TABLE IV

THE ENERGY DIFFERENCE BETWEEN SUBSTITUTED OXYALLYLS AND THE CORRESPONDING CYCLOPROPANONES

					ΔE, kcal/mol		
Registry no.[b]	R_1	R_2	R_3	R_4	MINDO α 70°	MINDO α 90°	INDO α 90°
5009-27-8	H	H	H	H	+36	+59	+232
39050-15-2	F	H	H	F	*a*	+20	+184
39050-16-3	F	F	H	H	−153	+15	+203
39050-17-4	CH_3	H	H	CH_3	+30	+50	+200
39050-18-5	CH_3O	H	CH_3O	H	−93	+13	+180
39050-19-6	CH_3O	CH_3O	H	H	−96	+2	+174
39050-20-9	CH_3	F	F	CH_3	*a*	+14	+190
39050-21-0	CH_3O	F	CH_3O	F	−31	+24	+153
39050-22-1	CH_3O	CH_3O	F	F	−32	+30	+150

[a] The oxyallyl calculation failed to converge. [b] For cyclopropanones.

unreasonable, but the values for the fluoro and methoxy derivatives are incorrect, and the major shortcoming of the semiempirical methods is that one never knows when to believe their predictions.

Registry No.—Oxyallyl, 39050-23-2.

Acknowledgment.—The authors gratefully acknowledge the National Science Foundation for its support.

Organic Reactions in Liquid Hydrogen Fluoride. IV.[1] The Fries Rearrangement of Aryl Benzoates

JOHN R. NORELL

Phillips Petroleum Company, Phillips Research Center, Bartlesville, Oklahoma 74004

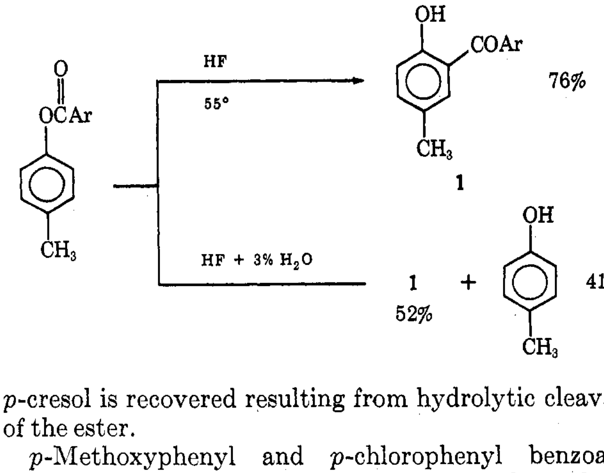
Received December 5, 1972

Phenyl and *p*-tolyl benzoates are converted to the corresponding hydroxybenzophenones in 70–75% yields when heated in anhydrous HF at 55°. With *p*-*tert*-butylphenyl benzoate the reaction product is the dealkylated *p*-hydroxybenzophenone, whereas the meta derivative gives 2-hydroxy-4-*tert*-butylbenzophenone in 40% yield. This appears to be the first example of a *tert*-butyl group being retained on a phenolic moiety during an acid-catalyzed Fries rearrangement. Comments on the mechanism and intermolecularity of the reaction are given.

Known as the Fries rearrangement,[2] the reaction of aryl esters in the presence of acidic type catalysts, usually $AlCl_3$, provides a convenient method for preparing hydroxybenzophenones. Hydrogen fluoride has received little attention as a catalyst for the rearrangement, although it has been reported to convert phenyl acetate[3] and some cresolic acetates[4] to the corresponding hydroxy ketones. The yields were low and a temperature of 100° for 24 hr was employed.[3] No work in HF has been reported with *tert*-butyl groups present on the phenolic ring; in fact, nothing in the literature could be found concerning favorable reactions with any *tert*-butylphenyl carboxylates employing any acid catalyst. Dealkylation always prevails, which led Kobsa[5a] to utilize the photo-Fries[5b] reaction for the rearrangement of *tert*-butyl esters.

Results

The present work describes our findings concerning rearrangement of some aryl benzoates in liquid HF, with special emphasis on the reactivity differences due to positions of *tert*-butyl groups on the phenolic ring. A summary of the experimental results is recorded in Table I. Phenyl and *p*-tolyl benzoate yield *p*-hydroxybenzophenone (70% yield) and 2-hydroxy-5-methylbenzophenone (76% yield), respectively, when shaken in liquid HF at 55° for 4–6 hr. The reaction is clean and the HF can easily be removed by distillation (bp 20°) or neutralization with base. No tars or insoluble residues often observed with $AlCl_3$ are obtained. If 3% water is present in the HF when *p*-tolyl benzoate is used as the starting ester, the isolated yield of ketone **1** drops to 52%, and 41% *p*-cresol is recovered resulting from hydrolytic cleavage of the ester.



p-Methoxyphenyl and *p*-chlorophenyl benzoates gave recovered starting material with *p*-methoxyphenol being obtained in the former case under the above con-

---

[1] For paper III, see J. R. Norell, *J. Org. Chem.*, **37**, 1971 (1972).

[2] For review articles, see (a) M. J. S. Dewar and L. S. Hart, *Tetrahedron*, **26**, 973 (1970); (b) H. J. Shine, "Aromatic Rearrangements," Elsevier, New York, N. Y., 1967, p 72; (c) A. Gerecs in "Friedel–Crafts and Related Reactions," Vol. III, Part I, G. A. Olah, Ed., Interscience, New York, N. Y., 1967, Chapter XXXIII, pp 499–533; (d) A. N. Blatt, *Org. React.*, **1**, 342 (1942).

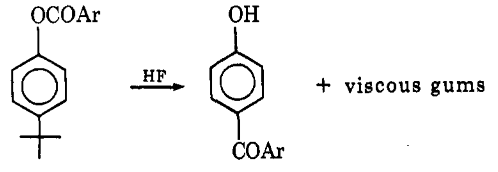
[3] J. H. Simmons, S. Archer, and D. I. Randall, *J. Amer. Chem. Soc.*, **62**, 485 (1940).

[4] O. Dann and G. Mylius, *Justus Liebigs Ann. Chem.*, **587**, 1 (1954).

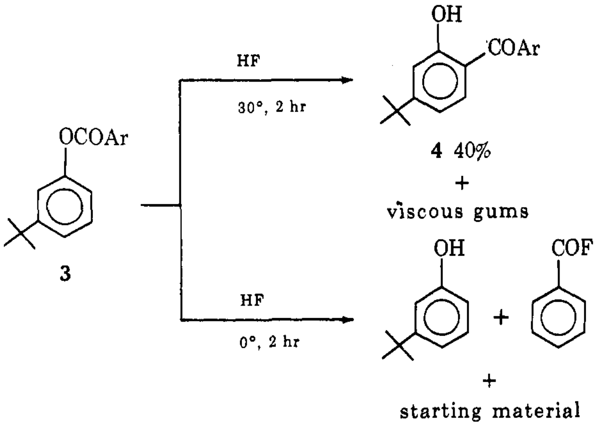
[5] (a) H. Kobsa, *J. Org. Chem.*, **27**,2 293 (1962); (b) D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967).

ditions. Little evidence was observed for the presence of rearranged ketone. The products isolated from a similar reaction with *p*-ethyl- and *p*-isopropylphenyl benzoates consisted of benzophenones with no unreacted starting materials.

The *tert*-butylphenyl benzoates, both mono- and disubstituted, vary in reactivity depending on the position of nuclear substitution. As equated below, *p*-*tert*-butylphenyl benzoate (**2**) gave only *p*-hydroxybenzophenone under a variety of conditions. The viscous gums are probably polybutylenes and highly substituted phenols. No reaction products were isolated or identified possessing the *tert*-butyl moiety. In contrast, the meta isomer (**3**) at room temperature gave a 40% yield of the desired 2-hydroxy-4-*tert*-butylbenzophenone (**4**). A striking temperature effect exists in that at 0° only the cleavage products, *m*-*tert*-butylphenol and benzoyl fluoride, are identified in addition to some starting material.



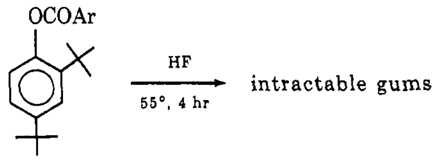
2



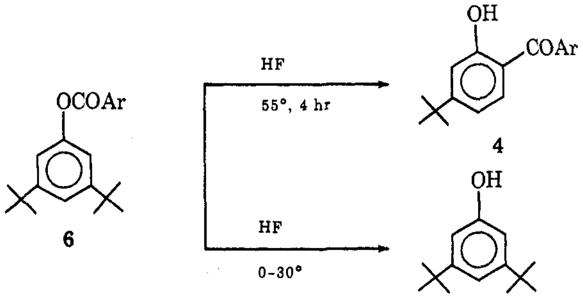
3

That the above reaction is clearly an artifact of the temperature difference gains credence from two simple observations during work-up. (1) No bands in the infrared attributable to the benzophenone (6.1 μ) are observed in the crude reaction mixtures when run at 0°. This band is very strongly present in the crude mixture of the 30° runs and is characteristic of **4**. (2) Compound **4** is bright yellow and imparts this color to the crude mixture in the 30° run, whereas at 0° the crude reaction mixture is cream colored. Whether or not this was a kinetically controlled run is not certain, but, in any case, cleavage products were observed at 0°. To our knowledge this is the first report of a *tert*-butyl group being retained on the phenolic ring under acid-catalyzed Fries rearrangement conditions.

With two *tert*-butyl groups in the molecule the reaction is even more complex. 2,4-Di-*tert*-butylphenyl benzoate (**5**) yields only a dark oil at 55° after 4 hr, which is typical of many reactions carried out at varying conditions with this isomer. If the *tert*-butyl groups are translated to the next succeeding carbons around the ring, *i.e.*, in **6**, the monoalkylated product, **4**, is isolated when run at 55° for 4 hr. As with compound **3**, a temperature-dependent reaction is observed, for, if **6** is allowed to react at 0° or 30°, the cleavage product, 3,5-di-*tert*-butylphenol, is recovered and none of the ketone is observed.



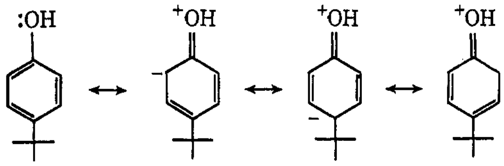
5



6

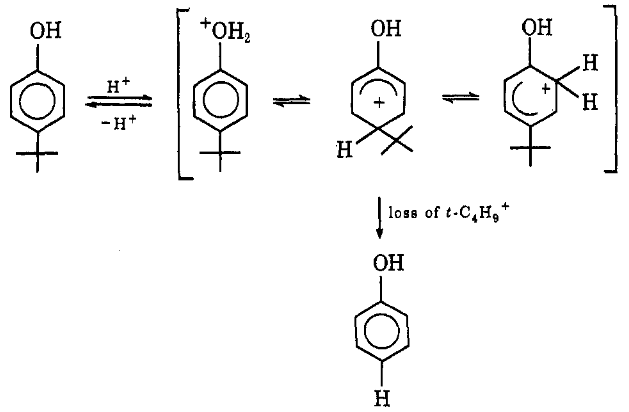
Discussion

The observation that *tert*-butyl groups in the meta position dealkylate to a lesser extent than those in the ortho or para position may be explained by invoking basic resonance and equilibrium principles of aromatic substitution on the free phenol. The electronegative sites on *p*-*tert*-butylphenol drawn in the canonical forms are shown.



The concept of using the free phenol appears valid, since in HF the cleavage products, the phenol and acyl fluoride, are observed. Dealkylation probably occurs on the free phenol, since a subsequent paper describes such a reaction of *tert*-butylphenols[6] in liquid HF.

On protonation of phenol a reversible attack of the proton can occur at any one of the three sites—two orthos and one para. If a labile group, *i.e.*, a *tert*-butyl, is also present in either the ortho or para position, then at a specific rate dealkylation will occur. The loss of a



---

[6] J. R. Norell, *J. Org. Chem.*, **38**, 1929 (1973).

TABLE I

REACTIONS OF ARYL BENZOATES IN HF

$\mathrm{ArO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{}_6\mathrm{H}_5$, Ar	Registry no.	Mmol	HF, ml	Temp, °C	Time, hr	Product		Description of product
						g	Recovery, %	
C_6H_5	93-99-2	76	150	55	4	14.8	99	Orange solids, recrystallized (hexane–$CHCl_3$), 10.5 g, *p*-hydroxybenzophenone (70% yield), mp 132–133.5°.
4-$CH_3C_6H_4$	614-34-6	71	150	55	6	14.5	97	Yellow solids, recrystallized (MeOH), 11.5 g, 2-hydroxy-5-methylbenzophenone (76% yield), mp 83.5–85°.
4-$CH_3C_6H_4$		71	150[a]	55	4	12.1	81	Yellow solids consisting of *p*-cresol (41%), 2-hydroxy-5-methylbenzophenone (52%), and *p*-tolyl benzoate (7%) by glc.
4-$C_2H_5C_6H_4$	3132-15-8	66	150	55	4	14.0	93	Yellow liquid, ir indicated mostly benzophenones; no attempt at characterization.
4-$CH_3OC_6H_4$	1523-19-9	66	150	55	4	11.2	75	Recrystallized (hexane + EtOH), pale yellow solid (6.0 g), mp 72–81°, infrared of crude indicated *ca.* 50% starting ester and 50% *p*-methoxyphenol, very little benzophenone.
4-ClC_6H_4	2005-08-5	64	150	55	4	13.0	87	Recrystallized (pentane), white crystals (8.1 g), mp 84–87°, mostly starting material.
4-*i*-$C_3H_7C_6H_4$	13936-99-7	62	150	55	4	15.2	100	Glc and ir indicated very little starting material, with the principal product being hydroxybenzophenones; no further characterization.
4-*t*-$C_4H_9C_6H_4$	14041-81-7	59	100	25	2	11.7	78	Yellow, viscous liquid, ir indicated no starting material, dilution with pentane gave 2.3 g of *p*-hydroxybenzophenone.
4-*t*-$C_4H_9C_6H_4$		59	150	55	1	14.2	95	Oil which crystallized on standing for several days, pentane trituration gave 3.9 g of *p*-hydroxybenzophenone, mp 131–133°.
3-*t*-$C_4H_9C_6H_4$	13189-56-5	59	100	25	2	13.1	87	Pale yellow liquid, recrystallized (MeOH), 5.6 g of yellow crystals, 2-hydroxy-4-*tert*-butylbenzophenone (37% yield), mp 80–81°.
3-*t*-$C_4H_9C_6H_4$		59	100	0	2	13.7	91	Yellow liquid, infrared indicated *m*-*tert*-butylphenol, PhCOF, and starting material, no indication of the desired product.
2,4-Di-*t*-$C_4H_9C_6H_3$	39000-49-2	48	150	55	4	12.6	84	Dark oil, very little starting material; no benzophenones were isolated.
3,5-Di-*t*-$C_4H_9C_6H_3$	5723-92-2	48	100	0	2	13.0	87	Pale yellow liquid, crystals separated, washed with pentane, gave 3,5-di-*tert*-butylphenol (3.9 g), mp 92–93.5°.
3,5-Di-*t*-$C_4H_9C_6H_3$		48	100	30	2	13.5	90	Yellow liquid, crystallized to give 3,5-di-*tert*-butylphenol (1.5 g); infrared of crude indicated phenols, Ph-COF, and unreacted ester with no indication of any benzophenone.
3,5-Di-*t*-$C_4H_9C_6H_3$		48	150	55	4	13.4	89	Yellow solids, recrystallized twice, from *i*-PrOH-H_2O then *i*-PrOH, gave 1.25 g of yellow solids, 2-hydroxy-4-*tert*-butylbenzophenone, mp 81–82°, no unreacted ester present.

[a] 5 ml of H_2O was added.

tert-butyl would be much less pronounced when placed in the meta position. The fate of the *tert*-butyl group is probably a combination of oligomerization and transalkylation, giving a large array of products. The disproportionation of *tert*-butylphenols has been studied over zeolites[7] and also was found to occur independently in HF.[6]

Theories and speculations on the mechanism of the Fries rearrangement are nearly as varied as the number of investigators in the field. Furthermore, the type of catalyst and even different quantities of the same catalyst at different temperatures provide interpretations of the reaction path which show little similarity.[2] Dewar and Hart[2a] have recently made an excellent attempt at clearing some of the confusion. The chief difference is whether the reaction is intermolecular or intramolecular, and even here terms such as "pseudo-intramolecular" are recorded.[2] No speculations or mechanistic studies using HF as the catalyst, which differs considerably from the usual aluminum halides,[8] have been recorded. From the data gathered thus far in this work and that gleaned from the literature, we presently favor the intermolecular path as shown below for the rearrangement of phenyl benzoates. The

---

(7) A. P. Bolton, M. A. Lanenala, and P. E. Pickert, *J. Org. Chem.*, **33**, 3415 (1968).

(8) Reference 2 provides a thorough review of the mechanism of the AlX_3 type of Fries rearrangements.

TABLE II

PREPARATION OF ARYL BENZOATES[a]

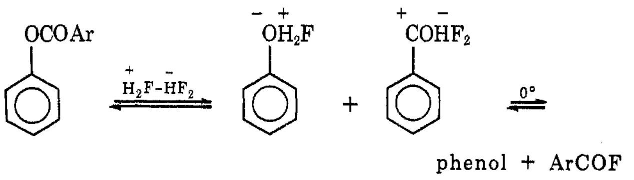
Aryl group	Substituted phenol, mol	C_6H_5COCl, mol	Pyridine, mol	Recrystn solvent	Yield, %	Mp, °C Found	Mp, °C Lit.
p-Tolyl	1.00	1.00	1.10	Hexane	82	70–71.5	70[d]
p-Ethylphenyl	1.00	1.00	1.10	Hexane	72	57–59	60[d]
p-Isopropylphenyl	0.50	0.50	0.50	Hexane	78	72–74	69–70[e]
p-*t*-Butylphenyl	1.00	1.00	1.00	Hexane–EtOH	81	81.5–83	83[f]
m-*t*-Butylphenyl	0.50	0.50	0.53	Liquid	78	136 (0.2 mm)[c]	[g]
2,4-Di-*tert*-butylphenyl	0.75	0.75	0.85	Hexane	45[b]	98–100	98[f]
3,5-Di-*tert*-butylphenyl	0.30	0.30	0.32	MeOH (9)–H_2O (1)	75	80–82	82.5–83[h]
p-Chlorophenyl	1.00	1.00	1.10	*i*-PrOH	83	86–87	88[d]
p-Methoxyphenyl	1.00	1.00	1.10	Hexane–EtOH	80	85–87	87[d]

[a] All reactions were run in toluene (1 l.) at reflux for 18–20 hr. [b] Run for 65 hr. [c] $n^{20}{}_D$ 1.555. [d] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd ed, Interscience, New York, N. Y., 1957, p 680. [e] R. L. Huang and F. Morsingh, *J. Chem. Soc.*, 160 (1953). [f] C. A. Sears, *J. Org. Chem.*, **13**, 120 (1948). [g] Bp 186–188 (11 mm). R. L. Van Etten, G. A. Clower, J. F. Sebastin, and M. L. Bender, *J. Amer. Chem. Soc.*, **89**, 3253 (1967). [h] J. W. Elders and R. P. Mariella, *Can. J. Chem.*, **41**, 1653 (1953).

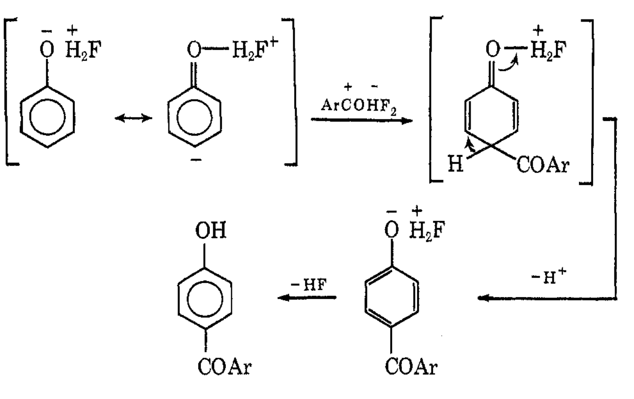
trimer form of HF is used here as the catalyst, since it displays the more ideal complexation forms, shown below.

$$3HF \rightleftharpoons H_2F\cdots HF_2$$

Initially a protonic cleavage step occurs, as follows.



Then, when carried out at 55°, an irreversible acylation takes place.



Although this paper is not intended to be mechanistically inclusive, the foregoing scheme is supported by the following observations.

(1) At 0° the cleavage products are readily isolated, and this step is reversible since benzoyl fluoride and phenol give phenyl benzoate in HF. In the $AlCl_3$ system, the counterpart to an acyl fluoride is not capable of isolation because it exists only as a complex. The reaction of benzoyl fluoride and a phenol in HF to form esters appears to be a novel reaction.

(2) HF is not as strong a π-type complexation agent as is $AlCl_3$ and will tend to be bound more to the oxygen atom rather than form π-coordination complexes with the aromatic ring. Also, HF possesses both Lewis and Brønsted type acid characteristics, which would tend to facilitate protolytic cleavage and an intermolecular reaction. $AlCl_3$ has only Lewis type of acidity.

(3) With phenyl benzoate in HF at 55°, *p*-hydroxybenzophenone is the major product with very little of the ortho derivative being obtained. Dewar and Hart suggest that an intramolecular reaction occurs only when the ortho/para ratio is close to unity. The benzoyl carbonium ion tends to go para in the intermolecular reaction because of the high charge due to the ^+H_2F cation complex in the vicinity of the ortho position.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord; nmr spectra were run on a Varian A-60 spectrometer and the mass spectra were obtained on a CEC mass spectrometer, Model 21-110. Gas chromatography was employed for studying the volatile components with an F & M Model 500 gas chromatograph using a 6-ft, 10% Apiezon L on Chromosorb W.

Chemicals.—*Caution!* When handling anhydrous HF, a face shield, rubber gloves with plastic arm bands, and a protective apron should be worn, and excellent hood facilities are required. Colorless hydrogen fluoride (99.9% from Air Products, Inc., Allentown, Pa.) was withdrawn in the liquid phase by inverting the cylinder and taking off liquid HF through a Monel Hoke valve in addition to the cylinder valve. The liquid HF was allowed to drip directly into a polyethylene graduate, where it readily condensed with very little loss as a fuming liquid; it was then poured into a 300-ml Monel transfer bomb.

Aryl Benzoates.—The starting esters (Table II) were all synthesized by reaction of benzoyl chloride with the appropriately substituted phenol (all commercially available) in refluxing toluene in the presence of pyridine. The example below illustrates a typical run taken from Table II with the other benzoates being prepared similarly.

4-*tert*-Butylphenyl Benzoate.—In a 2-l. flask equipped with a Trubore stirrer, thermometer, reflux condenser, and dropping funnel were placed successively 750 ml of toluene, 150.2 g (1 mol) of *p*-*tert*-butylphenol, and 79.1 g (1.0 mol) of pyridine. Benzoyl chloride (140.6 g, 1.0 mol) was added over a period of 15 min and the mixture was stirred at reflux temperature overnight. After being washed with an equal volume or water, then 10% HCl, water, 10% NaOH, and finally water, the toluene solution was dried over $MgSO_4$. Concentration on a rotating evaporator gave 235.8 g of crude ester. Recrystallization from *n*-hexane–ethanol yielded 205.5 g (81% yield) of white crystals, mp 81.5–83°.

General Procedure for Effecting the Fries Rearrangement in HF.—Either a 300-ml Monel reactor (for reactions above room temperature) or a 450-ml polyethylene vessel was cooled in ice and the specified amount of HF (usually 100–150 ml) was added under a nitrogen stream to exclude moisture. The ester was added and the mixture was shaken in a reciprocating shaker (Monel reactor) or stirred magnetically (polyethylene vessel) at the desired temperature and time. After completion of the reaction the mixture was poured into ice water and extracted with ether. The ether solution was shaken vigorously with saturated $NaHCO_3$ until neutral, washed with water, and dried over $MgSO_4$. Concentration gave the crude products as shown in

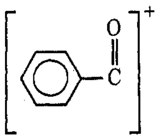
Table I. The residue was purified by crystallization, column chromatography, or distillation. Product characterization was made by comparison with authentically prepared samples, gas chromatography, ir, and nmr. The following two examples display the general method in detail.

2-Hydroxy-4-*tert*-Butylbenzophenone from 3-*tert*-Butylphenyl Benzoate.—Anhydrous HF (100 ml) was added to an ice-cooled 300-ml Monel reactor followed by dropwise addition of 3-*tert*-butylphenyl benzoate. The reactor was capped with a pressure head and shaken at 25° for 2 hr. Most of the HF was allowed to distil from the reactor and the contents were poured on ice. After extraction with ether, the combined organic layers were shaken with saturated NaOH and dried over $MgSO_4$. Concentration provided 14.0 g of a yellow liquid which tended to crystallize on standing. After vacuum distillation [maximum of pot 145° (0.5 mm)] to remove any volatiles, the pot residue, 10.5 g, was recrystallized from methanol to give 5.9 g (40% yield) of yellow crystals, mp 80.5–81.5°. Analysis is detailed below.

2-Hydroxy-4-*tert*-Butylbenzophenone from 3,5-Di-*tert*-Butylphenyl Benzoate.—The ester (15.0 g) was placed in 150 ml of HF in the Monel reactor and heated at 55° for 4 hr. The HF was allowed to evaporate and the residue was poured on ice, neutralized with $NaHCO_3$, extracted with ether, dried ($MgSO_4$), and concentrated to give 13.5 g of a yellow oil. Crystallization was achieved by dissolving the oil in 50% isopropyl alcohol and cooling in a Dry Ice–acetone bath. Recrystallization from isopropyl alcohol gave 1.25 g of yellow crystals: mp 81–82; uv max (EtOH) 3500 m; ir (3.5% $CHCl_3$) 6.17 μ (C=O).

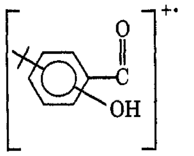
Anal. Calcd for $C_{17}H_{18}O$: C, 80.30; H, 7.12; mol wt, 254. Found: C, 80.23; H, 7.21; mol wt, 260 (osmometry).

Complete structure proof was as follows. The mass spectrum contained a parent ion at 254 with strong peaks observed for the fragments shown at *m/e* 105 and 177, respectively. Ir and nmr dilution studies indicated that the OH was in the 2 position because of strong intramolecular hydrogen bonding. This was evident by the strong downfield shifting of the hydroxyl proton, −728 Hz.



m/e 105

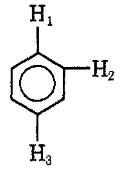
and



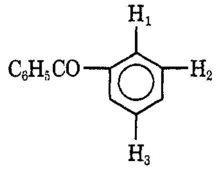
m/e 177

The position of the *tert*-butyl group was determined by nmr using an NMRIT analysis. An exact fit of the theoretical analysis of the aromatic protons with that of the experimental spectrum was obtained: $W_1 = -450.0$ Hz, $J_{12} = 8.6$ Hz; $W_2 = -410.5$ Hz, $J_{13} = 0.3$ Hz; $W_3 = -422.0$ Hz, $J_{23} = 1.9$ Hz.

It is well known[9] that the ortho coupling constants fall into the range of 7–9 Hz, meta 1–3 Hz, and para 0–1 Hz. Thus J_{12} is an ortho coupling constant, J_{13} para, and J_{23} meta. The proton arrangement is therefore identified as follows.



Irrespective of substituents, the proton ortho to the carbonyl group will experience the maximum of deshielding and will fall in the range of −440 to −470 Hz. Thus the carbonyl must be located as shown. Since the hydroxy group forms an intramolecular hydrogen bond, the structure is **4**.



3-*tert*-Butylphenyl Benzoate.—Anhydrous HF (100 ml) was placed in a 450-ml high-density polyethylene (Marlex) reactor[10] and cooled to −10°. Benzoyl fluoride (freshly distilled, 12.4 g, 0.10 mol) was added followed by *m-tert*-butylphenol (15.0 g, 0.10 mol). The mixture was stirred at −10° for 2 hr, poured on ice, and extracted with ether and the ether extracts were washed with saturated $NaHCO_3$. Drying with $MgSO_4$ and concentration provided 23.2 g of a pale yellow liquid. The infrared spectrum of the crude material indicated the presence of *m-tert*-butylphenol, benzoyl fluoride, 3-*tert*-butylphenyl benzoate, and a trace of 4-*tert*-butyl-2-hydroxybenzophenone. Distillation gave 13.4 g of the colorless product, bp 130–134° (0.2 mm). A similar run with *p-tert*-butylphenol at −40° gave a 75% yield of *tert*-butylphenyl benzoate, mp 81.5–83°. The pure compounds were characterized by comparison of their physical properties with those of authentically prepared esters.

Registry No.—Hydrogen fluoride, 7664-39-3; *p*-hydroxybenzophenone, 1137-42-4; 2-hydroxy-5-methylbenzophenone, 1470-57-1; 2-hydroxy-4-*tert*-butyl, benzophenone, 39000-51-6; 3,5-di-*tert*-butylphenol, 1138-52-9.

Acknowledgment.—The author wishes to acknowledge the capable laboratory assistance of Mr. Bill Loffer and the helpful discussions with Dr. John E. Mahan.

---

[9] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 770.

[10] See J. R. Norell, *J. Org. Chem.*, **35**, 1617 (1970), for a description of the reactor.