Aromatic Halogenation with Titanium(IV) Chloride in Presence of Peroxytrifluoroacetic Acid

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Titanium(IV) chloride in the presence of an oxidizing reagent such as peroxytrifluoroacetic acid is shown to chlorinate a variety of aromatic substrates. The substitution orientation patterns suggest that the reaction is an electrophilic substitution process, which possibly involves the intermediacy of hypochlorous acid. Chlorination fails to occur with ring systems bearing strongly deactivating substituents, but it proceeds very cleanly and in high yield with activated rings, *e.g.* phenol. The reaction conditions are mild and are adaptable for bromination or iodination as well as chlorination.

On montre que le chlorure de titanium(IV), en présence d'un agent oxydant tel l'acide péroxytrifluoroacétique, permet d'introduire un chlore sur plusieurs substrats aromatiques. Les modèles d'orientation de la substitution suggèrent que la réaction est un procédé de substitution électrophile, qui implique possiblement l'intermédiaire de l'acide hypochloreux. Il n'y a pas de substitution de chlore sur les noyaux portant des substituants fortement désactivants, mais elle se produit facilement, avec de bons rendements, dans le cas de noyaux activés, tel le phénol. Les conditions de réaction sont douces et peuvent être adaptées pour la bromuration et l'ioduration, aussi bien que pour la chloruration.

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Halogenation of aromatic rings is one of the more thoroughly investigated organic reactions, and it has been discussed in a wealth of chemical literature (1). Most reactions of this type fall into four general classes, *viz.* (*1*) reaction of electron-rich aromatic rings with molecular halogen; (*2*) reaction of less-activated rings with molecular halogen in the presence of a catalyst; (*3*) reaction of aromatic compounds with systems which furnish a positively charged halonium ion species (*e.g.* chlorine – silver acetate); and (*4*) direct halogenation of an aromatic molecule with halogen, apparently derived from reduction of a metal halide, but without the addition of any free halogen.

Of these four general approaches, the last-mentioned has been studied relatively little, although the use of iron(III) and antimony(V) chlorides as aromatic chlorinating agents has been known for over 100 years (2). Since that time, those metal halides which have received most attention include antimony(V), copper(II), iron(III), and vanadium(V) chlorides (3). It should be noted that metal halides may effect other transformations in addition to halogenation. Depending on the reaction conditions, nuclear coupling, side-chain attack in alkylbenzenes, disproportionation, and polymerization are known to occur (4, 5). In the nuclear chlorination of aromatic compounds with metal halides, various lines of evidence, including the predominant ortho/para orientation, point to an electrophilic substitution mechanism, although the actual attacking form of the metal halide is uncertain.

Titanium(IV) chloride by itself has never been reported to chlorinate aromatic compounds, but it has been used as a catalyst and as a solvent in the chlorination of aromatic rings by other metal halides (6). Previously, we reported that titanium(IV) chloride, in the presence of peroxytrifluoroacetic acid or *m*-chloroperbenzoic acid, will chlorinate aromatic compounds (7). In the present paper, we report further examples of aromatic chlorination with this system and present evidence for a proposed mechanism of the reaction.

Results and Discussion

In general, the chlorination reactions were performed in methylene chloride solvent at 0–20 °C with aromatic reactant – titanium(IV) chloride – peroxytrifluoroacetic acid in a 1 : 1 : 1 molar ratio. Aromatic substrates, which represent a range of different reactivities toward electrophiles, were chlorinated by this reaction; the results are presented in Table 1. The products

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TABLE 1. Chlorination of aromatic compounds with $TiCl_4$–CF_3CO_3H ([substrate]:[$TiCl_4$]:[CF_3CO_3H] = 1:1:1 for all experiments)

Substrate (mmol)	Reaction conditions: Time (h)	Reaction conditions: Temperature (°C)	Overall yield (%)	Isomer distribution
Benzene (3)	3	20	60	Chlorobenzene 100
Chlorobenzene (5)	9	20	40	*o*-Dichlorobenzene 40 *p*-Dichlorobenzene 60
Toluene (5)	3	20	90	*o*-Chlorotoluene 85 *p*-Chlorotoluene 15
Acetanilide (3)	4	20	76	*o*-Chloroacetanilide 27 *p*-Chloroacetanilide 48 2,4-Dichloroacetanilide 15 2,4,6-Trichlorophenol 10
p-Acetotoluidide (3)	10	20	86	2-Chloro-4-methylacetanilide 62 2,4,6-Trichloro-4-methylcyclohexa-2,5-dienone 15
p-Methoxyacetanilide (3)	6	20	85	3-Chloro-4-methoxyacetanilide 59 2,5-Dichloro-4-methoxyacetanilide 31 2,4,5-Trichloro-4-methoxycyclohexa-2,5-dienone 10
Mesitylene (3)	2	0	94	Trichloromesitylene 65 Mesitol 5 Unidentified products 30
p-Chloroacetanilide (2)	4	20	38	2,4-Dichloroacetanilide 100
Anisole (3)	3	20	94	*o*-Chloroanisole 52 *p*-Chloroanisole 28 2,4-Dichloroanisole 20
Phenol (5)	3	0	90	*o*-Chlorophenol 56 *p*-Chlorophenol 22 2,4-Dichlorophenol 22
Aniline (3)	4	20	64	*o*-Chloroaniline 34 *p*-Chloroaniline 23 2,4-Dichloroaniline 43
Biphenyl (3)	4	20	76	2-Chlorobiphenyl 68 4-Chlorobiphenyl 17
Benzoic acid (3)	28	64	—	Starting material
Nitrobenzene (3)	20	50	—	Starting material
Pyridine (3)	6	20	—	Starting material
Thiophene (3)	6	20	—	Starting material

were isolated and were identified by comparison with authentic materials or by their spectroscopic properties.

Benzene was converted to chlorobenzene with no detectable formation of dichlorobenzene. Toluene and chlorobenzene were monochlorinated also. Although there is considerable literature on chlorination of these two aromatics (8–10), it appears that the use of titanium(IV) chloride as a catalyst for chlorination with molecular chlorine has not been reported previously. In Table 2, we have included our results on this system, together with relevant literature data for other systems, in order to compare these with the reactions of the titanium(IV) chloride – peroxytrifluoroacetic acid reagent.

In the case of mesitylene, 94% was consumed and the products contained trichloromesitylene (65%) and mesitol (5%). Reaction of mesitylene with peroxytrifluoroacetic acid alone has been

TABLE 2. Chlorination reactions of toluene and chlorobenzene

Substrate	Catalyst	Chlorine source	Solvent	Reaction conditions Time (h)	Temperature (°C)	Overall yield (%)	Isomer distribution (%) *o*	*m*	*p*	Reference
Toluene	$HClO_4$ $AgClO_4$	$HOCl/H^+$	HOH	—	25.0	—	75	—	23	8
Toluene	$SbCl_5$	Cl_2	—	4.0	25–30	20*	72	2	26	9
Toluene	$FeCl_3$	Cl_2	—	2.3	25–30	5*	64	4	32	9
Toluene	—	$SbCl_5$	—	2.5	18–31	87	47	2	51	9
Toluene	$TiCl_4$	Cl_2§	CH_2Cl_2	3	25	95§	45	—	10†	‡
Toluene	$TiCl_4$	Cl_2‖	CH_2Cl_2	3	25	60‖	71	—	29	‡
Toluene	$TiCl_4$	$TiCl_4/CF_3CO_3H$	CH_2Cl_2	3	25	90‖	85	—	15	‡
Chlorobenzene	$HClO_4$	$ClClO_4$	CCl_4	1–8	25	—	36	—	62	10
Chlorobenzene	$FeCl_3$	Cl_2	—	3.5	40–55	35*	40	3	57	9
Chlorobenzene	—	$SbCl_5$	—	2.0	41–59	82	15	1	84	9
Chlorobenzene	$TiCl_4$	Cl_2§	CH_2Cl_2	9	25	90§	28	—	72	‡
Chlorobenzene	$TiCl_4$	Cl_2‖	CH_2Cl_2	3	25	37‖	30	—	70	‡
Chlorobenzene	$TiCl_4$	$TiCl_4/CF_3CO_3H$	CH_2Cl_2	9	25	40‖	40	—	60	‡

*Reaction not taken to completion.
†In addition, 45% 2,4-dichlorotoluene was obtained.
‡Present work.
§Excess of chlorine.
‖Molar ratio of reactants 1:1:1.

TABLE 3. Chlorination of aromatic compounds with $TiCl_4$–H_2O_2 at 20 °C

Substrate (mmol)	$TiCl_4$ (mmol)	H_2O_2 (90%) (mmol)	Reaction time (h)	Overall yield (%)	Isomer distribution			
					o	*p*	2,4-Dichloro	Residue
Acetanilide (3)	3	3	6	45	24	54	14	8*
Acetanilide (4)	3	6	6	52	29	56	9	6*
Acetanilide (1)	3	6	6	95	0	0	95	5*
Toluene (10)	10	10	7	40	75	25	0	0
Chlorobenzene (10)	10	10	9	21	40	60	0	0

*Shown to be 2,4,6-trichlorophenol.

reported to give mesitol in 45% yield, whereas this was increased to 88% by carrying out the same reaction in the presence of boron trifluoride (11). On the other hand, we have observed that aluminum(III) chloride – peroxytrifluoroacetic acid is a chlorinating system.[2] From these reactions it may be concluded that a Lewis acid will only enhance the reactivity of peroxytrifluoroacetic acid as a source of electrophilic hydroxyl if the Lewis acid itself will not become involved in a reaction to form a species less electrophilic than "HO^+".

Acetanilide gave a mixture of chloroacetanilides, in addition to 2,4,6-trichlorophenol.[3] With *p*-acetotoluidide, 2-chloro-4-methyl-acetanilide and 2,4,6-trichloro-4-methylcyclohexa-2,5-dienone were produced, the structure of this dienone being deduced from its spectral characteristics (see Experimental). On acetylation with acetic anhydride/*p*-toluenesulfonic acid, it rearranged to 3-methyl-2,4,6-trichlorophenyl acetate. This rearrangement rules out the possibility that the dienone might have been 3,4,5-trichloro-4-methylcyclohexa-2,5-dienone which, solely on spectral grounds, could not be unequivocally distinguished from the 2,4,6-trichloro-4-methyl isomer. Similarly, *p*-methoxyacetanilide gave 3-chloro-4-methoxyacetanilide, 2,5-dichloro-4-methoxyacetanilide and 2,4,5-trichloro-4-methoxycyclohexa-2,5-dienone, which proved to be much less stable than the similar dienone from *p*-acetotoluidide. The formation of 3-chloro- instead of 2-chloro-4-methoxyacetanilide is consistent with a dominance in substituent directive power of the methoxyl group over the *N*-acetylamino group (12).

Phenol was cleanly chlorinated with a mixture of titanium(IV) chloride and peroxytrifluoroacetic acid to give chlorophenols in 90% yield. No oxidation products of phenol, such as benzoquinone, could be detected; indeed, the reaction was remarkably smooth. Presumably, phenol first reacts with titanium(IV) chloride to form phenyl titanate (13) which is sufficiently nucleophilic to be chlorinated.

Aniline was chlorinated in 64% yield to *o*-chloroaniline (34%), *p*-chloroaniline (23%), and 2,4-dichloroaniline (43%). These products were identified by conversion to the corresponding chloroacetanilides which were analyzed by v.p.c. It is relevant to note that in this case too, no oxidation products could be detected, whereas the direct chlorination of most primary aromatic amines with free chlorine results in extensive oxidation (14).

Some aromatic compounds failed to undergo chlorination. Benzoic acid and nitrobenzene were too strongly deactivated to react, whereas pyridine and thiophene failed to react because of the nucleophilic heteroatoms which, on complexing with the titanium(IV) chloride, caused the ring to become highly deactivated toward electrophilic substitution (15).

Titanium(IV) chloride also chlorinates aromatic compounds in the presence of other peroxides. For example, acetanilide with titanium(IV) chloride – *m*-chloroperbenzoic acid in a 1 : 1 : 1 ratio gave a 56% yield of chloroacetanilides. Reaction with a mixture of titanium(IV) chloride and 90% hydrogen peroxide also gave chlorination products, although generally the yields were much lower than when using peroxytrifluoroacetic acid. Results for this system with three representative aromatic substrates are shown in Table 3.

Some conclusions concerning the mechanism of the chlorination reaction may be drawn at this point. The predominance of ortho/para

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[2] G. K. Chip and J. S. Grossert. Unpublished data.

[3] We had previously reported (7) the absence of *o*-chloroacetanilide in this reaction. This was due to the inadequacy of t.l.c. separation techniques, and the presence of the ortho isomer has since been demonstrated unequivocally by the use of v.p.c.

TABLE 4. Chlorination of acetanilide with $TiCl_4$–CF_3CO_3H in the presence of added anions

Added anions (mmol)	Reaction conditions		Overall yield (%)	Products
	Time (h)	Temperature (°C)		
$(C_2H_5)_4N^+Cl^-$ (24)	8	20	97	2,4-Dichloroacetanilide
$(C_2H_5)_4N^+Br^-$ (24)	24	20	98	4-Bromoacetanilide
$(C_2H_5)_4N^+I^-$ (6)	18	40	80	4-Iodoacetanilide
$(C_2H_5)_4N^+F^-$ (9)	48	20	50	2-Chloroacetanilide (25%) 4-Chloroacetanilide (54%) 2,4-Dichloroacetanilide (21%)

substitution and the lack of attack on alkyl side chains point to a reaction which is electrophilic rather than radical in nature. The possibility that the active species is molecular chlorine was considered unlikely on the grounds of the product isomer distribution (*cf.* Table 2), and the fact that the decomposition of titanium(IV) chloride into titanium(II) chloride and chlorine is not known (16). Examination of the substitution pattern for all the substrates investigated pointed to an active species of relatively low specificity (and hence of relatively high reactivity), with a relatively small steric factor (17); we suggest that this is best accounted for by postulating hypochlorous acid, or a titanate ester thereof, as the active chlorinating species. The formation of hypochlorous acid by reaction between a peroxy acid and titanium(IV) chloride may be readily rationalized by eq. 1, and a corresponding reaction with hydrogen peroxide by eq. 2.

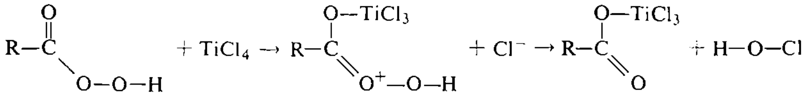
We have found two additional pieces of evidence to support eq. 1. Reaction of cyclohexene with titanium(IV) chloride – *m*-chloroperbenzoic acid gave 2-chlorocyclohexanol and *m*-chlorobenzoic acid as the only isolable products, eq. 3. No 2-chlorocyclohexyl *m*-chlorobenzoate or 1,2-dichlorocyclohexane could be isolated, which is in accord with the proposed mechanism.

Results from the addition of an excess of various halide anions to the reaction of acetanilide with titanium(IV) chloride – peroxytrifluoroacetic acid (3 mmol of each) are given in Table 4. On addition of an excess of chloride ions, the appearance of a greenish-yellow color in the reaction flask indicated the liberation of chlorine gas. The sole product was 2,4-dichloroacetanilide, formed in 97% yield. With an excess of bromide ions, 4-bromoacetanilide was formed in 98% yield, whereas addition of iodide ions gave 4-iodoacetanilide in 80% yield. Addition of fluoride ions gave no fluorination, but only a mixture of chloroacetanilides. These results are as would be expected for a hypochlorite as the active species (18).

The formation of dienones during chlorination of acetanilides is a novel reaction, although their formation during halogenation of phenols is known (19). We have depicted in Scheme 1 our speculation on how the reaction may convert the amide function into a leaving group.

Titanium(IV) chloride is known to form complexes with acetanilide, although the structure of these is in doubt.[4] However, an adduct of the Vilsmeier–Haack type, analogous to the one proposed in Scheme 1, has been postulated (21)

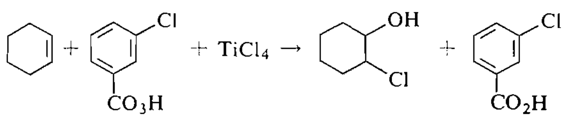
[1]



$$R{-}C(=O){-}O{-}O{-}H + TiCl_4 \rightarrow R{-}C(O{-}TiCl_3){=}O^+{-}O{-}H + Cl^- \rightarrow R{-}C(O{-}TiCl_3){=}O + H{-}O{-}Cl$$

[2] $$H{-}O{-}O{-}H + TiCl_4 \rightarrow H{-}O{-}TiCl_3 + H{-}O{-}Cl$$

[3]



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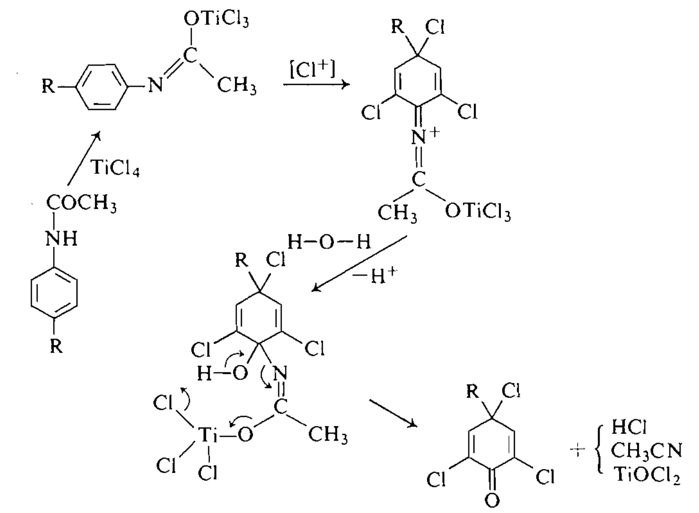
[4] We have prepared a red titanium(IV) chloride – acetanilide complex, m.p. 160–164° (dec.), from methylene chloride solutions. This does not correspond to complexes reported in the literature (20) and we are investigating its structure.



For R = —H or —CH_3; if R = —OCH_3, then chlorination pattern is changed

SCHEME 1

to decompose by expulsion of acetonitrile. As a result of this postulate, we examined the reaction mixture and did detect acetonitrile by v.p.c. and i.r. spectroscopy. On the basis of Scheme 1, mono- or dichlorinated dienones could have been expected but we have found no evidence of their presence.

We believe that this reaction offers a novel and versatile approach to the synthesis of halogenated aromatic compounds, and it may also have some potential for the synthesis of chlorohydrins. In particular, the reaction is easy to carry out, it occurs under mild, controlled conditions and it is applicable to chlorination of reactive molecules, such as aniline or phenol. We are exploring further its applicability to other systems.

Experimental

All melting points were recorded on a Fisher–Johns apparatus and are uncorrected. Infrared spectra were recorded (in $CHCl_3$) on a Perkin–Elmer Model 237B grating spectrophotometer. Ultraviolet spectra were obtained in 95% ethanol solutions on a Coleman–Hitachi Model 124 spectrophotometer. The n.m.r. spectra were determined in $CDCl_3$ on Varian Associates A-60 or T-60 spectrometers using tetramethylsilane as an internal standard. Mass spectra were taken on a C.E.C. Model 21-104 spectrometer operating at 70 eV. Vapor-phase chromatography was performed on a Hewlett–Packard Model 700 chromatograph, equipped with a flame ionization detector and a 6 ft × 1/8 in. stainless steel column (packed with a 15% DC-200/10% QF-1 mixture on 80–100 mesh acid-washed Chromosorb W) generally at 175°, with a nitrogen flow rate of 45 ml/min. Overall yields were calculated on the basis of consumption of starting aromatic substrate, and isomer ratios reflect the relative composition of the isolated product mixture.

Materials

Titanium tetrachloride (Matheson, Coleman & Bell) was refluxed over copper turnings for 4 h and then distilled, giving a colorless fraction, b.p. 136°. Methylene chloride was reagent grade (Fisher Scientific) and was dried over Linde molecular sieve 4A. Hydrogen peroxide (90%) was from the FMC Corporation, and chromatography was done using appropriate Merck products. Tetraethylammonium chloride was made by the method of Coppens *et al.* (22). All other materials were either reagent grade or were prepared by standard procedures.

Reaction of Acetanilide with Titanium(IV) Chloride and Peroxytrifluoroacetic Acid; General Procedure

An anhydrous solution of peroxytrifluoroacetic acid (11) was prepared by dissolving trifluoroacetic anhydride (0.63 ml, 3.2 mmol) in anhydrous methylene chloride (3 ml). After cooling to 0 °C, 90% hydrogen peroxide (0.09 ml, 3 mmol) was added while maintaining vigorous stirring until a homogeneous solution was obtained (15 min). The peracid solution was then added dropwise, during a 15 min period, to a cooled, well-stirred solution of acetanilide (405 mg, 3 mmol) and titanium(IV) chloride (0.33 ml, 3 mmol) in dry methylene chloride (15 ml), under N_2. After the addition of peracid was complete, the reaction mixture was stirred at room temperature for 4 h, during which time its color changed from dark orange to light yellow. The mixture was then hydrolyzed with cold water (50 ml). The product was extracted with methylene chloride, washed with water, 10% sodium bicarbonate, water again, and then dried over anhydrous sodium sulfate. The extract was concentrated and v.p.c. analysis showed that the product (formed in 76% overall yield) contained a mixture of *o*-chloroacetanilide (27%), *p*-chloroacetanilide (48%), 2,4-dichloroacetanilide (15%), and 2,4,6-trichlorophenol (10%). In some other experiments, the products were separated on preparative t.l.c. plates and the individual components were extracted and characterized by their melting points and spectroscopic properties.

Reactions of other aromatic substrates were carried out by a procedure identical with that described above. The reagent quantities, reaction conditions, yields, and isomeric distributions are presented in Table 1.

The aryl chlorides were identified by n.m.r. and v.p.c. techniques and in most cases by comparison of their physical properties with those of authentic samples.

Chlorination with Molecular Chlorine in the Presence of Titanium(IV) Chloride; General Procedure

A solution of chlorine (7 mmol) was prepared by bubbling molecular chlorine into methylene chloride (10 ml). This solution was then added to a mixture of acetanilide (7 mmol, 945 mg) and titanium(IV) chloride (7 mmol, 0.77 ml) in methylene chloride (20 ml). The reaction mixture was allowed to stir at room temperature for 5 h. After aqueous work-up, analysis of the organic fraction by v.p.c. indicated a mixture of ortho- and para-chloroacetanilide in the ratio 32:68 and in a 15% overall yield.

When a large excess of molecular chlorine was used in this reaction, only 2,4-dichloroacetanilide (in 96% yield) could be isolated. Similar reactions were carried out on toluene and on chlorobenzene. The results are reported in Table 2.

Reaction of Acetanilide with Titanium(IV) Chloride

The reaction of acetanilide and titanium(IV) chloride was repeated without the addition of peroxytrifluoroacetic acid. After aqueous work-up, the acetanilide recovery was essentially quantitative. No chloroacetanilides could be detected either by t.l.c. or v.p.c.

Reaction of p-Acetotoluidide with Titanium(IV) Chloride – Peroxytrifluoroacetic Acid

The same general procedure was followed. The crude reaction mixture (570 mg) was chromatographed on a column of neutral alumina, Brockman activity 1, 80–200 mesh. Elution with petroleum ether (b.p. 30–60°) gave a white solid (90 mg, 15%) which crystallized from petroleum ether (b.p. 30–60°), m.p. 89–90°. This was identified as 2,4,6-trichloro-4-methylcyclohexa-2,5-dienone from its spectral data: i.r. 1680, 1630 cm^{-1}, no NH or OH absorption; u.v. (95% EtOH) λ_{max} 251 nm (ε 8600), λ_{min} 288 nm; n.m.r. δ 1.98 (s, 3H), 7.21 p.p.m. (s, 2H); mass spectrum M$^+$ at 209.9399 a.m.u. (calculated for $C_7H_5OCl_3$, 209.9405 a.m.u.) with the isotopic ratio $M^+ + 2 : M^+ + 4 : M^+ + 6$ indicating three chlorine atoms. Further elution gave 2-chloro-4-methylacetanilide (340 mg, 62%, m.p. 117°, undepressed with an authentic sample) and 4-methylacetanilide (56 mg, 16%).

The cyclohexa-2,5-dienone was converted to its 2,4-dinitrophenylhydrazone by warming with an ethanolic solution of the hydrazine reagent. An orange solid precipitated immediately; water was added until the solution became cloudy, and the solid was extracted with chloroform, which was dried (Na_2SO_4). The solvent was evaporated and the residue was recrystallized from EtOH, giving orange–yellow plates, m.p. 160–161°, M$^+$ 390 a.m.u.

The dienone was converted to 3-methyl-2,4,6-trichlorophenyl acetate by refluxing with a mixture of acetic anhydride and *p*-toluenesulfonic acid for 20 h. The dark solution was poured into cold water and solid Na_2CO_3 added to neutralize excess acid. The product was extracted with chloroform, washed with water and dried (Na_2SO_4). Evaporation of the solvent gave a brown gum which was purified by column chromatography on silica gel. The product was recrystallized from petroleum ether (b.p. 30–60°) to give colorless prisms, m.p. 94–95°. The i.r. showed a band at 1760 cm^{-1} (ester C=O); n.m.r. showed a singlet at δ 2.3 (3H), a singlet at 2.08 (3H), and a singlet at 7.3 p.p.m. (1H).

Reaction of p-Methoxyacetanilide with Titanium(IV) Chloride – Peroxytrifluoroacetic Acid

The same general procedure was followed with *p*-methoxyacetanilide (495 mg, 3 mmol), titanium(IV) chloride (3 mmol), and peroxytrifluoroacetic acid (3 mmol). The crude reaction mixture (570 mg) was chromatographed on a column of neutral alumina, Brockman Activity 1, 80–200 mesh. Elution with petroleum ether (b.p. 30–60°)/benzene (3:1) gave a white solid (20 mg, 10%), m.p. 63–65°, identified as 2,4,5-trichloro-4-methoxycyclohexa-2,5-dienone by its spectral characteristics: i.r. 1665 and 1610 cm^{-1} (α,β-unsaturated C=O), no NH or OH adsorption; u.v. λ_{max} 235 nm (ε 8400); n.m.r. δ 3.84 (s, 3H, OCH_3), 6.83 (s, 1H), and 6.86 p.p.m. (s, 1H); mass spectrum M$^+$ 226 a.m.u. with the isotopic ratio indicating the presence of three chlorine atoms. This dienone was unstable and readily decomposed to a brown solid of undetermined composition, but which did appear to contain quinonoidal material.

Further elution gave 2,5-dichloro-4-methoxyacetanilide (153 mg, 31%) recrystallized from 95% ethanol, m.p. 194–195° (lit. (23) 189–190°), n.m.r. δ 2.20 (s, 3H, —CH_3), 3.87 (s, 3H, —OCH_3), 6.90 (s, 1H), 7.33 (broad s, 1H, NH, exchanged in D_2O), 8.17 p.p.m. (s, 1H); i.r. 3420 (NH), 1690 cm^{-1} (amide C=O), and 3-chloro-4-methoxyacetanilide (225 mg, 59%) recrystallized from ethanol, m.p. 92–93° (lit. (24) 94°).

Reactions with Titanium(IV) Chloride – Hydrogen Peroxide

The general procedure already outlined was followed, except that the appropriate amount of hydrogen peroxide (90%) was used in place of the peroxytrifluoroacetic acid. The two-phase system was stirred vigorously; the results are given in Table 3.

Reactions of Acetanilide with Titanium(IV) Chloride – Peroxytrifluoroacetic Acid in Presence of Added Anions

The same general procedure was followed, except that prior to the addition of the peroxytrifluoroacetic acid, a solution of tetraethylammonium chloride, bromide, or fluoride in methylene chloride was added. The results are presented in Table 4. Tetraethylammonium iodide was insoluble in methylene chloride and hence was added in methanol. At the end of this reaction, the solvent was evaporated, leaving a dark violet mass. This was thoroughly washed with cold water, leaving a violet solid which had m.p. 113° and smelled of iodine. The filtrate was extracted with benzene, and the extract was washed first with sodium thiosulfate, then with water, and dried (Na_2SO_4). Evaporation of the solvent gave *p*-iodoacetanilide, recrystallized from ethanol, m.p. 189–190° (lit. (25) 184°), The n.m.r. spectrum of this compound showed the characteristic AA′BB′ pattern of a 1,4-disubstituted benzene and the mass spectrum showed the molecular ion at *m/e* 261 (C_8H_8NOI has mol. wt. 261).

Reaction of Cyclohexene with m-Chloroperbenzoic Acid–Titanium(IV) Chloride

Cyclohexene (246 mg, 3 mmol) was added to a stirred solution of *m*-chloroperbenzoic acid (517.5 mg, 3 mmol) and titanium(IV) chloride (0.33 ml, 3 mmol) in methylene chloride (20 ml) under N_2. The reaction was allowed to proceed at room temperature for 4 h. The mixture was hydrolyzed with water and the organic product was extracted with methylene chloride. The extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent gave 493 mg of product which was washed with hot water to dissolve the *m*-chlorobenzoic acid. These washings were extracted with chloroform, which was dried and evaporated to give *m*-chlorobenzoic acid (212 mg, 45%), m.p. 155–156°, identical with an authentic sample.

The above product, having been washed with hot water, was extracted with methylene chloride, which was washed, dried and evaporated to give 2-chlorocyclohexanol (150 mg, 37%), the spectroscopic properties of which were identical to those of an authentic sample.

Identification of Acetonitrile

A reaction with acetanilide, as described in the general procedure, was repeated using 1,1,2,2-tetrachloroethane, b.p. 114°, as solvent. At the end of the reaction, the mixture was fractionated and the distillates were analyzed by v.p.c. and i.r. One fraction showed an absorption band in the i.r. spectrum at 2260 cm^{-1} and on the v.p.c. showed a peak corresponding to the retention time of authentic acetonitrile.

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