Esters and Amides of Fluorenone-4-Carboxylic Acid

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Preparation and melting points of fifteen esters and the amides of fluorenone-4-carboxylic acid are described. Of these compounds, 13 of the esters and all of the amides are new.

THE PURPOSE of this work was to prepare, analyze, and determine certain physical properties of some esters and amides of fluorenone-4-carboxylic acid which had not previously been described in the literature.

Three general methods for the preparation of the esters of fluorenone-4-carboxylic acid have been described. Underwood and Kochmann (*3*) prepared the methyl and ethyl esters in excellent yields by reacting fluorenone-4-carboxylic acid with the appropriate alcohol using concentrated sulfuric acid as a catalyst. Graebe and Aubin (*2*) prepared the methyl and ethyl esters by passing dry hydrogen chloride through a mixture of fluorenone-4-carboxylic acid and the appropriate alcohol.

Fluorenone-4-carbonamide has been prepared by heating either the mono-or diamide or the imide of 2,2′-diphenic acid with concentrated H_2SO_4 at 100° to 130° C. (*3*). Graebe (*1*) and Wegerhoff (*4*) prepared the unsubstituted amide by passing dry NH_3 through a solution of fluorenone-4-carboxylic acid chloride in benzene.

The esters were analyzed for carbon and hydrogen and the saponification equivalent determined. The percentage of nitrogen in the amides was determined by the Kjeldahl method. All melting points were corrected for emergent steam unless otherwise stated. Infrared spectra confirmed the identity of each compound prepared.

The compounds were prepared, their analyses and their physical properties are presented in Tables I and II. All attempts to prepare esters of tertiary alcohols by methods described in this paper as well as the silver salt method failed.

EXPERIMENTAL

Esters. The esters were prepared by one of the following three general methods. The method used and the physical properties of the esters prepared are given in Table I.

METHOD 1. Dry HCl was passed through a mixture of 0.018 mole of fluorenone-4-carboxylic acid in approximately 2.5 moles of the appropriate alcohol for 3 to 4 hours.

METHOD 2. A mixture of 0.022 mole of fluorenone-4-carboxylic acid, 50 ml. of the appropriate alcohol, and

Table I. Properties and Analyses of the Esters of Fluorenone-4-Carboxylic Acid

			Calculated			Found		
Ester	M.P., ° C.	Yield, %	C, %	N, %	Sapon. equiv.	C, %	H, %	Sapon. equiv.
Methyl[a, b]	132–132.5	81	75.62	4.23	. . .	75.38	4.37	. . .
Ethyl[a, b]	102–103	80	76.18	4.80	. . .	76.20	4.92	. . .
n-Propyl[b]	74.5–75.5	42	76.67	5.30	266	76.39	5.43	260
		32	76.67	5.30	266	76.66	5.50	265
n-Butyl[b]	61.0–615	60	77.12	5.75	280	77.60	5.74	272
sec-Butyl[c]	78.5–79.5	32	77.12	5.75	280	77.06	5.76	289
n-Amyl[c]	33.5–34.0	46	77.55	6.12	294	77.39	6.18	294
Isoamyl[c]	34.0–35.0	39	77.55	6.12	294	77.29	6.29	293
sec-Amyl[c]	57.0–58.0	25	77.55	6.12	294	77.62	6.23	297
n-Hexyl[c]	63.0–64.0	11	77.92	6.49	308	77.89	6.56	301
n-Heptyl[c]	35.0–36.0	46	78.26	6.83	322	78.05	6.69	318
n-Octyl[c]	45.5–46.5	14	78.57	7.14	336	78.83	6.88	330
Cyclopentyl[d]	99.0–100.0	50	78.08	5.48	292	78.00	5.57	278
Cyclohexyl[d]	108.0–109.5	45	78.43	5.88	306	78.17	6.05	299

[a] Previously described in the literature, but these data obtained in this laboratory.
[b] Prepared by Method 1.
[c] Prepared by Method 2.
[d] Prepared by Method 3.

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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.

LITERATURE CITED

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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