Experimental Section[9]

4-Acetoxycoumarin (**2a**) was prepared from **1** and acetic anhydride in 10% aqueous sodium hydroxide as outlined by Eisenhauer and Link.[2] 4-Benzoyloxycoumarin (**4a**) was obtained from **1** and benzoyl chloride in pyridine.[3]

Treatment of 4-Acetoxycoumarin (2a) with Trifluoroacetic Acid.—A solution of **2a** (20 g, 0.098 mol) in 60 ml of trifluoroacetic acid was refluxed for 15.5 hr and then poured into 400 ml of water. The mixture was chilled in ice for several hours, and the precipitated solid of 17.5 g, mp 76–184°, was collected by filtration. Tlc of this material with benzene–ethanol (3:2) indicated the presence of **1**, **3a**, and some unchanged starting material. The solid was extracted with three 100-ml portions of 5% aqueous Na_2CO_3; the insoluble portion was crystallized from ethanol to give 1.33 g of **2a**, whose melting point and mixture melting point with authentic **2a** was 111–112°. The carbonate extract was acidified with concentrated hydrochloric acid, and the solid of 14.0 g, mp 130–185°, which precipitated was filtered off. Recrystallization from *ca.* 75 ml of ethanol afforded 5.18 g of **3a**, mp 137–138°. The ethanol mother liquor was chilled in ice to give a second crop of material, which upon recrystallization from ethanol furnished an additional 0.53 g of **3a**, mp 137–138°. The combined yield of **3a** (5.71 g) was 28.6%; ir (KBr) 3.25 (aromatic CH), 3.4 (CH_3), 4.0 (broad, weak, chelated OH), 5.8 (lactone C=O), 6.23 (chelated acetyl C=O and C=C), 6.5 and 6.68 (aromatic C=C), 7.34 (CH_3CO), 8.55 (lactone C—O), 9.66, 10.24, 11.14, and 13.1 μ (4 adjacent aromatic hydrogens); nmr ($CDCl_3$) δ 2.73 (s, 3, $COCH_3$), 7.51 (complex m, 2, H-6 and H-8), 7.64 (t split into d, 1, H-7), 7.96 (d split into d, 1, H-5), and 17.60 (broad s, 1, intramolecularly chelated OH).

Anal. Calcd for $C_{11}H_8O_4$: C, 64.70; H, 3.95. Found: C, 64.71; H, 4.00.

The ethanol mother liquors from the above crystallizations were combined and the ethanol was evaporated under reduced pressure. Recrystallization of the residue thus obtained from water furnished 6.31 g (39.7%) of **1**, mp 210–212°. The mixture melting point with authentic **1** was not depressed.

Conversion of 3-Acetyl-4-hydroxycoumarin (3a) into 2-Methylchromone (13).—A mixture of 3-acetyl-4-hydroxycoumarin (**3a**) (3 g, 0.0245 mol), 150 ml of concentrated hydrochloric acid, and 90 ml of ethanol was heated under reflux for 67 hr. The ethanol and most of the hydrochloric acid were removed under reduced pressure. The pH of the solution was adjusted to 7 by adding 30% sodium hydroxide solution, and the oil which separated was extracted with ether. The ether extract was washed with 5% sodium bicarbonate solution; the ether layer was dried ($MgSO_4$), and after evaporation *in vacuo*, a solid residue was obtained. Recrystallization from hexane gave 1.1 g (47%) of 2-methylchromone, mp 70–71°. This material was identical with authentic 2-methylchromone prepared from *o*-hydroxybenzoylacetone as described by Badcock, *et al.*[10]

Treatment of 4-Benzoyloxycoumarin (4a) with Trifluoroacetic acid.—A solution of **4a** (10 g, 0.038 mol) in 30 ml of trifluoroacetic acid was heated under reflux for 15 $^2/_3$ hr and then poured into 200 ml of water. After chilling in ice for several hours, the mixture was filtered to give 10.0 g of a solid, mp 74–184°, which according to tlc (with benzene–ethanol 3:2) contained **1**, benzoic acid, and unchanged **4a**. This solid was extracted with two 100-ml portions of 5% aqueous sodium bicarbonate; the insoluble solid was recrystallized from ethanol to afford 3.07 g of **4a**, whose melting point and mixture melting point with authentic **4a** was 125–127°. The bicarbonate solution was acidified with concentrated hydrochloric acid, and the precipitated solid was filtered off and recrystallized from water to give 2.93 g (48.1%) of **1**, mp 210–213°. A mixture melting point with authentic **1** was not depressed. Evaporation of the aqueous mother liquor to small volume under reduced pressure furnished 1.2 g (26.2%) of benzoic acid, mp 118–120°. Recrystallization from water followed by sublimation *in vacuo* raised the melting point to 121–122°. No depression in melting point was observed on admixture with authentic benzoic acid. The materials were spectrally identical.

Registry No.—**2a**, 15059-36-6; **3a**, 2555-37-5; **4a**, 16709-58-3; trifluoroacetic acid, 76-05-1.

(9) Melting points are uncorrected. Ir spectra were determined with a Baird-Atomic 4-55 spectrometer using potassium bromide pellets of the compounds. Nmr spectra were obtained with a Varian HA-100 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed by Union Carbide Corporation, Analytical Department, South Charleston, West Virginia. Fluorescent silica gel (Eastman Chromatogram Sheet type K 301 R) was used for tlc. Visualization of spots was accomplished with uv light.

(10) G. G. Badcock, F. M. Dean, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 903 (1950).

Silicon Tetrachloride as a Coupling Reagent for Amide Formation

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Even though silicon tetrachloride is known to react vigorously with water[3] and the silicon–oxygen–silicon bond is extremely stable thermodynamically as exemplified by silica and the silicones,[4] the use of halosilanes as dehydrating agents for organic synthesis has not been fully explored.[5,6]

We report the use of silicon tetrachloride in pyridine as a coupling reagent for the formation of an amide from a carboxylic acid and an amine.[7] Thus, to a solution of 2.5 g (0.04 mole) of acetic acid and 3.8 g (0.04 mol) of aniline in 50 ml of pyridine, 4.0 g (0.023 mol) of silicon tetrachloride was added. A white precipitate was formed instantaneously. The mixture was stirred at room temperature for 10 hr, and was poured onto crushed ice. The acetanilide was obtained in 60% yield after recrystallization from water. Under these conditions, aromatic amines reacted with both aliphatic and aromatic acids to give good to moderate yields of amides. Aliphatic amines, however, gave only poor yields of amides at room temperature. The yield could be substantially improved by raising the reaction temperature to reflux (Table I).

This method of effecting the formation of a carbon–nitrogen bond appears to be simple and efficient. It offers the advantage that the other product of this

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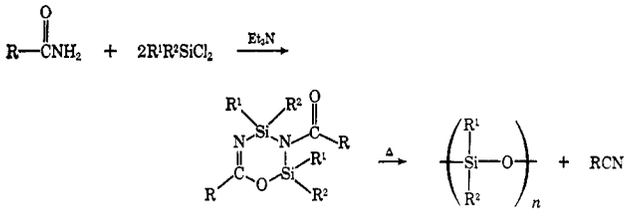
(2) Holder of National Research Council Studentship, 1968–1969.

(3) See for example, R. J. H. Voorhoeve, "Organohalosilanes," Elsevier Publishing Co., Amsterdam, 1967.

(4) See for example, E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley & Sons, New York, N. Y., 1946; and also, G. Fritz, *Angew. Chem. Intern. Ed. Engl.*, **7**, 1 (1968).

(5) The use of silanes for organic reactions has been reviewed by R. Calas, *Pure Appl. Chem.*, **13**, 61 (1966).

(6) J. F. Klebe [*J. Amer. Chem. Soc.*, **90**, 5346 (1968)] reported the reaction of acetamide or benzamide with dichlorosilanes and found that nitrile was eliminated on heating



(7) For a summary of reagents for amide formation, see J. P. Greenstein and M. Winitz, "The Chemistry of the Amino Acids," Vol. 2, John Wiley & Sons, New York, 1961.

TABLE I
AMIDE FORMATION FROM CARBOXYLIC ACID AND AMINE WITH SILICON TETRACHLORIDE–PYRIDINE AS COUPLING REAGENT

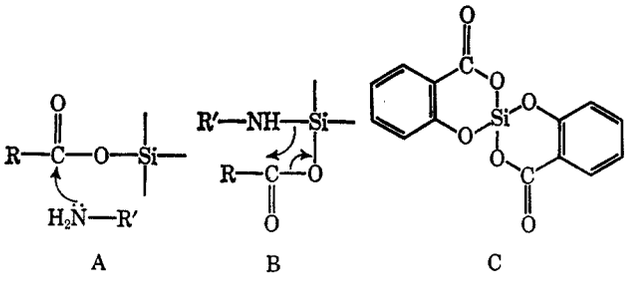
Acid	Amine	Conditions	Product (yield,[a] %)
Acetic	Aniline	R.t., 10 hr	Acetanilide (60)
Stearic	Aniline	R.t., 10 hr	Stearanilide (70)
Benzoic	Aniline	Reflux, 1 hr	Benzanilide (70)
p-Toluic	Aniline	R.t., 10 hr	*p*-Toluanilide (40)
p-Toluic	Aniline	Reflux, 1 hr	*p*-Toluanilide (70)
p-Hydroxybenzoic	Aniline	Reflux, 1 hr	*p*-Hydroxybenzanilide (50)
Salicylic	Aniline	Reflux, 1 hr	<1%[b]
Benzoic	Cyclohexylamine	R.t., 10 hr	N-Cyclohexylbenzamide, (25)
Benzoic	Cyclohexylamine	Reflux, 1 hr	N-Cyclohexylbenzamide (90)
Benzoic	*t*-Butylamine	Reflux, 1 hr	N-*t*-Butylbenzamide (65)
Benzoic	2,4,6-Mesidine	Reflux, 1 hr	N-2,4,6-Trimethylphenylbenzamide (80)
Acetic	N-Methylaniline	Reflux, 1 hr, N_2	N-Methylacetanilide (75)

[a] Isolated yield. [b] Salicylic acid was recovered quantitatively.

reaction is silica, which is insoluble in all common solvents, and thereby avoids the problem of contamination by side product.[8]

$$2RCO_2H + 2R'NH_2 + SiCl_4 \longrightarrow 2RCONHR' + (SiO_2)_n + HCl$$

Some comments can be made about the mechanism of this reaction. Both carboxylic acids[9] and amines[10] are known to displace chlorine from chlorosilanes to form the acyloxy- or aminosilanes. Two modes of condensation can be postulated to take place. One involves a nucleophilic attack by amine on what may be considered as a mixed anhydride (A). The other involves an intramolecular four-centered reaction (B). At present, we favor the latter mode of reaction. This is based on the observation that *p*-hydroxybenzoic acid reacted with aniline to give the anilide, whereas under identical conditions, salicyclic acid was recovered after hydrolysis.[11] Salicyclic acid forms a stable chelate with silicon (C)[12] and thus prevents the formation of B.



A B C

Experimental Section

Example A. Acetanilide.—To a solution of acetic acid (2.5 g) and aniline (3.8 g) in anhydrous pyridine (50 ml), silicon tetrachloride (4.0 g) was introduced. The mixture was stirred at room temperature for ten hours and was poured onto crushed ice. The precipitate was filtered and the filtrate was concentrated to yield 3.3 g of crystalline acetanilide, mp 113°.

Example B. N-*t*-Butylbenzamide.—To a solution of benzoic acid (1.0 g) and *t*-butylamine (0.60 g) in anhydrous pyridine (30 ml), silicon tetrachloride (1.0 g) was introduced. The mixture was refluxed for one hour, and was poured onto crushed ice. The precipitate was filtered and triturated with hot ethanol. The ethanol solution was concentrated to yield 0.90 g of N-*t*-butylbenzamide, mp 134–136°.

Registry No.—Silicon tetrachloride, 10026-04-7.

Acknowledgment.—We gratefully acknowledge financial support from the National Research Council of Canada.

(8) For example, the well-known coupling reagent dicyclochexylcarbodiimide sometimes gives acylurea as a side product which is difficult to separate.

(9) R. C. Mehrotra, *Pure Appl. Chem.*, **13**, 111 (1966).

(10) R. O. Sauer and R. H. Hasek, *J. Amer. Chem. Soc.*, **68**, 241 (1946).

(11) This differs from phosphonitrilic chloride, which activated salicyclic acid to form amide: L. Caglioti, M. Poloni and G. Rosini, *J. Org. Chem.*, **33**, 2979 (1968).

(12) R. C. Mehrotra and B. C. Pant, *J. Indian Chem. Soc.*, **40**, 623 (1963).

Perchloric Acid Catalyzed Acylations. Occurrence of Carbon Acylation in Enol Lactones[1]

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We have published earlier a versatile procedure for preparing the enol lactones and enol acetates using a reagent composed of acetic anhydride and perchloric acid in ethyl acetate.[3,4] After detailed experimentation with reaction times and reagent composition, we have established that a 5-min reaction at room temperature with a reagent composed of 1 *M* acetic anhydride and 10^{-3} *M* perchloric acid in ethyl acetate converts a δ-keto acid such as 17β-hydroxy-4-nor-5-oxo-3,5-seco-3-andro-

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(2) (a) To whom all correspondence should be addressed. (b) Taken from the M.S. Thesis submitted by J. E. B. to St. Mary's University, San Antonio, Tex., May 1968.

(3) (a) P. Narasimha Rao and L. R. Axelrod, *Chem. Ind.* (London), 1838, (1963); (b) P. Narasimha Rao and L. R. Axelrod, *J. Chem. Soc.*, 1356 (1965).

(4) B. E. Edwards and P. Narasimha Rao, *J. Org. Chem.*, **31**, 324 (1966).