

tion cooled. The pale yellow crystals of trimer (**13**, R = CH<sub>3</sub>O) were filtered: yield 2.0 g (50%), mp 167–169°.

This material was identical with the trimer prepared by the ferricyanide oxidation.

**Ag<sub>2</sub>O Oxidation of 4-Phenyl-2,6-xyleneol.**—A mixture of benzene (75 ml), silver oxide (5.0 g, 0.022 mol), and 4-phenyl-2,6-xyleneol (3.96 g, 0.02 mol) was stirred for 3 hr. The solution was dried (MgSO<sub>4</sub>). The benzene was removed on a film evaporator and the residue recrystallized from acetone–water. Light yellow solids were obtained (3.5 g, 88%).

Several recrystallizations gave white crystals, mp 198–200°, of the trimer **13** (R = C<sub>6</sub>H<sub>5</sub>).

*Anal.* Calcd for C<sub>24</sub>H<sub>36</sub>O<sub>3</sub>: C, 85.8; H, 6.1; mol wt, 588. Found: C, 85.9; H, 6.0; mol wt, 609.

**4-*t*-Butylanisole.**—Commercial 4-*t*-butylphenol was methylated with dimethyl sulfate after conversion into its salt with sodium. The yield was 81% colorless anisole, bp 51° (0.7 mm).

**Li-NH<sub>3</sub> Reduction of 4-*t*-Butylanisole.**—The general procedure of Wilds and Nelson<sup>16</sup> was followed for the Birch reduction of 4-*t*-butylanisole.

A 500-ml three-necked flask was insulated with vermiculite. The flask was charged with 4-*t*-butylanisole (8.2 g, 0.05 mol) and anhydrous ether (75 ml). Anhydrous ammonia (100 ml) was distilled into the flask, which was equipped with a Dry Ice–acetone condenser. Lithium wire (2.2 g, 24 g-atoms) was added over 5 min. After 0.5-hr stirring of the solution, methanol (20 ml) was added slowly. When the ammonia had evaporated the ether solution was washed with water and dried (MgSO<sub>4</sub>). The product remaining after removal of the ether was distilled, yielding 5.2 g (63%) of the colorless dihydroanisole, bp 43° (0.4 mm).

*Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>O: C, 79.5; H, 10.8; mol wt, 166. Found: C, 79.7; H, 10.5; mol wt, 178.

**Hydrolysis of 2,5-Dihydro-4-*t*-butylanisole.**—A cold (0–5°) mixture of sulfuric acid (25 ml) and water (75 ml) was added dropwise to a cold (5°) solution of 2,5-dihydro-4-*t*-butylanisole (2.8 g) in benzene (100 ml). This mixture was allowed to warm to 25° after the addition of the acid was complete. The layers were separated; the benzene layer was washed with water, sodium bicarbonate solution, and water, then dried (MgSO<sub>4</sub>). The

yellow oil obtained after removal of the benzene was distilled, giving 1.9 g (74%) of 4-*t*-butyl-3-cyclohexenone, bp 45° (0.4 mm), *n*<sub>D</sub><sup>20</sup> 1.4816.

*Anal.* Calcd for C<sub>10</sub>H<sub>16</sub>O: C, 79.0; H, 10.5; mol wt, 152. Found: C, 78.8; H, 10.2; mol wt, 166.

The infrared spectrum of this material revealed that it consisted of both the conjugated (24%) and unconjugated ketones (76%). Preparative vpc was used to obtain a small but pure sample of 4-*t*-butyl-3-cyclohexenone.

**Conjugation of 4-*t*-Butyl-3-cyclohexenone.**—Samples of the pure ketone were refluxed for 1 and 2 hr in absolute methanol containing ~1% concentrated HCl. The ketone was reisolated by extraction into ether, washing with water, dilute base, and water, and then drying. The 1-hr sample gave 41% conjugation, while the 2-hr sample gave 63% conjugation. The reaction is evidently slow.

**2,4-Dinitrophenylhydrazone of 4-*t*-Butyl-3-cyclohexenone.**—The method of Shriner and Fuson<sup>18</sup> was used. A yield of 0.155 g (29%) of the purified dinitrophenylhydrazone was obtained from 0.25 g of the ketone, mp 163–165°.

*Anal.* Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>N<sub>4</sub>: C, 57.8; H, 6.0; N, 17.0; mol wt, 332. Found: C, 57.7; H, 6.1; N, 17.0; mol wt, 332.

**Registry No.**—**13**, R = *t*-butyl, 22566-50-3; **13**, R = CH<sub>3</sub>O, 21856-90-6; **13**, R = C<sub>6</sub>H<sub>5</sub>, 22566-51-4; **17**, 22566-52-5; **21**, 22566-53-6; **22**, 5234-62-8; 2,4-dinitrophenylhydrazone of **22**, 22566-55-8.

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## Chlorination of Aromatic Systems with Trichloroisocyanuric Acid under Polar and Free-Radical Conditions<sup>1</sup>

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Trichloroisocyanuric acid (I) was found to be an effective laboratory reagent for nuclear or side-chain halogenation of aromatic systems. Chlorination of common aromatic, polynuclear, and mixed aromatic–aliphatic systems was investigated. A charge-transfer intermediate appears to be involved in the reaction.

The use of trichloroisocyanuric acid (1,3,5-trichloro-2,4,6-trioxohexahydro-*s*-triazine) as an allylic halogenating agent was described by Ziegler,<sup>3</sup> and we have previously reported examples of  $\alpha$  halogenation of saturated cyclic ethers.<sup>4</sup> N-Halogen compounds, such as N-bromosuccinimide, N-chlorosuccinimide, N-bromoacetamide, etc., were previously described as nuclear<sup>5</sup> and side-chain<sup>6</sup> halogenating agents. The use

of trichloroisocyanuric acid in this capacity has not been described. As part of our continued study of the use of this reagent as a convenient laboratory substitute for chlorine, we now report its reactions with a number of common aromatic compounds. Other examples of the synthetic variety offered by this reagent are its use as a hypohalogenating agent<sup>4</sup> and the novel and direct conversion of ethers into esters.<sup>7</sup>

The reaction of trichloroisocyanuric acid (Scheme I) with benzene in the presence of anhydrous ferric chloride or 50% aqueous sulfuric acid as catalytic reagents yielded chlorobenzene. It is analogous to the reaction of benzene with molecular chlorine, which requires Lewis acid catalysis. In addition, naphthalene also required Lewis acid catalysis to effect good yields of the 1-chloro product, and only small amounts of product were obtained when no catalyst was employed

(1) Taken in part from the M.S. theses of D. A. Beal and W. P. Duncan, Kansas State College of Pittsburg, 1968 and 1966, respectively.

(2) To whom all inquiries should be addressed.

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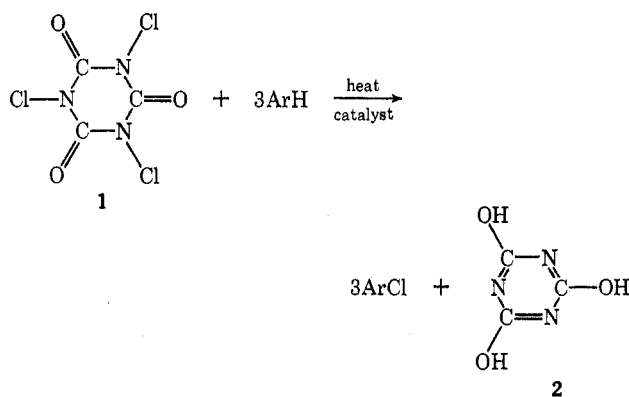
TABLE I  
 MONOSUBSTITUTION OF AROMATIC COMPOUNDS

Compd	Time, hr	Temp, °C	Solvent	Catalyst	Chloro product, <sup>a</sup> %
Benzene	2	40-80	Benzene	FeCl <sub>3</sub>	62
Benzene	5	65-80	Benzene	50% H <sub>2</sub> SO <sub>4</sub>	80
Naphthalene	5	78	CCl <sub>4</sub>	None	2.7 (1-Cl)
Naphthalene	3	78	CCl <sub>4</sub>	FeCl <sub>3</sub>	58 (1-Cl)
Naphthalene	1	95	None	50% H <sub>3</sub> PO <sub>4</sub>	44 (1-Cl)
Toluene	16.5	20-90	None	FeCl <sub>3</sub>	9.4 (2-Cl), 36 (4-Cl)
Toluene	4	65-80	None	50% H <sub>2</sub> SO <sub>4</sub>	66 (2-Cl + 4-Cl)
Toluene	3	78	CCl <sub>4</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub>	44 (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl)
<i>t</i> -Butylbenzene	3	78	CCl <sub>4</sub>	FeCl <sub>3</sub>	4.8 (2-Cl), 35 (4-Cl)
Phenol	1	40-78	CCl <sub>4</sub>	None	7.5 (2-Cl), 48 (4-Cl)
Aniline	5.75	40-78	CCl <sub>4</sub>	None	2.3 (2-Cl), 25 (4-Cl)
Benzoic acid	3	78	CCl <sub>4</sub>	FeCl <sub>3</sub>	None
Nitrobenzene	4	78	CCl <sub>4</sub>	FeCl <sub>3</sub>	None

<sup>a</sup> Yields based on the amount of trichloroisocyanuric acid used.

SCHEME I

## GENERALIZED CHLORINATION REACTION



in the reaction (Table I). This is in direct contrast to the reaction of naphthalene with molecular chlorine, in which such catalysis is not required to obtain the 1-chloro product in good yield.<sup>8</sup>

In order to investigate mechanistic control in the chlorination of mixed aromatic-aliphatic systems, toluene was chlorinated under ionic and free-radical conditions. As shown in Table I, the use of anhydrous ferric chloride or 50% aqueous sulfuric acid as catalytic agents yielded 2- and 4-chlorotoluene, while reaction in the presence of benzoyl peroxide yielded benzyl chloride. Treatment of *t*-butylbenzene under the conditions shown (Table I) gave rise to 2- and 4-chloro-*t*-butylbenzene, with the yield of chlorinated product being nearly the same as that obtained in the toluene reaction.

A mechanism involving charge-transfer complexes and, thus, differing from that usually postulated for electrophilic chlorination of aromatic substrates (presence of Cl<sub>2</sub>, formation of Cl<sup>+</sup> or Cl<sup>+</sup>-Cl<sup>-</sup>·MX<sub>3</sub> dipole) might be operating when trichloroisocyanuric acid was employed as a source of chlorine. In an effort to find evidence for such a mechanism and to study the application of the chlorination reaction in organic synthesis, some benzene derivatives which display widely differing electron densities were subjected to reaction. It was found that no catalytic agents were necessary to effect the production of 2-chloro- and 4-chloro-substituted products from phenol or aniline and trichloroisocyanuric acid. In contrast, when attempts were made to

chlorinate nitrobenzene and benzoic acid, no chlorinated products were obtained, despite the fact that suitable catalysis and extensive reflux were employed in both reactions (Table I). Thus trichloroisocyanuric acid can be used as an effective monochlorinating agent for substances which tend to give polysubstitution, such as phenols and anilines. Moreover, failure to produce polyhalogenation of phenol and aniline in contrast to the reaction with chlorine suggests that destabilization of the complex through monohalogenation may account for the lack of 2,4,6 trisubstitution of reactive aromatics and may support the argument for a charge transfer complex intermediate. Complete lack of reactivity of some aromatic compounds may be accounted for in terms of poor electron-donor properties of the aromatic compounds.

In all reactions producing chlorinated products, intense coloration of the reaction mixture was noted. In the aniline reaction, this color developed immediately upon addition of the chlorinating agent to a stirring solution of aniline in carbon tetrachloride at room temperature. These colors or transient colors occurring during the course of the reaction suggested a molecular complex as a participatory agent in the reactions. That this idea is not unreasonable is indicated by the facts that Lewis acid molecular complexes are well documented<sup>9</sup> and that substituted triazines have been proposed as strong electron acceptors, capable of forming donor-acceptor charge-transfer complexes.<sup>10</sup> Trichloroisocyanuric acid may undergo rehybridization to a conjugated triazine *via* concomitant electron shifts. An electronic rearrangement of this type has been shown for a similar species, cyanuric acid (2), in solution.<sup>11</sup>

In order to investigate the facility with which such a complex might form, four compounds were selected which were considered to have good electron-donor properties. The spectra of these compounds in the presence of trichloroisocyanuric acid (1:1 molar ratio) were recorded, and pertinent assignments appear in Table II. An attempt at determining the formulation of the complexes by mole ratio method spectroscopy<sup>12</sup> was proved unsatisfactory. From solutions of suitable

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(10) P. R. Hammond, *Nature*, **206**, 891 (1965).

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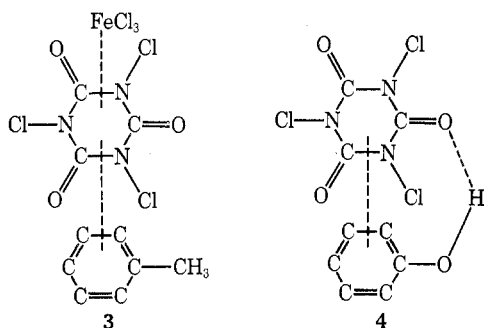
TABLE II<sup>a</sup>  
SPECTRAL ASSIGNMENTS OF MOLECULAR COMPLEXES

Donor compd <sup>b,c</sup>	Major band, nm <sup>d,e</sup>	Minor band, nm
Aniline	285 (241)	298 (285)
2,4,6-Trichlorophenol	249 (227)	293-304 (287)
2,4,6-Trichloroaniline	223 (213)	278-303 (245)
Pentachlorophenol	261 (231)	304 (303)

<sup>a</sup> Data are given for solutions of reactants. <sup>b</sup> Trichloroisocyanuric acid absorbs at 216, 239, and 253 nm. <sup>c</sup> All spectra were taken in acetonitrile, 1-cm cell path. <sup>d</sup> No complex showed absorption beyond 350 nm. <sup>e</sup> Values in parentheses are for absorptions of donors alone.

concentration were isolated solids which gave spectra very similar to or identical with those obtained when the donor compounds were mixed with trichloroisocyanuric acid solutions. All were brilliantly colored, ranging from bright yellow (trichlorophenol) to deep red (aniline). Only in the case of aniline was it possible to isolate a stable, crystalline complex as an analytically pure compound.

The aniline complex was examined to determine whether a chloroaniline could be generated from it. A quantity of this red material was taken up in carbon tetrachloride and decomposed under reflux. Gas chromatographic analysis of the reaction mixture showed that 4-chloroaniline had been produced, suggesting that the molecular-addition complex observed probably lies along the reaction path. In conclusion, for those reactants requiring Lewis acid catalysis, such as toluene (see structure 3), the catalyst would contribute to the acidity of the electron acceptor. Stabilization of phenol (see structure 4) or aniline would be

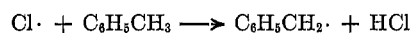
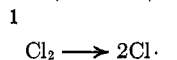
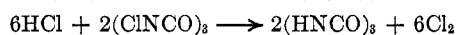


promoted by their high electron density and possibly through hydrogen bonding placing the *ortho* and *para* positions of phenol in juxtaposition with the transferable halogens of the trichloroisocyanuric acid. Under reaction conditions conducive to free-radical attack (presence of peroxides or other radical initiators, nonpolar solvents), trichloroisocyanuric acid (1) may be considered to react in the manner proposed by Goldfinger and coworkers<sup>13</sup> and supported by the work of McGrath and Tedder,<sup>14</sup> where nascent HCl results in the steady-state formation of Cl<sub>2</sub> with subsequent production of Cl radicals (Scheme II).

The reactions in Scheme II serve to illustrate the versatility and occasional specificity of the reactions of trichloroisocyanuric acid as a chlorinating agent in addition to its use, already described, as an oxidant<sup>7</sup> and a hypohalogenating agent.<sup>4</sup>

A detailed account of the properties of trichloro-

SCHEME II  
CHAIN-REACTION SEQUENCE PROPOSED BY GOLDFINGER APPLIED TO TOLUENE WITH TRICHLOROISOCYANURIC ACID



isocyanuric acid as an oxidizing agent and its specificity in oxidation is in preparation and will appear in the near future.

### Experimental Section

All reactants were reagent grade chemicals and were used as received with the exception of benzene and toluene, which were purified by distillation to give materials with boiling points of 80-81° (760 mm) and 110-111° (760 mm), respectively. After triple distillation under vacuum, aniline, bp 76° (10 mm), was obtained. *t*-Butylbenzene, bp 60° (3 mm), was prepared by established procedures.<sup>15</sup> Gas chromatographic separations were made on Aerograph A-90P and A-700 gas chromatographs, under the conditions noted. Infrared spectra were recorded on Perkin-Elmer 137 and 337 infrared spectrophotometers. Melting points, obtained on a Fisher-Jones apparatus, are uncorrected. Yields are based on the amount of trichloroisocyanuric acid used.

**Reaction of Trichloroisocyanuric Acid with Benzene Using Anhydrous Ferric Chloride as the Catalyst.**—To 110 ml (99.7 g, 1.26 mol) of benzene mixed with 8.11 g (0.05 mol) of anhydrous ferric chloride was added 11.62 g (0.05 mol) of trichloroisocyanuric acid over a 1-hr period at such a rate so as to maintain the temperature at 40-80°. After all of the trichloroisocyanuric acid had been added, the reaction mixture was allowed to stir for 1 hr. The cyanuric acid, which precipitated almost quantitatively, and the ferric chloride were removed by filtration. The filtrate distilled through a 16-cm Vigreux column to give 10.5 g (62%) of chlorobenzene, bp 132-133° (760 mm), *n*<sub>D</sub><sup>20</sup> 1.5250. The physical constants of the product were identical with those reported in the literature for chlorobenzene, and the infrared spectrum of the product was identical with the spectrum of an authentic sample of chlorobenzene.

**Reaction of Trichloroisocyanuric Acid with Benzene Using 1:1 Sulfuric Acid-Water as the Catalyst.**—To 50 ml (44 g, 0.57 mol) of benzene mixed with 100 ml of 1:1 sulfuric acid and water was added 11.62 g (0.05 mol) of trichloroisocyanuric acid. The temperature was adjusted to 65-80°, and vigorous stirring was maintained throughout the entire 5-hr reaction period. The cyanuric acid, which precipitated almost quantitatively, was removed by filtration. The organic layer was separated and distilled through a 16-cm Vigreux column to give 13.4 g (80%) of chlorobenzene, bp 132-133° (760 mm), *n*<sub>D</sub><sup>20</sup> 1.5253. The physical constants of the product were identical with those reported in the literature for chlorobenzene, and the infrared spectrum was identical with the spectrum of an authentic sample of chlorobenzene.

**Reaction of Naphthalene with Trichloroisocyanuric Acid in the Absence of Catalysis.**—To a stirring solution of 22.6 g (0.175 mol) of naphthalene in 50 ml of CCl<sub>4</sub> was added in one portion 11.62 g (0.05 mol) of trichloroisocyanuric acid. The mixture was refluxed for 5 hr. The reaction mixture was filtered, and the CCl<sub>4</sub> was removed with a rotary evaporator. The residue was distilled to give 0.8 ml (0.67 g, 2.7%) of 1-chloronaphthalene, bp 103° (3 mm), *n*<sub>D</sub><sup>20</sup> 1.6305. The physical constants of the product were identical with those reported in the literature for 1-chloronaphthalene, and the infrared spectrum of the product matched that of an authentic sample of 1-chloronaphthalene.

**Chlorination of Naphthalene by Trichloroisocyanuric Acid Utilizing Lewis Acid Catalysis.**—To a three-neck flask fitted with reflux condenser, mechanical stirrer, and thermometer were added 10.14 g (0.08 mol) of naphthalene and 50 ml of carbon tetrachloride. To this solution was added 4.06 g (0.025 mol) of anhydrous ferric chloride and 5.81 g (0.025 mol) of trichloroisocyanuric acid, in one portion. Stirring was initiated and the reaction mixture was heated to reflux for 3 hr. After cooling, the reaction mixture was filtered to remove the ferric chloride

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(14) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).

(15) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 513.

and spent cyanuric acid. The filtrate was placed in a rotary evaporator and the solvent was removed. Distillation of the residual liquid under vacuum gave 5.9 ml (7.04 g, 57.8%) of 1-chloronaphthalene, bp 97° (3 mm), which was identified by its picrate derivative, mp 136° (lit. mp 137°).

**Reaction of Trichloroisocyanuric Acid with Naphthalene under Mineral Acid Catalysis (43% Aqueous  $H_3PO_4$ ).**—To 22.56 g (0.175 mol) of naphthalene in a reaction flask was added 100 ml of 43% aqueous phosphoric acid. The flask was placed in a water, stirring was initiated, and 11.62 g (0.05 mol) of trichloroisocyanuric acid was added in one portion. The temperature of the reaction mixture was raised to 95° by a thermostat hot plate for 1 hr. The water bath was then removed and the reaction mixture was allowed to cool to room temperature. To the flask was slowly added 200 ml of a saturated aqueous solution of  $KHCO_3$  to make the mixture neutral to litmus. After removal of suspended solids by filtration, the mixture was filtered and aqueous filtrate was extracted with carbon tetrachloride, evaporation of which left no residue. The solid material which had been removed by filtration was vigorously stirred with ca. 150 ml of carbon tetrachloride to dissolve adsorbed 1-chloronaphthalene. After removal of the former by distillation, 9 ml (10.8 g, 44%) of 1-chloronaphthalene, bp 77° (2 mm), was obtained.

**Reaction of Trichloroisocyanuric Acid with Toluene under Lewis Acid Catalysis.**—To a stirred suspension of 8.11 g (0.05 mol) of anhydrous ferric chloride in 50 ml (43.4 g, 0.47 mol) of toluene was added, in small portions so as to keep the temperature of the reaction mixture below 90°, 11.62 g (0.05 mol) of trichloroisocyanuric acid. The reaction mixture was allowed to stir for 16 hr after the last portion of trichloroisocyanuric acid had been added. The cyanuric acid which precipitated in the course of the reaction and the spent ferric chloride were removed by filtration. Distillation of the filtrate gave 8 ml of isomeric chlorotoluenes, bp 55° (17 mm). Analysis of this sample by refractive-index measurements showed it to be composed of 79% 4-chlorotoluene and 21% 2-chlorotoluene. The yield of the reaction was thus 6.85 g (6.33 ml, 36.2%) of the 4-chloro isomer and 1.79 g (1.67 ml, 9.42%) of the 2-chloro isomer.

**Reaction of Trichloroisocyanuric Acid with Toluene Using 1:1 Sulfuric Acid-Water as the Catalyst.**—To 70 ml (60.7 g, 0.66 mol) of toluene mixed with 100 ml of 1:1 sulfuric acid-water was added 23.24 g (0.10 mol) of trichloroisocyanuric acid. The reaction mixture was stirred vigorously at 65–80° for a 4-hr period. The cyanuric acid, which precipitated almost quantitatively, was removed by filtration. The organic layer was separated and the resulting mixture was distilled through a 16-cm Vigreux column to give 25.10 g (66%) of a mixture of 2- and 4-chlorotoluene, bp 157–163° (760 mm),  $n_D^{20}$  1.5215.

**Reaction of Trichloroisocyanuric Acid with Toluene Using Benzoyl Peroxide as the Catalyst.**—To 15.43 g (0.2 mol) of toluene mixed with 0.6 g of benzoyl peroxide and 100 ml of carbon tetrachloride was added 11.62 g (0.05 mol) of trichloroisocyanuric acid. The reaction mixture was refluxed for 3 hr and the cyanuric acid, which precipitated almost quantitatively, was removed by filtration. The resulting reaction mixture was distilled through a 16-cm Vigreux column to give 11.5 g (44%) of benzyl chloride, bp 179–180° (760 mm),  $n_D^{20}$  1.5420. The physical constants obtained were identical with those reported in the literature, and the infrared spectrum was identical with the spectrum of an authentic sample of benzyl chloride.

**Reaction of *t*-Butylbenzene with Trichloroisocyanuric Acid Using Lewis Acid Catalysis.**—To 20.0 ml (20.1 g, 0.15 mol) of *t*-butylbenzene in 40 ml of carbon tetrachloride was added 8.1 g (0.05 mol) of anhydrous ferric chloride and 11.62 g (0.05 mol) of trichloroisocyanuric acid. Stirring was initiated and the mixture was refluxed for 3 hr. The mixture was allowed to cool and the spent ferric chloride and cyanuric acid were removed by filtration. The filtrate was stripped of solvent with a rotary evaporator. Distillation of the residue gave 1.40 g (0.008 mol, 4.8%) of 2-chloro-*t*-butylbenzene, bp 62° (3 mm), and 9 g (0.053 mol, 35%) of 4-chloro-*t*-butylbenzene, bp 75–76° (3 mm).

**Reaction of Phenol with Trichloroisocyanuric Acid in the Absence of Catalysis.**—To 50 ml of carbon tetrachloride was added 14.1 g (0.15 mol) of phenol. Stirring was initiated, and trichloroisocyanuric acid (11.62 g, 0.05 mol) was added in three equal portions over a 10-min period. The last addition produced a violent evolution of chlorine of short duration. After this gas evolution, the temperature of the reaction mixture was maintained at the reflux point of carbon tetrachloride with stirring for 1 hr. The reaction mixture was allowed to cool and the

cyanuric acid was filtered off. Analysis of the filtrate by gas chromatography using a 20 ft × 0.375 in. 20% Carbowax 20M column on 60–80 mesh Chromosorb P showed that the reaction produced 0.05 mol (6.38 g, 48%) of 4-chlorophenol and 0.008 mol (1.12 g, 7.5%) of 2-chlorophenol, wherein peaks were identified by comparison of retention times with those of known samples of 2-chloro- and 4-chlorophenol. No evidence could be found in the gas chromatographic analysis for 2,4-dichloro- and 2,4,6-trichlorophenol.

**Reaction of Aniline with Trichloroisocyanuric Acid in the Absence of Catalysis.**—The reaction of 13.7 ml (14 g, 0.15 mol) of aniline and 11.62 g (0.05 mol) of trichloroisocyanuric acid in 400 ml of carbon tetrachloride and work-up were similar to that used for phenol above. The carbon tetrachloride was removed with a rotary evaporator. Vacuum distillation of the liquid residue gave two fractions: a, 7.3 ml, bp 52° (4 mm), and b, 0.5 ml, bp 56° (3 mm). Analysis of these fractions by gas chromatography on a 20 ft × 0.375 in. 20% Carbowax 20M column on 60–80 mesh chromosorb P showed that fraction a contained 71% aniline and 29% 4-chloroaniline, while fraction b contained 50.6% aniline, 42% 4-chloroaniline, and 7.4% 2-chloroaniline. The total yield of chloro anilines was 25% 4-chloroaniline and 2.3% 2-chloroaniline. No evidence for 2,4-dichloro- and 2,4,6-trichloroaniline could be found in the gas chromatographic analysis or by extraction procedures of the distillation residue.

**Preparation and Decomposition of Addition Complex of Trichloroisocyanuric Acid and Aniline.**—To 80 ml of acetonitrile (Matheson Spectroquality) in an erlenmeyer flask equipped with magnetic stirring bar was added 2.35 g (0.01 mol) of trichloroisocyanuric acid. Stirring was initiated and the trichloroisocyanuric acid went into solution. To the stirred solution was slowly added a 20% (v/v) solution of freshly distilled aniline in acetonitrile. Addition was discontinued when the solution, which became orange-red on addition of the aniline solution, reached a point of turbidity which could not be cleared by further stirring. This required ca. 2 ml of the aniline solution. The solution was then placed in a separatory funnel and partitioned between water-benzene phases. The benzene-soluble phase was decanted, washed with water, dried ( $Na_2SO_4$ ), and allowed to air evaporate on a large watch glass. There remained after evaporation a large quantity of crystals, which melted with decomposition at 47–51° and evolved chlorine gas when treated with concentrated HCl (a phenomenon observed for trichloroisocyanuric acid itself). Ca. 1 g of these crystals was added to 15 ml of  $CCl_4$  and the mixture was refluxed for 30 min. At the end of that time, a flocculent white precipitate collected at the bottom of the flask. The solution was filtered and the precipitate was found to give a positive test for cyanuric acid.<sup>19</sup> Analysis of the solution by gas chromatography on a Varian Aerograph A-700, 5 ft × 0.375 in. 20M Versamide 900 column on 80–120 mesh Chromosorb P showed that it contained 9.2% (v/v) 4-chloroaniline. No evidence of a peak for 2-chloroaniline could be found from the chromatogram.

**Attempted Chlorination of Benzoic Acid by Trichloroisocyanuric Acid in the Presence of Lewis Acid Catalysis.**—The attempt to chlorinate benzoic acid in refluxing carbon tetrachloride with anhydrous ferric chloride catalyst was unsuccessful, and unreacted benzoic acid was recovered in quantitative yield.

**Attempted Chlorination of Nitrobenzene by Trichloroisocyanuric Acid in the Presence of Lewis Acid Catalysis.**—The attempt to chlorinate nitrobenzene in refluxing carbon tetrachloride with anhydrous ferric chloride catalyst was unsuccessful, and a quantitative yield of nitrobenzene was recovered by distillation.

**Registry No.**—1, 87-90-1; benzene, 71-43-2; naphthalene, 91-20-3; toluene, 108-88-3; *t*-butylbenzene, 98-06-6; phenol, 108-95-2; aniline, 62-53-3.

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