

dropwise to a precooled ( $-70^{\circ}$ ) solution of 2,3,5,6-heptafluorotoluene (21.8 g., 0.10 mole) in 200 ml. of anhydrous tetrahydrofuran. The temperature was maintained below  $-60^{\circ}$ . The solution was carbonated by bubbling gaseous carbon dioxide through the reaction mixture for 1 hr. The reaction was allowed to warm to room temperature with continued carbonation. The mixture was then hydrolyzed with 300 ml. of 6 *N* hydrochloric acid. The two-phase solution was distilled until only the aqueous phase remained. This solution was cooled, yielding a white precipitate which on recrystallization from benzene afforded 20.3 g. (77%) of white crystalline product, m.p.  $107.5-110.5^{\circ}$ . The analytical sample, m.p.  $110-111.5^{\circ}$  was obtained by an additional recrystallization from benzene.<sup>15b</sup>

Anal. Calcd. for  $C_8HF_7O_2$ : C, 36.66; H, 0.38; F, 50.7. Found: C, 36.72; H, 0.41; F, 50.6.

#### 2,2',3,3',5,5',6,6'-Octafluorobiphenyl-4,4'-dicarboxylic Acid.

—A solution of 2,2',3,3',5,5',6,6'-octafluorobiphenyl (28.9 g., 0.1 mole) in 55 ml. of anhydrous tetrahydrofuran was added dropwise over a period of 18 min. to a precooled ( $-70^{\circ}$ ) solution of *n*-butyllithium (137 ml. of a hexane solution, 0.2 mole) in 250 ml. of anhydrous tetrahydrofuran. Thirty minutes after the addition was complete, Color Test IIA was negative. After an additional 30 min., carbon dioxide was bubbled through the reaction mixture for 0.5 hr. The mixture was then allowed to warm to room temperature with continued carbonation and then hydrolyzed with 250 ml. 6 *N* HCl, and the resulting mixture was phase separated. The aqueous layer was then washed three times with diethyl ether, combined with the organic layer, and dried over magnesium sulfate. After drying, solvents were removed by aspiration, yielding 38.4 g. (96.7%) of the desired 2,2',3,3',5,5',6,6'-octafluorobiphenyl-4,4'-dicarboxylic acid, m.p.  $313-319^{\circ}$ . The analytical sample, m.p.  $318-320^{\circ}$  dec., was

obtained by slurring the above product in boiling petroleum ether, yielding 35.5 g. (91.9%).

Anal. Calcd. for  $C_{14}H_8F_8O_4$ : C, 43.54; H, 0.52; F, 39.36. Found: C, 43.24; H, 0.62; F, 39.40.

**Attempted Preparation of 4-Cyano-2,3,5,6-tetrafluorobenzoic Acid.**—To a cooled ( $-70^{\circ}$ ) stirred solution of 2,3,5,6-tetrafluorobenzonitrile (10.0 g., 0.057 mole) dissolved in 220 ml. of diethyl ether was added 0.057 mole of *n*-butyllithium (37 ml. of a hexane solution) over a period of 1 hr. During the addition the color of the reaction mixture changed from pale yellow to amber and finally to brown. Forty-five minutes after the addition was complete, Color Test I was positive and Color Test IIA was negative. The reaction was stirred another 45 min. and then carbon dioxide was bubbled in. During carbonation the appearance of the mixture became much lighter. The mixture was then warmed to room temperature, hydrolyzed with ice, acidified, extracted with diethyl ether, and dried over magnesium sulfate. Distillation of the dried organic layer yielded a pale yellow semisolid. Attempted crystallization from a variety of solvents as well as silica gel chromatographic separation produced no tractable material. Infrared analysis of the crude materials indicated the presence of a nitrile band at  $2250\text{ cm.}^{-1}$ .

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## The Acylation of 1,3,5-Triphenylbenzene. The Solvent Effect

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The aluminum chloride catalyzed acetylation of 1,3,5-triphenylbenzene gives only the peripheral-ring *para*-substitution product in nitrobenzene, dichloroethane, and carbon disulfide. Benzoylation of 1,3,5-triphenylbenzene gives only central-ring substitution in carbon disulfide and dichloroethane. The central-ring:peripheral-ring product ratio for benzoylation decreases by at least  $10^3$  as the solvent is changed from dichloroethane through various dichloroethane-nitrobenzene mixtures. The ratio is unity at a solvent composition containing between 15 and 20% nitrobenzene (nitrobenzene:benzoyl chloride molar ratio of approximately 5). The mechanism of the solvent effect is discussed.

It had been shown previously<sup>1</sup> that the normal position of electrophilic attack on 1,3,5-triphenylbenzene (**1**) is the central ring, but that Friedel-Crafts acetylation in nitrobenzene gives only an abnormal orientation product, 1-(*p*-acetylphenyl)-3,5-diphenylbenzene (**6**), resulting from attack at a *para* position of one of the peripheral rings. In contrast to this result, the literature records, for reactions of 1,3,5-triphenylbenzene, acetylation, phthaloylation, and aminoforylation giving only central-ring products (no yields or solvents recorded);<sup>2</sup> benzoylation giving a 90% yield of central-ring product (no solvent recorded);<sup>3</sup> benzoylation in carbon disulfide giving a 75% yield of central-ring product;<sup>4</sup> and benzoylation in carbon disulfide giving a 98% yield of central-ring product.<sup>5</sup>

In this laboratory acetylation with acetic anhydride has been found to give only 1-(*p*-acetylphenyl)-3,5-diphenylbenzene in each of the solvents, nitrobenzene, 1,2-dichloroethane, and carbon disulfide. These results are summarized in Table I. The examination

TABLE I  
ACETYLATION OF 1,3,5-TRIPHENYLBENZENE<sup>a</sup>

Solvent	Recovered 1, %	Yield of 6, %
CS <sub>2</sub>	63	36
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	31	60
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	30	72

<sup>a</sup> At  $20^{\circ}$  for 2 hr; triphenylbenzene and acetic anhydride 0.015 *M*; AlCl<sub>3</sub> 0.053 *M*. Percentages are  $\pm 2\%$ .

by nmr of the crude reaction mixtures in each solvent confirmed the specificity of the reaction. Only a single methyl signal, that of the peripheral-ring *p*-acetyl derivative at  $\tau$  7.45,<sup>1</sup> was observed under conditions that would have produced a detectable signal (at  $\tau$  8.11<sup>1</sup>) for a 2% yield of the central-ring isomer.

(1) G. E. Lewis, *J. Org. Chem.*, **30**, 2798 (1965).

(2) H. Hopff, H. A. Schweizer, A. Ghertos, A. Heer, and A. Solarsky, *Chimia (Aarau)*, **12**, 143 (1958).

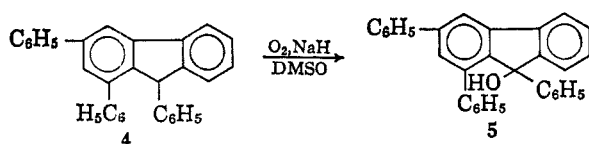
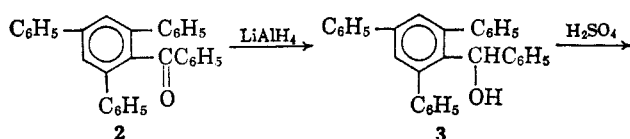
(3) E. P. Kohler and L. W. Blanchard, Jr., *J. Am. Chem. Soc.*, **57**, 367 (1935).

(4) N. S. Kozlov, P. N. Fedoseev and I. Drabkin, *J. Gen. Chem. USSR*, **6**, 1686 (1936); *Chem. Abstr.*, **31**, 2592 (1937).

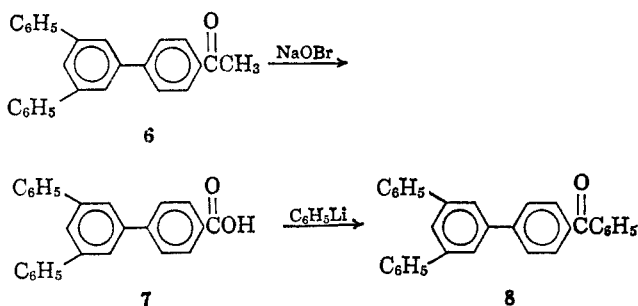
(5) D. Ivanov and C. Ivanov, *Chem. Ber.*, **77**, 173 (1944).

Acetylation in dichloroethane or carbon disulfide (but not in nitrobenzene) gives a deep yellow reaction mixture, suggesting that further reaction takes place. This allows the possibility that some central-ring product was formed and escaped detection because of further reaction. In a separate experiment treatment of the central-ring isomer with aluminum chloride and hydrogen chloride in dichloroethane did indeed lead to the rapid formation of a mixture of yellow materials. However, the high material balances shown in Table I indicate that this is at worst a small source of error.

The benzoylation of 1,3,5-triphenylbenzene is also complicated by further reaction, but in this instance further reaction gives only a single product, one which may be quantitatively determined and isolated. This product has been identified as 1,3,9-triphenylfluorene (5), the cyclization product of 1-benzoyl-2,4,6-triphenylbenzene (2),<sup>3</sup> by the sequence of reactions shown (2 → 5). The previously unknown peripheral-ring



*para* benzoylation product, 1-(*p*-benzoylphenyl)-3,5-diphenylbenzene (8), was characterized by synthesis from 1-(*p*-acetylphenyl)-3,5-diphenylbenzene (6 → 8). Unlike the case of the peripheral-ring *p*-



acetyl derivative, it was not possible to identify 8 directly through the characteristic  $A_2B_2$  coupling pattern in its nmr spectrum. Although the substituted peripheral-ring protons are shifted downfield by the acetyl group sufficiently to appear outside of the general mass of aromatic protons at  $\tau$  2.2–2.7, this is not true for the benzoyl derivative.<sup>6</sup>

(6) A more general diagnostic tool for the orientation of substitution was developed during this study. All 1,3,5-triphenylbenzene derivatives have a moderately intense infrared absorption band around 11.3  $\mu$  which can be attributed to an out-of-plane deformation of an aromatic hydrogen with no adjacent hydrogens (*i.e.*, a central-ring hydrogen).<sup>7</sup> All derivatives having a single electron-withdrawing substituent on the peripheral ring were found to absorb between 11.26 and 11.30  $\mu$  (five examples); all derivatives having a single electron-withdrawing substituent on the central ring absorbed between 11.20 and 11.23  $\mu$  (four examples); 1,3,5-triphenylbenzene absorbed at 11.32  $\mu$ .

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 79.

In accord with the results of Ivanov and Ivanov<sup>5</sup> we find that benzoylation of 1,3,5-triphenylbenzene in carbon disulfide is a clean reaction, giving the central-ring benzoyl derivative in nearly quantitative yield. Benzoylation in dichloroethane gives a mixture of the central-ring benzoyl derivative and its cyclization product, 5.<sup>8</sup> In nitrobenzene the product is a mixture of the peripheral-ring *p*-benzoyl derivative and a small amount of 5. These data and the data for mixtures of dichloroethane and nitrobenzene are given in Tables II and III.

TABLE II  
BENZOYLATION OF 1,3,5-TRIPHENYLBENZENE.  
PRODUCT COMPOSITIONS<sup>a</sup>

Solvent, (v/v)	Recovery			
	of 1, %	8	2	5
CS <sub>2</sub>	5	0	93	0
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	14	0	76	9
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (5:95)	10	7	68	10
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (10:90)	59	11	9	18
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (15:85)	54	23	0	26
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (20:80)	57	26	0	18
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (30:70)	52	31	0	15
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (50:50)	52	38	0	9
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	45	46	0	6

<sup>a</sup> At 20° for 2 hr; triphenylbenzene and benzoyl chloride 0.015 M; AlCl<sub>3</sub> 0.053 M. Percentages are  $\pm 2\%$ .

TABLE III  
BENZOYLATION OF 1,3,5-TRIPHENYLBENZENE.  
REACTANT AND PRODUCT MOLAR RATIOS

Solvent (v/v)	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> / C <sub>6</sub> H <sub>5</sub> COCl	Central- ring <sup>a</sup> / peripheral ring
CS <sub>2</sub>	0	Very high
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0	Very high
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (5:95)	1.6	11
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (10:90)	3.1	2.4
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (15:85)	4.6	1.1
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (20:80)	6.3	0.7
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (30:70)	9.3	0.5
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (50:50)	15	0.2
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	31	0.1

<sup>a</sup> Central-ring value includes both 1 and 4; see footnote 8.

Careful infrared examination of each of the several dozen elution chromatography fractions of the product from reaction in dichloroethane revealed no trace of the peripheral-ring *p*-benzoyl derivative, indicating that the total yield of 8 must certainly be less than 1%. Therefore, the change in central-ring:peripheral-ring attack is at least 10<sup>3</sup> in going from nitrobenzene to dichloroethane.

Two explanations have been proposed in the past for abnormal orientations in Friedel-Crafts acylations run in nitrobenzene: One involves equilibrium control and the other, steric effects owing to bulky complex

(8) It is conceivable that 1,3,9-triphenylfluorene could arise from cyclization of a peripheral-ring *ortho* product. However, in view of the acetylation results shown in Table I and in view of the fact that benzoylation in a far less hindered molecule, toluene, gave only 7–9% *ortho* substitution in both dichloroethane and nitrobenzene,<sup>9</sup> any significant amount of *ortho* substitution in this reaction seems rather unlikely. In this study all of the 1,3,9-triphenylfluorene has been assigned to central-ring attack.

(9) H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719 (1957); H. C. Brown and G. Marino, *J. Am. Chem. Soc.*, **81**, 3308 (1959).

formation with nitrobenzene.<sup>10</sup> It is evident that in the present case the abnormal orientation in nitrobenzene is not due to equilibrium control. Treatment of 1-benzoyl-2,4,6-triphenylbenzene with aluminum chloride and hydrogen chloride in nitrobenzene produced no trace of the peripheral-ring isomer; the central-ring compound was recovered contaminated only with a slight amount of 1,3,9-triphenylfluorenol. Similar results were obtained with the central-ring acetyltriphenylbenzene.

The data do fit the bulky complex model quite satisfactorily. Regardless of whether the actual electrophile is the benzoyl chloride-aluminum chloride complex or the benzoyl acylium ion, both are highly charged species and would be expected to freeze out several polar nitrobenzene molecules from the surrounding medium. The resulting large unit might well offer an abnormal hindrance to attack at the sterically crowded central-ring positions, particularly since the high selectivity of benzoylation<sup>11</sup> indicates that covalent bonding between electrophile and substrate is well advanced in the transition state. The data in Table III do indeed indicate that only a small number of nitrobenzene molecules for every molecule of benzoyl chloride is necessary to reverse the orientation from peripheral ring to central ring.

Recently Jensen and Goldman<sup>12</sup> have proposed an alternative explanation for the solvent effect in the benzoylation of naphthalene. Their explanation is based on the assumption of an unusual stability for the  $\sigma$  complex at the 1-position and third-order kinetics for attack at that position. In their view nitrobenzene inhibits attack at the 1-position by complexing the aluminum chloride which assists in deprotonation of the  $\sigma$  complex. Without kinetic evidence as to the over-all order of benzoylation of 1,3,5-triphenylbenzene, it is impossible to determine the applicability of this latter explanation to the present case.

Although no evidence has been obtained in this study to support the explanation of Jensen and Goldman, observations concerning the cyclization of **2** are difficult to rationalize other than in terms of a relatively stable central-ring  $\sigma$  complex. The data in Table II show that very little of **2** cyclized during the benzoylation reaction in  $C_2H_4Cl_2$ , but that all of it does in nitrobenzene. Treatment of the central-ring benzoyl compound with aluminum chloride and hydrogen chloride in nitrobenzene under the previous reaction conditions produced only a 6% conversion to 1,3,9-triphenylfluorenol; a 3-day reaction time was required for 46% conversion. Therefore, neither the ketone-aluminum chloride complex **10** nor any of its more accessible conjugate acids (peripheral-ring protonated isomers of **9**) is the species that cyclizes during

the benzoylation reaction. The most reasonable cyclizing species is the aluminum chloride-central-ring  $\sigma$  complex **9**, which is stabilized in the more polar nitrobenzene relative to dichloroethane.

By comparison of the data in Tables II and III it can be seen that when the nitrobenzene content in the nitrobenzene-dichloroethane solvent mixture is reduced to 15%, the majority of the reaction is taking place on the central ring. However, the rate, as measured by the amount of unreacted triphenylbenzene, has not changed commensurately. Only when the nitrobenzene content is reduced to 5% is there a dramatic increase in rate. It can be seen from the fixed molar ratio of aluminum chloride to benzoyl chloride (3.5) in each solvent mixture, that the number of moles of aluminum chloride and nitrobenzene are approximately equivalent in the 10:90 nitrobenzene-dichloroethane mixture. Since aluminum chloride is probably extensively complexed with nitrobenzene,<sup>12</sup> then only at solvent mixtures containing more than 10% nitrobenzene are there significant amounts of free nitrobenzene and only at solvent mixtures containing less than 10% nitrobenzene are there significant amounts of free aluminum chloride. Apparently the orientation is more sensitive to the concentration of nitrobenzene than the rate is to the concentration of aluminum chloride.

The pronounced differences in orientation between acetylation and benzoylation in the different solvents are difficult to assess. The question of the actual acylating species has never been settled<sup>12</sup> and it is not known whether acid anhydrides and acid chlorides react through common intermediates. Therefore, discussions based on the present data concerning the relative steric effects of acetylation and benzoylation are premature.

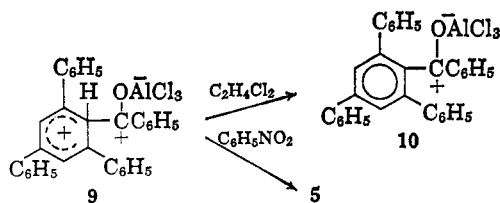
### Experimental Section

The infrared measurements were determined in  $CCl_4$  solutions on a Beckman IR-5 instrument calibrated against polystyrene. The nmr measurements were determined in  $CDCl_3$  solutions on a Varian A-60 instrument, using tetramethylsilane as an internal standard. Melting points were taken on a Fisher-Johns block and are corrected. Elemental analyses were performed by Alfred Bernhardt, Mülheim, Germany.

The aluminum chloride used was from a single new container of reagent grade anhydrous material waxed between uses. The nitrobenzene used was reagent grade material that was washed with concentrated hydrochloric acid and then water, dried over Drierite, and distilled. The 1,2-dichloroethane used was purified by the method of Brown, Marino, and Stock.<sup>13</sup> Acetic anhydride and benzoyl chloride were freshly distilled before each run.

**Acylation of 1,3,5-Triphenylbenzene.**—To a solution of 4.60 g (0.015 mole) of 1,3,5-triphenylbenzene and 1.53 g (0.015 mole) of acetic anhydride or 2.12 g (0.015 mole) of benzoyl chloride in 50 ml of solvent was added with vigorous stirring 7.0 g (0.053 mole) of anhydrous aluminum chloride. An ice-water bath was adjusted during addition and thereafter so that the reaction temperature remained between 19 and 21°. After 2 hr the deeply colored solutions were poured on ice, the layers were separated, and the aqueous layers were extracted with dichloromethane. The combined organic layers were steam distilled if nitrobenzene was present or, if not, were concentrated on a rotary evaporator. The resulting residues were then analyzed.

**Methods of Product Analysis.**—Infrared working curves were determined by base-line methods in  $CCl_4$  solutions of known



(10) For a recent discussion, see P. H. Gore, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, pp 5-8, 64-66.

(11) L. M. Stork and H. C. Brown *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(12) F. R. Jensen and G. Goldman, ref 10, pp 1003-1032.

(13) H. C. Brown, G. Marino, and L. M. Stock, *J. Am. Chem. Soc.*, **81**, 3310 (1959).

concentration over a large concentration range. The following wavelengths were used: 1, 7.05, 9.27, 9.67, and 11.32  $\mu$ ; 2, 5.95, 7.90, 10.68, and 11.22  $\mu$ ; 5, 2.82  $\mu$ ; 6, 5.90, 7.05, 7.15, 7.33, 7.87, 8.41, 10.43, and 11.28  $\mu$ ; and 8, 5.99, 7.05, 7.58, 7.80, 10.61, 10.79, 11.28, and 11.72  $\mu$ . Reproducibilities were  $\pm 2\%$ . Not all of these wavelengths were equally reliable owing to multiple interferences. The values of 2 below 10% in mixtures with 8 are questionable for this reason.

The dried residue of every reaction was carefully ground until homogeneous. Several weighed aliquots were dissolved in standard volumes of  $\text{CCl}_4$ , and the infrared absorption values were compared with the working curves.

Several of the mixtures were further analyzed by elution chromatography through a column of Woelm activity grade I alumina. In a typical example, the product from benzylation in 1,2-dichloroethane gave the following fractions (three chromatograms were required for complete resolution): A, eluted with petroleum ether (bp 30–60°), 0.64 g (14%) of triphenylbenzene; B, eluted with benzene, 4.50 g (73%) of 1-(*p*-benzoylphenyl)-3,5-diphenylbenzene; C, eluted with 20:1 benzene-ether, 0.55 g (9%) of 1,3,9-triphenylfluorene. Infrared analyses of the same mixture showed 15, 76, and 9%, respectively. Infrared examination of all the fractions showed no trace of 2, which in other mixtures was eluted with benzene-petroleum ether mixtures appearing in the eluate between 1 and 8.

1-(*p*-Benzoylphenyl)-3,5-diphenylbenzene (8) was recrystallized from ethanol: mp 145.0–145.5°;  $\lambda$  5.99 (C=O) and 11.28  $\mu$ .<sup>6</sup>

*Anal.* Calcd for  $\text{C}_{25}\text{H}_{20}\text{O}$ : C, 90.81; H, 5.41. Found: C, 90.71; H, 5.35.

1,3,9-Triphenylfluorene (5) was recrystallized from petroleum ether (bp 90–120°): mp 204.5° (lit.<sup>3</sup> mp 207°);  $\lambda$  2.82 (O-H) and 11.31  $\mu$ .<sup>6</sup>

**Preparation of 1-Benzoyl-2,4,6-triphenylbenzene (2).**—Several attempts to prepare 2 by a Grignard method<sup>3</sup> failed. The following alkyllithium exchange method was found to be both convenient and reliable. To 7.67 g (0.0200 mole) of 1-bromo-2,4,6-triphenylbenzene<sup>3</sup> dissolved in 50 ml of dry toluene was added 12.5 ml of 1.6 *M* butyllithium solution. After stirring for 30 min, 2.82 g (0.0200 mole) of freshly distilled benzoyl chloride was added in small portions; the mixture was stirred for another 30 min as the temperature returned to 25° and then poured on ice. The residue remaining after concentration of the organic layer was filtered and washed with ether: 4.74 g (58%) of material; mp 169–170° (lit.<sup>3</sup> mp 168–169°), unchanged on recrystallization from benzene-ethanol;  $\lambda$  5.95 (C=O) and 11.22  $\mu$ .<sup>6</sup>

**Conversion of 1-(*p*-Acetylphenyl)-3,5-diphenylbenzene (6) to 1-(*p*-Benzoylphenyl)-3,5-diphenylbenzene (8).**—1-(*p*-Acetylphenyl)-3,5-diphenylbenzene<sup>1</sup> was oxidized with sodium hypobromite to 1-(*p*-carboxyphenyl)-3,5-diphenylbenzene (7) in 75% yield by the method of Edwards and Cashaw.<sup>14</sup> An analytical sample was recrystallized from acetonitrile: mp 247–248°;  $\lambda$  5.89 (C=O) and 11.28  $\mu$ .<sup>6</sup>

*Anal.* Calcd for  $\text{C}_{25}\text{H}_{18}\text{O}_2$ : C, 85.79; H, 5.18. Found: C, 85.99; H, 5.42.

1-(*p*-Carboxyphenyl)-3,5-diphenylbenzene was converted to 1-(*p*-benzoylphenyl)-3,5-diphenylbenzene in 51% yield by the method of Cram and Fischer.<sup>15</sup> This material was identical in infrared spectrum and melting point with the benzylation product in nitrobenzene; their mixture melting point showed no depression.

**2,4,6-Triphenylbenzhydrol (3).**—To 4.00 g of 1-benzoyl-2,4,6-triphenylbenzene dissolved in 200 ml of anhydrous ether was added 1.0 g of lithium aluminum hydride. The reaction mixture was allowed to stir overnight and then quenched with methanol. Water was added and the liquid phases were decanted and separated. The residue was extracted with dichloromethane. The combined organic layers were concentrated to give 3.73 g (93%) of 2,4,6-triphenylbenzhydrol, mp 154–157°. Chromatography through a Florisil column produced an analytical sample, mp 158–158.5° (lit.<sup>3</sup> mp 158°).

**1,3,9-Triphenylfluorene (4).**—To 30 ml of concentrated sulfuric acid was added 3.73 g of 2,4,6-triphenylbenzhydrol. The mixture was heated until the solid material melted (100–105°). The resulting dark brown solution was allowed to cool and poured on ice. The filtered solid material was washed thoroughly with sodium carbonate solution and then water. The yield of 1,3,9-triphenylfluorene, mp 148–149° (lit.<sup>3,16</sup> mp 149°), was 2.19 g (62%).

**1,3,9-Triphenylfluorene (5).**—To a solution of 2.19 g of 1,3,9-triphenylfluorene dissolved in 100 ml of dimethyl sulfoxide was added a spatula of a 50% sodium hydride dispersion in mineral oil. Dry air was passed into this cherry red solution until the color faded to yellow (40 min). The solution was poured on ice and filtered. The filtered material was washed with water and then petroleum ether (bp 30–60°). The yield of 1,3,9-triphenylfluorene, mp 204–205°, was 1.90 g (84%). The infrared spectrum of this product was identical with that isolated from the benzylation reaction, and the mixture melting point showed no depression.

**Reaction of 1-Acetyl- and 1-Benzoyl-2,4,6-triphenylbenzene with Aluminum chloride.**—Treatment of 1-acetyl-2,4,6-triphenylbenzene<sup>1</sup> with aluminum chloride and hydrogen chloride in dichloroethane for 30 min produced a yellow gum which could not be resolved by repeated elution chromatograms. Infrared examination of the chromatography fractions showed that the starting material had been completely destroyed and that there was no trace of the peripheral-ring *p*-acetyl derivative.

Treatment of 1-benzoyl-2,4,6-triphenylbenzene with aluminum chloride and hydrogen chloride in nitrobenzene for 2 hr led to recovery of starting material. Careful infrared examination of the product showed the presence of 6% of 1,3,9-triphenylfluorene and no peripheral-ring *para* isomer. Lengthening of the reaction time to 3 days produced no peripheral-ring *para* isomer, 46% of 1,3,9-triphenylfluorene, and recovered starting material.

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