TMSMA) in the presence of potassium fluoride and crown ether gave triazine, methanediamine, and benzamide derivatives, while the reaction of acid anhydride with TMSMA gave tertiary amine together with methanediamine and benzamide under similar conditions.

We are currently interested in the reactivities and the synthetic utilities of azide compounds containing silicon atoms.[1] Trimethylsilylmethyl azide (TMSMA) has various reaction sites and a synthetic applicability as a synthon for the amination of aromatic halides,[1b] 1,3-dipolar cycloaddition,[2] or heterocumulenes.[3] In this paper, we describe unexpected reactions involving TMSMA with acid derivatives to give triazine, methanediamine, tertiary amine, and benzamide derivatives.

Results and Discussion

A mixture of benzoyl chloride and TMSMA in the presence of potassium fluoride and a catalytic amount of 18-crown-6 in benzene was heated to reflux for 50 h. Surprisingly, the extract with dichloromethane gave 30% of 1,3,5-tribenzoylhexahydro-1,3,5-triazine (**1a**) and 34% of *N,N'*-dibenzoylmethanediamine (**2a**) together with 16% of benzamide.



1

2

a, Ar = C_6H_5
b, Ar = *p*-$NO_2C_6H_4$
c, Ar = *p*-MeC_6H_4

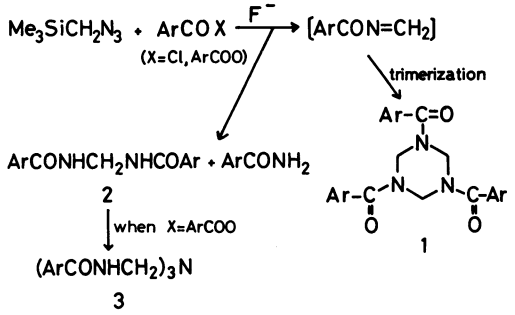
Without either potassium fluoride or crown ether, no products were formed. Other aroyl chlorides were treated in a similar manner and the results are listed in the Table. With *p*-nitrobenzoyl chloride, both triazine **1b** and methanediamine **2b** along with *p*-nitrobenzamide were isolated, though the product distribution was different from that of benzoyl chloride itself. When *p*-methylbenzoyl chloride was employed, only triazine **1c** was obtained in a much higher yield (73%) as the sole product. As for the formation of these compounds, it has been reported that benzonitrile, 1,3,5-trioxane, and a catalytic amount of concd sulfuric acid gave either triazine **1a**[4] or methanediamine **2a**,[5] depending on the conditions.

As a reaction pathway, we assumed that the

Table. Reaction of TMSMA with aroyl chlorides and benzoic anhydride[a]

Substrate	KF	Yield/%[b]			ArCONH$_2$
		1	**2**	**3**	
C_6H_5COCl	1 equiv	30	34		16
p-$NO_2C_6H_4COCl$	1 equiv	9	38		7
p-MeC_6H_4COCl	1 equiv	73			
$(C_6H_5CO)_2O$	1 equiv	0	28	3	4
	3 equiv	0	10	22	4

a) Reaction conditions were cited in experimental section. b) Based on used acid derivatives.



Scheme

desilylation of TMSMA induced by fluoride ions gave $K^+[CH_2N_3]^-$, followed by an evolution of nitrogen to form $K^+[CH_2{=}N]^-$ at the temperature, which afforded *N*-benzoylmethanimine (ArCON=CH_2) *via* a nuclereophilic attack on acid chloride. The triazine derivative **1** would be obtained by a trimerization of the species. Such a trimerization of methanimine has been reported;[6] 1,3,5-tris(benzylsulfonyl)hexahydro-1,3,5-triazine was transformed from phenylmethanesulfonamide and 1,3,5-trioxane *via* *N*-(benzylsufonyl)methanimine ($PhCH_2SO_2N{=}CH_2$), in which 3,4-dihydro-1*H*-2,3-benzothiazine 2,2-dioxide was also obtained as a thermodynamically controled product. In our case, however, the intramolecular cyclization product, 1-isoindolinone, was not detected even when the reaction time was prolonged.

When benzoic anhydride was employed, 28% of methanediamine **2a**, 3% of tris(benzoylaminomethyl)-amine (**3a**), and 4% of benzamide, along with the

$(RCONHCH_2)_3N$ **3**, a, R = Ph; b, R = Me

starting material, were obtained. With a three-fold excess of potassium fluoride to benzoic anhydride, the yield of **2a** was decreased to 10%, while that of amine **3a** was increased to 22%. Ethyl benzoate and acetic anhydride gave neither **1**, **2**, nor **3**.

From reported investigations[4,5,6] and these results, the reaction pathway to **1** and **2** might be competitive (as shown in the Scheme) and the formation of **3** would be rationalized by a nucleophilic attack of benzoyloxy anions towards **2**. However, it was not easy to confirm the reaction course.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were determined with a Hitachi R-600 or a JEOL PS-100 spectrometer using tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-10 infrared spectrometer and mass spectra were measured with a JEOL DX-300 spectrometer. Aroyl chlorides, potassium fluoride, and 18-crown-6 were commercial products and were purified when necessary. Trimethylsilylmethyl azide was prepared from trimethylsilylmethyl chloride and sodium azide according to a reported method.[1d]

Reaction of Aroyl Chloride with TMSMA. A mixture of benzoyl chloride (1.40 g, 10 mmol), TMSMA (1.94 g, 15 mmol), KF (0.58 g, 10 mmol), and 18-crown-6 (26 mg, 0.1 mmol) in benzene (10 cm^3) was heated to reflux for 50 h with stirring. To the reaction mixture was added a 10% sodium carbonate solution (30 cm^3). Stirring was continued for 24 h. The reaction mixture was extracted with dichlromethane. After drying over magnesium sulfate and evaporating the solvent *in vacuo*, the residual solid was chromatographed on alumina. Rapid elution with benzene/chloroform gave 405 mg (30%) of 1,3,5-tribenzoylhexahydro-1,3,5-triazine (**1a**), recrystallized from ethanol, colorless prisms, mp 216—218 °C (lit,[4] 220—222 °C), mass spectrum *m/z* 399 (M^+), and 435 mg (34%) of *N,N'*-dibenzoylmethanediamine (**2a**), recrystallized from methanol, colorless needles, mp 215—216 °C (lit,[5] 216—218 °C), *m/z* 254 (M^+). Further elution with methanol afforded 197 mg (16%) of benzamide. ^{1}H NMR spectra of **1a** and **2a**: **1a** ($CDCl_3$) δ=5.41 (6H, s) and 7.48 (15H, m); **2a** (DMSO-d_6) δ=5.08 (2H, t, J=6 Hz), 7.5—8.1 (10H, m) and 9.15 (2H, t, J=6 Hz).

Other aroyl chlorides were similarly treated unless otherwise mentioned. With *p*-nitrobenzoyl chloride (1.85 g, 10 mmol), the reaction time was prolonged to 120 h. To the reaction mixture was added chloroform and water. A precipitated solid was filtered and then washed with hot acetonitrile, giving 160 mg of a colorless solid, which was found to be 1,3,5-tris(*p*-nitrobenzoyl)hexahydro-1,3,5-triazine (**1b**, 9%), mp >260 °C, ν_{max} 1650 and 1530 cm^{-1}. The ^{1}H NMR spectrum in DMSO-d_6 showed at δ=5.38 (6H, s) and 7.76, 8.26 (12H, AA'BB'q, J=8 Hz). Found: C, 53.46; H, 3.33; N, 15.60%. Calcd for $C_{24}H_{18}N_6O_9$: C, 53.93; H, 3.39; N, 15.73%. Column chromatography on alumina of the combined filtrate gave 650 mg (38%) of *N,N'*-bis(*p*-nitrobenzoyl)methanediamine (**2b**), recrystallized from acetonitrile, colorless needles, mp 245—246 °C, *m/z* 344 (M^+), ^{1}H NMR (DMSO-d_6) δ=5.08 (2H, t, J=6 Hz), 8.35, 8.54 (12H, AA'BB'q, J=9 Hz), and 9.65 (2H, t, J=6 Hz), ν_{max} 3290, 1630, and 1510 cm^{-1}. Found: C, 51.97; H, 3.42; N, 16.27%. Calcd for $C_{15}H_{12}N_4O_6$: C, 52.33; H, 3.51; N, 16.27%. *p*-Nitrobenzamide along with unidentified products was also obtained.

When *p*-methylbenzoyl chloride (1.55 g, 10 mmol) was employed, 1,3,5-tris(*p*-methylbenzoyl)hexahydro-1,3,5-triazine (**1c**) was obtained in 73% (1.07 g) yield. The compound was recrystallized from ethanol to give colorless needles, mp 211—212 °C, *m/z* 441 (M^+). The IR spectrum showed at 1660 and 1640 cm^{-1} and the ^{1}H NMR spectrum in $CDCl_3$ showed signals at δ=2.40 (9H, s), 5.40 (6H, s), and 7.28 (12H, m). Found: C, 73.23; H, 6.07; N, 9.48%. Calcd for $C_{27}H_{27}N_3O_3$: C, 73.45; H, 6.17; N, 9.52%.

Reaction of Acid Anhydride with TMSMA. The reaction of benzoic anhydride (2.26 g, 10 mmol) with TMSMA (1.94 g, 15 mmol) was carried out as metioned above. Extraction with CH_2Cl_2 and column chromatography eluted by benzene/chloroform gave 350 mg (28%) of **2a** and 41 mg (3%) of tris(benzoylaminomethyl)amine (**3a**), recrystallized from ethanol, colorless plates, mp 188—189 °C, *m/z* 416 (M^+), ν_{max} 3320 and 1645 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=4.73 (6H, d, J=7 Hz), 7.0—7.7 (15H, m), and 8.10 (3H, t, J=7 Hz). Found: C, 69.05; H, 5.71; N, 13.28%. Calcd for $C_{24}H_{24}N_4O_3$: C, 69.21; H, 5.80; N, 13.45%. Benzamide (48 mg, 4%) was also obtained by elution with methanol on alumina. With 3 equiv of KF, yields of **2a**, **3a**, and benzamide were 127 mg (10%), 305 mg (22%), and 48 mg (4%), respectively.

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