Fluoro- and Trifluoromethyl-Substituted 2,4-Dimethoxybenzophenones and 2-Hydroxy-4-methoxybenzophenones

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SOME DERIVATIVES of 2-hydroxy-4-methoxybenzophenone have been prepared for evaluation as ultraviolet absorbers for space applications (*3*). Some members of this series are nearly colorless and impart low initial solar absorptivities to white pigmented coatings (*5*), and 3′-fluoro-, 2′-trifluoromethyl-, and 4′-trifluoromethyl-2-hydroxy-4-methoxybenzophenone have lower evaporation rates than the parent compound (*4*).

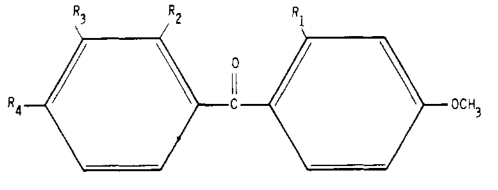
2′, 3′, and 4′-Fluoro-, and 2′, 3′, 4′-trifluoromethyl-2-hydroxy-4-methoxybenzophenones were prepared conveniently via acylation of resorcinol dimethyl ether with the appropriate benzoyl chloride in contact with anhydrous aluminum chloride or titanium tetrachloride in refluxing *n*-hexane. Low yields were obtained in the preparation of trifluoromethyl-substituted 2-hydroxy-4-methoxybenzophenones using aluminum chloride; however, by using the same mole ratio of titanium tetrachloride, considerably improved yields were noted. The activity of aluminum chloride is greater than that of titanium tetrachloride in the acylation of toluene by acetyl chloride (*2*). Cullinane, Chand, and Leyshon (*1*) have studied the benzoylation of anisole with titanium tetrachloride and aluminum chloride and report comparable yields for both. The improved yields obtained with titanium tetrachloride (Table I) probably can be attributed to greater solubility of the benzoyl chloride–titanium tetrachloride complex in *n*-hexane. The 2,4-dimethoxybenzophenones (R_1 = OCH_3) were prepared in a similar fashion using carbon disulfide as the solvent.

EXPERIMENTAL

The fluoro- and trifluoromethylbenzoyl chlorides (Pierce Chemical Co.) and resorcinol dimethyl ether (Koppers Co.) were distilled before use. Fresh aluminum chloride and titanium tetrachloride were used. Technical grade *n*-hexane was distilled from concentrated sulfuric acid prior to use.

3′-Trifluoromethyl-2-hydroxy-4-methoxybenzophenone. Aluminum chloride (29.3 grams, 0.22 mole) was covered with 100 ml. of *n*-hexane using anhydrous conditions. When titanium tetrachloride was used, it was injected below the surface of the *n*-hexane with a glass syringe. In the 2,4-dimethoxy series, carbon disulfide was the solvent. *m*-Trifluoromethylbenzoyl chloride (20.8 grams, 0.1 mole) was added with stirring. A yellow complex formed from resorcinol dimethyl ether (15.1 grams, 0.11 mole) dissolved in 50 ml. of *n*-hexane was added slowly at a rate which caused gentle reflux. The resulting dark-brown mixture was refluxed with stirring for 8 hours. Water (100 ml.) was added followed by 100 ml. of 6*N* HCl. The resulting dark-brown oil was taken up in diethyl ether, dried with calcium sulfate, and subsequently distilled through a short, unpacked column. After a forecut of 1.5 grams of resorcinol dimethyl ether, 4.1 grams (14%) of a light-yellow oil (b.p. = 170–176° C. at 3.0 mm.) was obtained which solidified after being cooled for several days at −20° C. One recrystallization from 80% ethanol gave white crystals which contained less than 0.01% impurities on the basis of vapor phase chromatography analysis. In the monofluoro series (R_1 = OCH_3 or OH, R_2, or R_3 or R_4 = F) the ether was removed on a steam bath, and the oily residue was taken up in 80% ethanol (95% ethanol was used for the fluoro-2, 4-dimethoxy-

Table I. Properties and Analytical Data for the Fluoro- and Trifluoromethylbenzophenones



R_1	R_2	R_3	R_4	M.P.[a]	Yield,[b,c] %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Fluorine, % Calcd.	Fluorine, % Found
OCH_3	F	d		75.7- 76.5	53[b]	$C_{15}H_{13}O_3F$	69.22	68.85	5.04	4.89	7.3	7.3
OCH_3		F		40.0- 41.5	58[b]	$C_{15}H_{13}O_3F$	69.22	69.17	5.04	5.06	7.3	7.4
OCH_3			F	102.0-102.8	72[b]	$C_{15}H_{13}O_3F$	69.22	69.62	5.04	5.08	7.3	7.3
OH	F			49.0- 50.0	24[c]	$C_{14}H_{11}O_3F$	68.29	68.29	4.50	4.40	7.7	7.6
OH		F		88.5- 89.5	39[c]	$C_{14}H_{11}O_3F$	68.29	68.46	4.50	4.44	7.7	7.8
OH			F	88.0- 89.0	43[c]	$C_{14}H_{11}O_3F$	68.29	68.08	4.50	4.67	7.7	7.6
OCH_3	CF_3			45.0- 47.0	63[b]	$C_{16}H_{13}O_3F_3$	61.94	61.99	4.22	4.25	18.4	17.8
OCH_3		CF_3		85.5- 86.0	64[b]	$C_{16}H_{13}O_3F_3$	61.94	62.03	4.22	4.30	18.4	18.0
OCH_3			CF_3	92.5- 93.0	60[b]	$C_{16}H_{13}O_3F_3$	61.94	62.06	4.22	4.12	18.4	18.0
OH	CF_3[e]			95.0- 95.5	71[b], 29[c]	$C_{15}H_{11}O_3F_3$	60.81	60.96	3.74	3.73	19.2	19.1
OH		CF_3[f]		65.5- 66.0	78[b], 14[c]	$C_{15}H_{11}O_3F_3$	60.81	60.83	3.74	3.51	19.2	18.8
OH			CF_3[g]	66.5- 67.0	76[b], 24[c]	$C_{15}H_{11}O_3F_3$	60.81	60.74	3.74	3.68	19.2	19.3

[a] Melting points determined by the Kofler microscopic method (*6*). [b] $TiCl_4$. [c] $AlCl_3$. [d] Where there are no entries in the table, the substituent is hydrogen. [e] B.p. 162–174° C. (2.7 mm.). [f] B.p. 170–176° C. (3.0 mm.). [g] B.p. 180–186° C. (3.9 mm.).

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benzophenones), treated with decolorizing carbon, and cooled to induce crystallization.

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Synthesis of Aromatic Glycidyl Esters

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An improved procedure for the preparation of aromatic glycidyl esters uses simultaneous addition of triethylamine and acid chloride to glycidol at 0° to 5° C. Several new di-, tri-, and tetraglycidyl esters are described. *m*-Chloroperbenzoic acid can be used for the peroxidation of diallyl esters to diglycidyl esters.

GLYCIDYL ESTERS of aromatic acids appear to have been relatively unexplored, compared to those of the aliphatic acids (*4*), except for descriptions in some patents (*1, 2, 3, 5, 7, 8, 9, 11, 12, 13*). The patents have described the preparation of these materials rather crudely, except for one case where carbon and hydrogen analyses have been reported for crystalline diglycidyl terephthalate (*2, 8*). The object of this investigation was to synthesize pure glycidyl esters of aromatic acids, in order to explore their use for adhesives.

Diglycidyl phthalate and diglycidyl terephthalate are described in detail in a procedure (*2, 8*) which recommends addition of the acid chloride to a mixture of glycidol in the presence of triethylamine at 0° to 5° C. in benzene or toluene solution. This procedure suffers from the disadvantage that glycidol itself polymerizes exothermically in the presence of basic materials and, thus, contaminates the products, which are subsequently isolated in low yields. The products are easily polymerized by the application of heat in the presence of basic catalysts such as triethylamine. Some investigators (*2, 8*) have neglected this fact and give procedures wherein the products are heated to 160° at 10-mm. pressure in vessels which originally contained basic catalysts. Therefore, to prepare purer products with acceptable analyses, a modified procedure was developed which utilized low temperatures and separate addition of triethylamine. Many of the crystalline products obtained in this investigation have been reported by earlier investigators as resins. The melting points and analyses for the glycidyl esters prepared by this method appear in Table I. The general procedure is illustrated below, utilizing the preparation of diglycidyl isophthalate. as an example. The properties of diglycidyl hexahydroterephthalate are shown for comparison, although this is not an aromatic system.

An additional method that is useful for the preparation of glycidyl esters is the reaction of the allyl esters of aromatic acids with *m*-chloroperbenzoic acid. Although peracetic acid (*1*) has been reported to peroxidize diallyl esters, the epoxy esters decomposed in the presence of acetic acid. *m*-Chloroperbenzoic acid gave a clean product and was separated from the by-product *m*-chlorobenzoic acid by washing the organic layer with dilute sodium carbonate or sodium hydroxide. Recently other investigators (*6*) have also found *m*-chloroperbenzoic acid useful for preparing volatile epoxides. The procedure for preparing diglycidyl tile epoxides.The procedure for preparing diglycidyl terephthalate from diallyl terephthalate is given below.

EXPERIMENTAL

Glycidyl Esters from Glycidol and an Acid Chloride—Diglycidyl Isophthalate. A 1-liter resin kettle was fitted with a stirrer, thermometer, condenser with drying tube, and two 300-ml. dropping funnels. All the equipment was carefully dried and flushed with nitrogen for 10 minutes. Glycidol (74.1 grams, 1.0 mole) and 200 ml. of benzene were placed in the flask and cooled, with stirring, to 0° C. in an ice water-methanol bath. A solution of isophthaloyl chloride (101.5 grams, 0.5 mole) in 150 ml. of benzene was placed in one dropping funnel and a solution of triethylamine (101 grams, 1.0 mole) in 150 ml. of benzene in the second funnel. The dropwise addition of the acid chloride was begun first, then dropwise addition of the triethylamine solution. The rates were controlled so that the pot temperature did not exceed 5° C. and the acid chloride addition was slightly faster than that of the triethylamine. Complete addition required 3 hours. Stirring was continued for 3 hours longer while the pot reached room temperature. The solids (triethylamine hydrochloride) were filtered, rinsed with 50 ml. of benzene, and dried. The weight of triethylamine hydrochloride was 123 grams (theoretical weight 137.5 grams).

The filtrates were washed in a separatory funnel with 200 ml. of saturated aqueous sodium chloride, twice with 200-ml. portions of distilled water, and dried over anhydrous calcium chloride. The salt was removed by gravity filtration and the benzene was stripped from the filtrate by means of a vacuum pump and a warm water (40° to 45° C.) bath. The residue, a white solid, was mixed with petroleum ether and filtered. The crude product weighed 111 grams (theoretical yield 139 grams) and melted at 48° to 53° C. The product was dissolved in 700 ml. of petroleum ether-benzene (1 to 1) solution, stirred with about 5 grams of activated charcoal, filtered, and cooled. About 25 ml. of petroleum ether was added. The recrystallized material was filtered and dried in a vacuum oven at room temperature. Final yield was 36 grams (m.p. 60-63° C.).

Glycidyl Esters by Peroxidation of Diallyl Esters with *m*-Chloroperbenzoic Acid—Glycidyl Terephthalate. The reaction of diallyl terephthalate with *m*-chloroperbenzoic acid consisted of cooling to 0° to 3° C. a solution of the acid (0.4 mole) in chloroform (700 ml.) and adding the diester (0.2 mole) in small portions with gentle agitation over a period of 4 hours. The stoppered reaction flask was stored