The reaction of ethylene oxide with p-aminoarylaryl-acetonitriles apparently is susceptible to steric hindrance from groups substituted ortho to the amino group. After the usual reaction time, 24 hours, the mono-2-hydroxy-ethyl derivatives for the compounds containing the methyl group and the methoxy group ortho to the amine function were isolated, while the compounds without a substituent ortho to the amino group produced the bis-(2-hydroxy-ethyl) derivatives in good yield. After an 8-day reaction time using a large excess of ethylene oxide, the bis-(2-hydroxyethyl) derivative of 4-amino-3-methylphenyl-phenylacetonitrile was obtained as an oil. Subsequent reactions showed the oil to be authentic. Prolonged reaction time in the presence of ethylene oxide failed to hydroxyethylate 4-amino-3-chlorophenylphenylacetonitrile; the starting material was recovered unchanged. Both steric hindrance and the weaker basicity of the amine may be responsible for this failure to react.

A number of attempts to isolate and identify nitrogen mustard derivatives of 4-aminophenyl-4-methoxyphenyl-acetonitrile and 4-amino-3-methoxyphenylphenylaceto-nitrile were unsuccessful.

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Trifluoroacylation

Synthesis of ω-Trifluororesacetophenone and ω-Trifluorophloroacetophenone

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The aluminum chloride–catalyzed reaction of trifluoroacetic anhydride with resorcinol and with phloroglucinol afforded ω-trifluororesacetophenone and ω-trifluorophloro-acetophenone, respectively.

SINCE large quantities of ω-trifluororesacetophenone (I) were needed, possible methods of synthesis were explored. The reported Hoesch reaction of resorcinol with relatively expensive trifluoromethyl cyanide involves several steps (6). Furthermore, Whalley (6) has reported that trifluoromethyl cyanide fails to react with orcinol, pyrogallol, and phloroglucinol. Accordingly, a more convenient synthesis for ω-trifluororesacetophenone was undertaken. The acylation of aromatics with trifluoroacetic anhydride has been cited by Parish and Stock (3) and by Tedder (5). In the present investigation, relatively inexpensive, commercially available trifluoroacetic anhydride was caused to react with resorcinol in 1,2-dichloroethane in the presence of aluminum chloride to afford compound I in 68 to 73% yields.

To establish the generality of this reaction, it was extended to phloroglucinol. Under similar experimental conditions, aluminum chloride catalyzed the trifluoro-acylation of phloroglucinol with trifluroacetic anhydride in 1,2-dichloroethane to give ω-trifluorophloroacetophenone (II, α,α,α-trifluoro-2,4,6-trihydroxyacetophenone) in 40% yield. Infrared and nuclear magnetic resonance data are reasonable for the proposed structure. Further evidence for the structure of compound II is the formation of phloroglucinol on heating with alkali (2).

EXPERIMENTAL

Melting points were taken with a Thomas Hoover capillary melting point apparatus and are corrected. The infrared spectra were taken with a Perkin-Elmer Model 21 spectrophotometer. Proton magnetic resonance spectra were taken with a Varian model A-60 instrument. Values are reported in τ units using tetramethylsilane as internal reference. Fluorine magnetic resonance spectra were taken with a Varian model V-4300-2 40 mc. per sec. spectrometer. Values are reported in θ^* (CFCl₃ reference). Analyses were performed by the Microanalytical Section of these laboratories.

Materials. Resorcinol (Mallinckrodt) was dried at room temperature in a vacuum desiccator at 0.5 to 1 mm. of Hg for several days before use. Phloroglucinol (Eastman white label) was dried in an oven at 100° C. and stored in a Drierite-containing desiccator. 1,2-Dichloroethane was distilled from phosphoric anhydride at atmospheric pressure, b.p. 82-83° C. Aluminum chloride (anhydrous) (Matheson, Coleman, and Bell) was used from a freshly opened bottle. Trifluoroacetic anhydride was distilled from phosphoric anhydride at atmospheric pressure, b.p. 40-42° C. It was prepared in this study by dehydration of trifluoroacetic acid (3M Company) with phosphoric anhydride. Trifluoroacetic anhydride is available commercially (Matheson, Coleman, and Bell).

Apparatus. A three-necked, round-bottomed flask of suitable size was equipped with a high-torque mechanical stirrer, pressure-equalizing addition funnel, and a water-cooled condenser topped with a dry ice–acetone condenser (to condense volatile trifluoroacetic anhydride). To the top condenser was attached a calcium chloride drying tube followed by a hydrogen chloride gas trap (1). To ensure dryness, the apparatus was purged with dry nitrogen for 1 to 2 hours and discontinued before a reaction was conducted.

ω-Trifluororesacetophenone (I). To effect a maximum solubility of resorcinol in 1,2-dichloroethane at ice bath tem-

perature, 110.1 grams (1 mole) of resorcinol with 1.5 liters of 1,2-dichloroethane was heated under reflux for 10 minutes and cooled then by means of an ice bath. To this efficiently stirred slurry at 0–5° C. was added in one portion 320 grams (2.4 moles) of anhydrous aluminum chloride followed by the dropwise addition over 2 hours of 169 ml. (252.1 grams. 1.2 moles) of trifluoroacetic anhydride. The ice bath was removed after addition of the anhydride was complete. The resulting yellow solution was allowed to warm to room temperature of its own accord with stirring for 4 hours. It was poured onto an excess of chipped ice and extracted with methylene chloride several times. The combined organic extract was washed with water, dried (anhydrous magnesium sulfate), and filtered. Concentration of the filtrate to a small volume (steam bath) afforded a light yellow solid which was purified by recrystallization from carbon tetrachloride to afford 140–150 grams (68 to 73%) of compound I, m.p. 106–108° C. [lit. (6), m.p. 103° C.]. This yield represents the average of four such experiments. An additional 10 to 20 grams (5 to 10%) of compound I was obtained by sublimation (100–120° C./0.5–1 mm. of Hg) of the residue from the combined filtrates. [Impure ketone (I) may develop a yellow color in storage. Recrystallization and/or sublimation yields pure, white compound.] Compound I gives a red-brown color with ferric nitrate. Methylation of this ketone according to the procedure of Whalley (6) gave the dimethyl ether, m.p. 51–53° C. [lit. (6), m.p. 52° C.].

ω-Trifluorophloroacetophenone (II). Following the above procedure, 6.3 grams (0.05 mole) of phloroglucinol with 150 ml. of 1,2-dichloroethane was heated under reflux for several minutes and cooled. The reaction was conducted then at room temperature. To the efficiently stirred mixture was added in one portion 22.7 grams (0.17 mole) of anhydrous aluminum chloride followed by the dropwise addition over 20 minutes of 8.1 ml. (12.1 grams, 0.058 mole) of trifluoroacetic anhydride. After addition, it was stirred for 1 day and poured onto ice. After one extraction with methylene chloride (to remove a small amount of tar), the aqueous layer was extracted with ether. The ether layer was separated, dried (anhydrous magnesium sulfate), and filtered. Concentration of the filtrate to dryness (steam bath) left a yellow solid which was dissolved in benzene and filtered to remove benzene-insoluble phloroglucinol. Chilling of the filtrate deposited 4.4 grams (40%) of yellow crystals, m.p.

174–177° C. dec. Anal. calcd. for $C_8H_5F_3O_4$: C, 43.3; H, 2.3; F, 25.7; mol. wt., 222. Found: C, 42.9; H, 2.6; F, 25.3; mol. wt., 213.

An alcoholic solution of this ketone with ferric nitrate gives a brown color. Infrared and nuclear magnetic resonance studies are reasonable for compound II. IR data show two distinct strong absorptions in the carbonyl region (6.07 μ and 6.20 μ). Proton magnetic resonance spectra show two absorptions. One absorption at −2.02 τ is assigned to hydroxyl; the other at +3.76 τ is assigned to aromatic protons (relative areas of 3 to 2). Fluorine magnetic resonance data show a single absorption at 7.26 θ^* assigned to CF_3. Both spectra were taken in a mixture composed of 50 mg. of compound II in 0.36 ml. of pyridine with 0.11 ml. of $CFCl_3$.

Alkaline Degradation of ω-Trifluorophloroacetophenone (II). A mixture of 0.5 gram (2 mmoles) of compound II, with 0.8 gram (20 mmoles) of sodium hydroxide in 10 ml. of water was heated under reflux for one-half hour and cooled (ice bath). Acidification (pH 3) afforded a white solid, m.p. 217–219° C., which was identified as phloroglucinol by undepressed mixture melting point and superimposable infrared spectra.

Both ketones failed to give a 2,4-dinitrophenylhydrazone under the usual conditions or according to a newer technique (4).

ACKNOWLEDGMENT

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(5) Tedder, J.M., Chem. Revs. 55, 787 (1955).
(6) Whalley, W.B., J. Chem. Soc. 1951 p. 665.

CORRECTION:

In the article "Heat of Solution, Heat Capacity, and Density of Aqueous Urea Solutions at 25° C." by Edward P. Egan, Jr., and Basil B. Luff [J. CHEM. ENG. DATA 11, 192 (1966)], the formula given for urea is incorrect. The first sentence of the text should read, "Urea, $CO(NH_2)_2$ is used..."

CORRECTION:

In the article "On Latent Heat of Vaporization, Surface Tension, and Temperature," [J. CHEM. ENG. DATA 11, 69–72 (1966)], there were errors which should be corrected as follows:

Page 69, line 8 should read, "Figure 1 shows [λ (1 − $1/T_r$)]/ T_c plotted as a function of . . . . "

Page 71, Equation 10 should be

$$\frac{\gamma^{1/4}}{\gamma_B^{1/4}} = \frac{\lambda}{\lambda_B} \frac{TP_B}{T_B P} \frac{\rho_l \rho_g}{(\rho_l \rho_g)_B}$$

Page 71, Equation 11 should be

$$\gamma/\gamma_B = (\lambda/\lambda_B)^4 \tag{11}$$

Page 71, line 8 should read, "Figure 2 shows the validity of the relation $\gamma/\gamma_B = f(\lambda/\lambda_B)$ . . . . "

Page 71, line 4 should read, "γ_o (1 − T_r)^m after fitting the the equation using the avaliable . . . . "

Page 71, Equation 12 should be

$$\gamma/\gamma_B = 1.02 \ (\lambda/\lambda_B)^{3.16} \cong (\lambda/\lambda_B)^{3.16} \tag{12}$$