Table II. Properties and Analyses of the Amides of Fluorenone-4-Carboxylic Acid

Amide	M.P., °C.	N, % Calcd.	N, % Found	Yield, %
N-Methyl	232.5–233.5	5.91	6.00	40
N,N-Diethyl	91.5– 92.5	5.02	5.16	62
N-*n*-Propyl	176.0–177.0	5.28	5.35	50
N,N-Di-*n*-propyl	101.5–102.5	4.56	4.65	80
N-*n*-Butyl	139.0–140.0	5.02	5.19	75
N-Isobutyl	186.5–187.5	5.02	5.15	42
N-*tert*-Butyl	168.0–169.0	5.02	5.11	70
N-Phenyl	214.5–215.5	4.68	4.76	60
N-*p*-Tolyl	221.0-222.0	4.47	4.65	72

approximately 1.5 ml. of concentrated H_2SO_4 was refluxed for 9 hours. The reaction mixture was diluted with ether, washed with 5% aqueous Na_2CO_3, and dried over anhydrous Na_2SO_4. The ether and excess alcohol were removed by evaporation under reduced pressure.

METHOD 3. Approximately 0.018 mole of fluorenone-4-carboxylic acid chloride and 60 ml. of the appropriate alcohol were refluxed for 2 hours. Twenty five milliliters of pyridine were used as a hydrogen chloride acceptor in the preparation of the cyclopentyl fluorenone-4-carboxylate. The pyridine hydrochloride was precipitated by the addition of absolute ether. The mother liquor from the reaction solution was evaporated under reduced pressure and the residue recrystallized from petroleum ether.

Amides. The amides were prepared by slowly adding the calculated weight of the appropriate amine in 50 ml. of dry benzene to 0.021 mole of fluorenone-4-carboxylic acid chloride. This solution was refluxed gently for approximately 20 minutes. The refluxed solution was transferred to a separatory funnel and washed with 25 ml. of water. The aqueous layer was removed and the benzene layer washed successively with 25 ml. of 5% HCl, 25 ml. of 5% aqueous NaOH, and 25 ml. of water. The benzene solution was evaporated over a steam bath. The yellow residue was decolorized with Norit and recrystallized from absolute ethanol. All the amides were yellow solids. The physical properties of the amides prepared are given in Table II.

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COMMUNICATION

N-Substituted Trifluoroacetamidines

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The properties are reported of N-substituted trifluoroacetamidines, prepared from the interaction of primary and secondary amines (C_2H_5 through C_6H_{13}) with trifluoroacetonitrile.

REILLY AND BROWN (*4*) and Grivas and Taurins (*1*) have described the synthesis of some N-substituted trifluoroacetamidines from the interaction of primary and secondary amines with trifluoroacetonitrile:

$$RR'NH + CF_3CN \rightarrow CF_3C(=NH)NRR'$$

We report the preparation and physical properties of additional representatives of the series (Table I).

All the amidines, when pure, were colorless liquids (except N-*n*-propyltrifluoroacetamidine, which crystallized to a white solid). They were soluble in common organic solvents but insoluble in water. If protected from the atmosphere in sealed vials, they were very stable. Only a slight color change was noted over 6 months.

The hydrochlorides were white solids, soluble in water, ethanol, propanol, and alcohol-ether mixtures, and insoluble in pure ether. They were stable, if protected from the atmosphere.

Attempts to isolate products from the reaction of trifluoroacetonitrile with diisopropylamine and diisobutylamine resulted only in the recovery of the starting materials.

EXPERIMENTAL

Reagents. Amines were purchased from Distillation Products Industries. Ethylamine was recovered from 60% aqueous solution by dropping the solution slowly on to NaOH pellets and condensing the gas evolved in a dry ice trap.

Trifluoroacetonitrile was purchased in cylinders from Peninsular Chem. Research Co., Gainesville, Fla. For use in a reaction, the gas was liquefied by passing it into a trap surrounded by a dry ice–trichloroethylene mixture. The trap containing the liquid could be weighed without appreciable loss of gas. The delivery tube of the trap was connected to the admission tube of the apparatus described below and the trap allowed to warm up spontaneously. Generally this caused the gas to pass into the reaction vessel at an appropriate rate and no auxiliary heating or cooling was necessary.

Apparatus. A 50 to 100 ml. round-bottom flask arranged for magnetic stirring, was attached by a 10-inch jacketed tube to a Dewar condenser. The well of the condenser was

Table I.[a] Properties of Trifluoroacetamidines, $CF_3(=NH)NRR'$

R	R'	Yield, %	B.p.	Mm. Hg	n_D^{25}	Empirical Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. F	Found C	Found H	Found N	Found F	M.p.	Hydrochloride Calcd. N	Hydrochloride Calcd. Cl	Hydrochloride Found N	Hydrochloride Found Cl
C_2H_5	H	58	58–9	46	1.3967	$C_4H_7N_2F_3$	34.3	5.0	20.0	40.7	34.9	5.3	19.8	37.7[b]	193–5	15.9	20.1	15.6	19.9
n-C_3H_7	H	80	47–50	152		$C_5H_9N_2F_3$	39.0	5.8	18.2	37.0	39.2	5.9	18.0	36.7	141–4	14.7	18.6	15.0	18.4
	H	63	122–4		1.3945	$C_5H_9N_2F_3$	39.0	5.8	18.2	37.0	39.4	5.9	18.0	34.2[b]	189–91	14.7	18.6	14.5	18.5
	H	66	58–8.5	10	1.4048	$C_6H_{11}N_2F_3$	42.9	6.5	16.7	33.9	43.2	6.7	16.5	33.6	[c]				
	H	75	53–55	31	1.4034	$C_6H_{11}N_2F_3$	42.9	6.5	16.7	33.9	43.0	6.8	16.5	33.7	[d]				
tert-C_4H_9	H					$C_6H_{11}N_2F_3$									204–5[e]	13.7	17.4	13.5	17.2
n-C_6H_{13}	H	60	81–4	5	1.4265	$C_8H_{15}N_2F_3$	49.0	7.7	14.3	29.1	49.3	7.8	14.2	29.3	[d]				
C_2H_5	C_2H_5	55	43–4	39	1.3943	$C_6H_{11}N_2F_3$	42.9	6.5	16.7	33.9	42.7	6.6	16.6	33.6	[f]	13.7	17.4	13.4	17.2
n-C_3H_7	n-C_3H_7	60	55–7	22	1.3870	$C_8H_{15}N_2F_3$	49.0	7.7	14.3	29.1	49.0	7.8	14.0	28.8	[d]				
n-C_4H_9	n-C_4H_9	67	65–6	22	1.4115	$C_{10}H_{19}N_2F_3$	53.6	8.5	12.5	25.4	53.5	8.5	12.3	25.6	[d]				
n-C_6H_{13}	n-C_6H_{13}	60	70–1	1	1.4300	$C_{14}H_{27}N_2F_3$	60.0	9.6	10.0	20.4	61.4	10.0	10.0	18.0	[g]				

[a] Boiling points and melting points uncorrected. N and Cl analyses carried out in our laboratory. C, H, and F analyses performed by a commercial laboratory. [b] Considerable difficulty was experienced in obtaining F analyses consistent with C, H, and N. However, no compound was sent out for analyses unless the N found was within acceptable limits. Grivas and Taurins (*1*) reported only N analyses presumably did not run C, H, and F. [c] Cf. Grivas and Taurins (*1*). Hydrochloride too unstable to analyze. [d] Hydrochloride could not be recovered. [e] Free base could not be purified. Yield as hydrochloride, 40%. Additional analyses on hydrochloride; Calcd. for C, 35.2; H, 5.9; F, 27.9. Found: C, 35.0; H, 5.4; F, 28.1. [f] M.p. uncertain. Original value 224–5 dropped to 113° after several weeks. Grivas and Taurins (*1*) reported 133–5°. [g] No derivative could be made to offset the rather poor analysis. However, C, H, and F determinations were made several weeks after the N determination. I.R. spectrum of free base showed absorptions for CF_3 and N,N-dialkylamidine (*2, 3*).

filled with a dry ice–trichloroethylene mixture, and it was surrounded by a metal container filled with dry ice. (Otherwise much CF_3CN was lost.) Trifluoroacetonitrile was admitted to the system through a side tube about halfway between the flask and the condenser. Standard taper ground glass joints were used throughout.

Reactions. The reaction of isopropylamine with trifluoroacetonitrile is representative of most of the amines. A 50-ml. reaction flask containing 20 grams (0.34 mole) of isopropylamine was attached to the condenser system and stirred by a magnetic stirrer. No external heating or cooling was employed during the entire run. Trifluoroacetonitrile (9.8 grams; 0.103 mole) was passed into the system through the side tube at a rate such that the heat generated by the reaction caused brisk refluxing. (A cloud appeared above the surface of the liquid as soon as the CF_3CN was admitted.) Twenty minutes was required to introduce the nitrile.

Stirring was continued for 1 hour longer, after which the clear, homogeneous reaction mixture was taken up in 75 ml. of ether and dried over anhydrous sodium sulfate. Fractional distillation at atmospheric pressure, using a 2 × 20 cm. temperature-controlled column, packed with glass helices, produced a fraction boiling at 122–4° and weighing 9.8 grams (63% yield, based on CF_3CN).

Hydrochlorides of these compounds were normally prepared by one of two methods.

About 5 grams of the free base was dissolved in 25 ml. of dry ether at 0°. To this was slowly added a saturated solution of dry hydrogen chloride in ether, also at 0°, until no further precipitate formed. The white solid was washed with cold anhydrous ether and recrystallized from a suitable organic solvent (usually an alcohol or alcohol-ether pair).

Dry hydrogen chloride gas was bubbled through the ether solution of the amidine, as long as a precipitate formed, and the solid was worked up as above.

Procedure for Specific Cases. ETHYLAMINE. The reaction flask was maintained at dry ice temperature during the addition of the CF_3CN. Considerable heat was generated near the top of the flask. When all the nitrile had been added, the flask was allowed to warm to room temperature and stirred for 1 hour.

n-PROPYLAMINE. Distillation of the reaction mixture at 152 mm. produced a fraction boiling at 46.5–50°. On mild agitation, the liquid crystallized to a while solid which was purified by recrystallization from petroleum ether. The only successful method for preparing the hydrochloride of the amidine was to pass dry hydrogen chloride intermittently over the surface of an anhydrous ether solution of the base (maintained at 0°) and shake it in. An oil separated, but crystallized when the flask was cooled to dry ice temperature and scratched vigorously. The solid was recrystallized from a 2-propanol–ether pair and dried in vacuo.

N-DIETHYLTRIFLUOROACETAMIDINE. A stoichiometric amount of dry hydrogen chloride was passed into an absolute ether solution of the base at 0°. The white solid which separated had to be quickly recrystallized from absolute ethanol; otherwise, it absorbed water and decomposed. When pure and dry (105° for 0.5 hour) it was stable.

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