Highly Selective Aromatic Chlorination. Part 1. The 4-Chlorination of Anisole and Phenol with *N*-Chloroamines in Acidic Solution

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Anisole and phenol are rapidly and efficiently chlorinated by *N*-chlorodialkylamines and *N*-chlorotrialkylammonium salts in trifluoroacetic acid at room temperature. Product analyses reveal that these reactions have a very marked selectivity for monochlorination of the 4-position. The reactions can also be carried out in aqueous sulphuric acid and under these conditions the selectivity is found to decrease with decreasing acidity of the solvent. The nature of the chlorinating species is discussed and it is proposed that the selective agents in these systems are *N*-chloroammonium ions.

Chlorine or hypochlorous acid is commonly used for the chlorination of electron-rich aromatic compounds; with less reactive substrates the electrophilicity of these reagents can be increased with a Lewis or protic acid respectively.[1] Although these reactions are simple to carry out, they are rarely selective for one isomeric monochlorinated product (site-selective)[2] and with more reactive substrates polychlorination can also occur.

The need for isomerically pure chloroaromatics as intermediates for the synthesis of bio-active compounds, with such applications as pesticides and medicinal chemicals, has led to investigations into more selective chlorinating agents. Crocker and Walser[3] developed a method for the 4-chlorination of phenols and anilines using concentrated hydrochloric acid, oxygen, and catalytic quantities of copper(II) chloride. However, they gave no explanation for the site-selectivity of this system. Watson[4] reported that catalytic amounts of aluminium trichloride and diphenyl sulphide will enhance the selectivity of sulphuryl chloride for chlorinating the 4-position of phenols and phenol ethers. This effect was attributed to the bulk of the chlorinating species which prefers to attack the 4- rather than the less accessible 2-position. Very recently Olah *et al.*[5] have described the efficient 4-chlorination of activated aromatics with *S*-chlorodimethylsulphonium chloride in dichloromethane. Other approaches that have been used to increase the selectivity of chlorination have employed α-cyclodextrin,[6] micelles,[7] zeolites,[8] and complexes between substrate and chlorinating agent[9] to direct the reaction predominantly to one position in the aromatic substrate.

In this paper we describe the highly selective and efficient monochlorination of anisole and phenol with *N*-chlorinated amines in acidic media.

Results

When anisole is added to an equivalent amount of a solution of *N*-chloropiperidine (NCP) in trifluoroacetic acid (TFA) at room temperature, there is a rapid and quantitative formation of monochloroanisoles and the piperidinium ion (reaction is complete in < 5 min). This reaction is unaffected by the presence of light; identical results are obtained when the chlorination is carried out in the dark or in diffuse daylight. The very high selectivity for 4-chlorination and for monosubstitution is immediately apparent from ^{1}H n.m.r. spectra of the reaction mixture (Figure) and this is readily confirmed by g.c. analysis after work-up (Table 1). Almost identical results are obtained when *N*-chloropiperidine is replaced by a selection of *N*-chlorodialkylamines or *N*-chlorotrialkylammonium salts (Table 1).

When the reactions are repeated using *N*-chloropyridinium acetate or four of its methylated derivatives, the selectivity for 4-chlorination is less remarkable (Table 2). However, methylation of the pyridine ring has no significant effect on the chloroanisole isomer distribution. Another difference between *N*-chlorotrialkylammonium and *N*-chloropyridinium salts is the poor conversion of the pyridines into their *N*-chloro-derivatives; conditions that give good

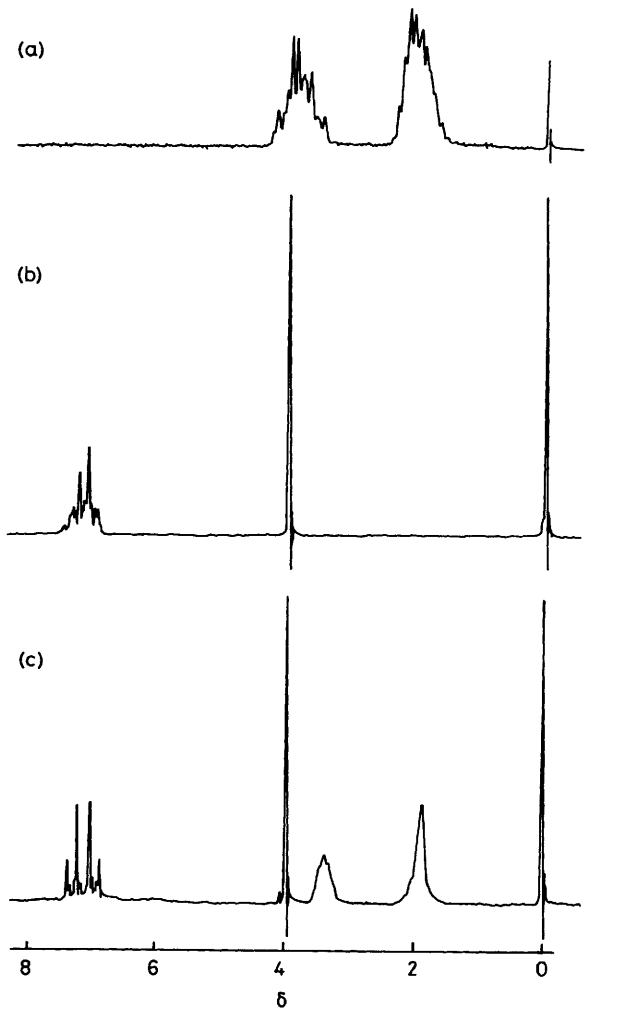


Figure. ^{1}H N.m.r. spectra of TFA solutions of (a) *N*-chloropiperidine, (b) anisole, and (c) an equimolar mixture of *N*-chloropiperidine and anisole, 5 min after mixing

Table 1. Chlorination of anisole with *N*-chlorodialkylamines and *N*-chlorotrialkylammonium salts in TFA

Chlorinating agent	Yield (%)[a]	Monochloroanisole isomer distribution (%) 2-	4-	Ratio of 4- to 2- chlorination
N-Chloropiperidine	97	1	99	99
N-Chloro-*N*-methylcyclohexylamine	—	1.5	98.5	66
N-Chloro-*N*-methylbenzylamine	66	2	98	49
N-Chloromorpholine	100	5	95	19
N-Chloro-1-azoniabicyclo[2.2.2]octane acetate	89	0.2	99.8	499
N-Chlorotriethylammonium chloride	97	1	99	99
N-Chlorotriethylammonium perchlorate	—	1	99	99
N-Chlorotrimethylammonium acetate	99	3	97	32

[a] Based on *N*-chlorinated amine.

Table 2. Chlorination of anisole with *N*-chloropyridinium acetates in TFA

Chlorinating agent	Monochloroanisole isomer distribution (%) 2-	4-	Ratio of 4- to 2- chlorination
N-Chloropyridinium	16	84	5.3
N-Chloro-2-methylpyridinium	18	82	4.6
N-Chloro-4-methylpyridinium	14	86	6.1
N-Chloro-3,5-dimethylpyridinium	12	88	7.3
N-Chloro-2,4,6-trimethylpyridinium	15	85	5.7

Table 3. Chlorination of anisole with some chlorinating agents other than *N*-chlorinated amines

Chlorinating agent	Solvent	Monochloroanisole isomer distribution (%) 2-	4-	Ratio of 4- to 2- chlorination
Cl_2	TFA	32	68	2.1
Cl_2–CF_3CO_2Ag	TFA	40	60	1.5
Cl_2–CF_3CO_2Ag	TFA–TFAA	42	58	1.4
HOCl	H_2O	40	60	1.5[a]
Bu^{t}OCl	AcOH–H_2SO_4	35.5	64.5	1.8[b]

[a] Reference 11. [b] Reference 12.

Table 4. Chlorination of phenol with *N*-chlorinated amines in TFA and with some other chlorinating agents

Chlorinating agent	Monochlorophenol isomer distribution (%) 2-	4-	Yield (%)[a]	Ratio of 4- to 2- chlorination
NCP	3	97	100	32
NCTA	3	97	98	32
Cl_2–CCl_4	57	43	93	0.75[b]
NaOCl–pH 4 buffer	39	61	22	1.6[c]
Bu^{t}OCl–H_2O–MeCN	48	52	100	1.1[d]

[a] Based on chlorinating agent. [b] Reference 13. [c] Reference 11. [d] Reference 7*a*.

yields of *N*-chlorotriethylammonium salts (NCTA) yield *ca.* 15—35% of the *N*-chloropyridium salts.

For comparison with the *N*-chloroamine reactions we studied the chlorination of anisole with chlorine in TFA. We also attempted to make chlorine trifluoroacetate, following the procedures used to make bromine and iodine trifluoroacetate,[10] and to use it to chlorinate anisole. In these experiments anisole was added to solutions of chlorine and silver(I) trifluoroacetate in TFA and in TFA–TFA anhydride (TFAA). Chlorine and the chlorine-derived species show a relatively low selectivity for 4-chlorination of anisole (Table 3).

The reaction of phenol with NCP or NCTA in TFA is also rapid and gives quantitative yields of monochlorophenols with a very high site-selectivity for the 4-isomer (Table 4). The results from some other chlorinations of phenol are included in Table 4 for comparison.

Table 5. Chlorination of anisole with NCP in aqueous sulphuric acid

Solvent composition H_2SO_4–H_2O (v/v)	Acidity H_0[a]	Monochloroanisole isomer distribution (%) 2-	4-	Yield (%)[b]
50:50	−3.38	1	99	79
20:80	−1.01	3	97	53
10:90	−0.31	10	90	30

[a] H_0 values from reference 14, the value for TFA is −3.03. [b] Based on NCP when ^{1}H n.m.r. analysis showed all NCP had been consumed.

Table 6. Chlorination of anisole with NCTA in aqueous sulphuric acid

Solvent composition H_2SO_4–H_2O (v/v)	Monochloroanisole isomer distribution (%) 2-	4-	Yield (%)[a]
50:50	0.5	99.5	73
20:80	3	97	73
10:90	4	96	79
0:100	5	95	70

[a] Based on NCTA when ^{1}H n.m.r. analysis showed all chloroammonium salt had been consumed.

Table 7. Chlorination of phenol with NCP in aqueous sulphuric acid

Solvent composition H_2SO_4–H_2O (v/v)	Chlorophenol product distribution (%) Monochlorophenols 2-	4-	Mono- and di-chlorophenols[b]		Yield (%)[a]
50:50	3	97	97	3	98
20:80	9	91	97	3	99
10:90	13	87	95	5	99
0:100	63	37	67	33	64

[a] Based on NCP. [b] 2,4-Dichlorophenol.

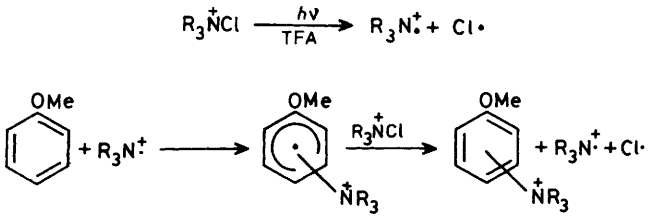
The reactions in TFA, described above, can also be carried out in aqueous sulphuric acid to give similar high selectivities. TFA and 50:50 (v/v) aqueous sulphuric acid have comparable acidities [14] and reactions in these two solvents show very similar product distributions. However, because the latter chlorination mixtures are not homogeneous they require vigorous mixing and longer reaction times.

Changing the proportions of water and sulphuric acid reveals that the reactions of *N*-chloropiperidine are more sensitive to changes in acidity than those of the *N*-chloroammonium ion, NCTA. Decreasing the acidity with both leads to a decrease in selectivity and yields (Tables 5, 6, and 7). With phenol and NCP in the absence of added acid, 2-chlorination becomes the dominant reaction and significant dichlorination occurs.

Since the chloroamine reactions in aqueous sulphuric acid can take several hours to reach completion, it is important to consider the stability of chloroamines under these conditions. NCP is stable in water and aqueous sulphuric acid, however ^{1}H n.m.r. analyses show that NCTA is converted cleanly into triethylamine in a strongly acid dependent reaction. Assuming pseudo-first-order kinetics for this decomposition, the half-life of the chloroammonium ion in 50 and 20% (v/v) aqueous sulphuric acid at 20 °C is *ca.* 100 and 12.5 days respectively. It is noteworthy that these results are in marked contrast to the half-life of 1—2 h reported by Deno *et al.* for this salt in 40 and 70% aqueous sulphuric acid at 25 °C.[15] In water NCTA shows significant decomposition within 10 min (Deno *et al.* report a half-life of 20 min for NCTA in water [15]).

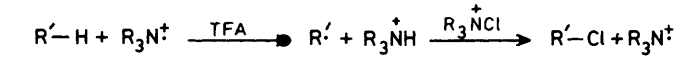
Discussion

Extensive studies by Minisci and his co-workers have shown that mono- and di-alkylaminium radicals, generated by metal ion-catalysed reduction of *N*-chloroamines in acid solution, can aminate aromatic compounds in high yield.[16] Based on these observations, we attempted to aminate anisole with trialkylaminium radicals obtained by photolysis of solutions of *N*-chlorotrialkylammonium salts in TFA [17] (Scheme 1). The



Scheme 1.

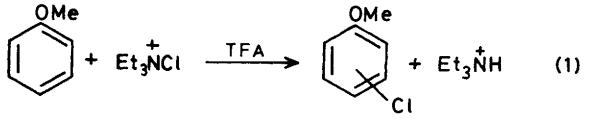
conditions were comparable to those used in our laboratory for the successful chlorination of alkanes with *N*-chlorotrialkylammonium salts,[18] a reaction which involves hydrogen-atom abstraction by trialkylaminium radicals (Scheme 2). The anisole



Scheme 2.

reactions, however, give chloroanisoles and are unaffected by illumination. Indeed mixing equimolar quantities of anisole and NCTA in TFA in the dark gives a quantitative conversion into chloroanisoles and protonated amine [equation (1)].

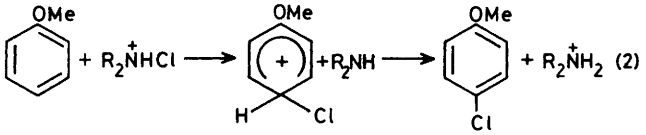
The kinetics of the chlorination of aromatic compounds with *N*-chloroalkylamines in acidic media were studied briefly in the 1950s [19] and the authors concluded that the chlorinating agent



(1)

is the protonated *N*-chloroamine. More recently, the research of Minisci and his co-workers,[16] into redox-initiated aromatic amination using *N*-chloroamines, has shown that chlorination can occur as a side reaction in these systems with the more electron-rich substrates. In none of the investigations above was the isomeric composition of the chloroaromatics reported.

The most striking feature of the chlorinations with *N*-chlorinated amines in strongly aidic media is the extremely high site-selectivity for 4-chlorination and the negligible extent of further reaction leading to dichloro-anisole or -phenol. If these reactions are typical arenium ion electrophilic substitutions [equation (2)], chlorination at the 2-position must be prevented

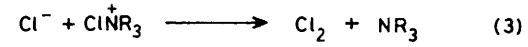


(2)

either through the bulk of the attacking species or because the reagents form a complex that directs substitution to the 4-position. Alternatively the reactions may proceed by some other mechanism.

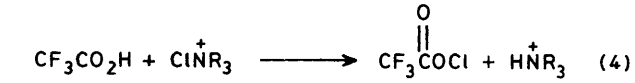
A detailed discussion of the mechanism of this and related chlorinations will be the subject of another paper in this series. However, it is appropriate here to eliminate some of the possible chlorinating agents.

The data are inconsistent with three species namely chlorine, chlorine trifluoroacetate, and protonated chlorine trifluoroacetate. The first species would be formed by nucleophilic displacement by chloride on the *N*-chloroammonium ion [equation (3)]. However, chlorine can be rejected as the active



(3)

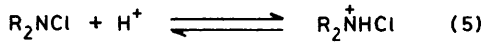
species in these reactions because the presence of chloride ion has no effect on the product distributions and, more importantly, chlorine in TFA leads to relatively unselective chlorination. The other two species, which might be generated by equation (4), can also be eliminated since the solvent TFA



(4)

can be replaced by aqueous sulphuric acid. Furthermore, reactions under conditions that should favour the formation of chlorine trifluoracetate show poor site-selectivity. However, solutions of *N*-chloropyridinium ions in TFA are much less stable than those of aliphatic chloroammonium ions. It is possible that with the former their lower selectivity could be due to partial coversion into chlorine or chlorine trifluoroacetate in the reaction medium. Alternatively these reactions could generate some other less selective attacking species.

The most likely selective chlorinating species are the *N*-chloroammonium ions formed by protonation of *N*-chlorodialkylamines by the acidic solvent [equation (5)]; with *N*-



(5)

chlorotrialkylammonium salts protonation is unnecessary. In agreement with this conclusion the reactions of NCP show a stronger dependence on acidity than those of NCTA. The decrease in yield and selectivity with decreasing acidity observed in NCP reactions might be attributed to equilibrium (5) assuming that the protonated species is the selective chlorinating agent. Consequently at the lower acid concentrations the smaller proportions of protonated NCP will lead to slower chlorination and alternative, less selective chlorinating agents (such as chlorine or NCP) can compete for the substrate. With NCTA the yield of chloroanisoles decreases because decomposition of NCTA begins to compete effectively with aromatic chlorination as the acidity is lowered. Although the mechanism of the decomposition is not clearly understood, the products are probably triethylamine and chlorine and hypochlorous acid. Chlorination by either of the latter two species would account for the decrease in selectivity observed in the low-acidity reactions.

The absence of dichlorination in the reactions of anisole and most of the reactions of phenol arises predominantly from an electronic and to a lesser extent a steric effect of the chlorine in the primary product. Thus competitive chlorinations of anisole and 2-chloroanisole with NCP in TFA show that the former substrate is *ca.* 600 times more reactive than the latter. 4-Chloroanisole is even less reactive than the 2-isomer. These and other aspects of the influence of substituents on these reactions will be discussed in a subsequent paper.

Experimental

Materials.—All the materials were commercial reagent grade unless otherwise stated and were obtained from Aldrich Chemical Co. Ltd., B.D.H. Ltd., or Fisons Scientific Apparatus Ltd.

N-Chlorotriethylammonium chloride was prepared by a modification of the method of Böhme and Krause.[20] A solution of triethylamine (0.1 g) in tetrachloromethane (5 cm^3, spectroscopic grade) was frozen to −78 °C and a saturated solution of chlorine in tetrachloromethane (10 cm^3) was similarly frozen. The latter was allowed to commence thawing and was added to the frozen amine solution. The mixture was agitated without cooling and when completely melted a fine suspension of *N*-chlorotrimethylammonium chloride was obtained. This was frozen and then trifluoroacetic acid (TFA) was added dropwise, with shaking, to the thawing mixture. The TFA solution was separated and the yield of the *N*-chloroammonium salt was determined (92 ± 5%) by ^{1}H n.m.r. spectroscopy [δ 1.60 (t, 9 H) and 3.95 (q, 6 H)] using acetic acid as the internal standard.

N-Chlorotriethylammonium perchlorate was obtained by stirring a TFA solution of the chloride salt with silver perchlorate and removing, by filtration, the silver chloride.

N-Chlorotrimethylammonium acetate was obtained by adding a 10% molar excess of silver acetate in TFA to an ice-cold suspension of the chloride salt[20] in tetrachloromethane. The solutions were thoroughly mixed and the TFA layer was removed and the yield of *N*-chlorotrimethylammonium acetate (70 ± 5%) was measured by ^{1}H n.m.r. spectroscopy [δ 4.05 (s)] using nitrobenzene as the internal standard.

N-Chloro-1-azoniabicyclo[2.2.2]octane acetate was prepared from 1-azabicyclo[2.2.2]octane by the method used for *N*-chlorotrimethylammonium acetate. ^{1}H N.m.r. spectroscopy [δ(TFA) 2.00—2.60 (m, 7 H) and 3.95—4.40 (m, 6 H)] was used to calculate the yield (56 ± 5%).

N-Chloropiperidine, *N*-chloro-*N*-methylcyclohexylamine, and *N*-chloro-*N*-methylbenzylamine were prepared following the method of Spanswick and Ingold.[21] *N*-Chloropiperidine had b.p. 34.5 °C at 15 mmHg (lit.,[22] 43 °C at 20 mmHg); δ(TFA) 1.5—2.3 (m, 6 H) and 3.4—4.3 (m, 4 H). *N*-Chloro-*N*-methylcyclohexylamine had b.p. 63 °C at 14 mmHg; δ(TFA) 1.10—2.50 (m, 10 H), 3.6 (s, 3 H), and 3.8 (m, 1 H). *N*-Chloro-*N*-methylbenzylamine was not distilled and had δ($CDCl_3$) 2.9 (s, 3 H), 4.0 (s, 2 H), and 7.35 (s, 5 H).

N-Chloromorpholine was obtained by adding morpholine (0.34 mol) dropwise to a stirred cold (< 10 °C) solution of 1.5M sodium hypochlorite (250 cm^3). After 5 min the *N*-chloromorpholine was extracted into diethyl ether (4 × 50 cm^3). The combined extracts were dried ($MgSO_4$), then concentrated with a rotary evaporator (below 30 °C). Distillation gave *N*-chloromorpholine (35.5 g, 85%), b.p. 54—55 °C at 27 mmHg (lit.,[23] 52—53 °C at 17 mmHg); δ($CDCl_3$) 3.2 (br t, 4 H) and 3.8 (br t, 4 H).

N-Chloropyridinium chlorides were prepared from the pyridine and chlorine in TFA, by the method used for *N*-chlorotrimethylammonium chloride, and were converted into acetate salts by the procedure above for *N*-chlorotrimethylammonium acetate. The TFA solutions which contained a mixture of pyridinium and *N*-chloropyridinium salts were used without purification. Although the yields (15—35%) could be measured by ^{1}H n.m.r. spectroscopy, overlap of the absorptions from the protonated and the *N*-chlorinated pyridines made a complete spectral assignment of the latter impossible.

Solutions of the *N*-chloroammonium salts were freshly prepared for each experiment. To avoid problems arising from their thermal instability,[15] the salts were never isolated as solids. The *N*-chloroamines after purification were stored in the dark at −20 °C.

Silver trifluoroacetate was obtained quantitatively by dissolving silver acetate (0.2 g) in TFA (5 cm^3) and then removing the acids by rotary evaporation to give a white solid. ^{1}H N.m.r. spectroscopy showed that the product was free of silver acetate.

Instrumentation.—^{1}H N.m.r. spectra for $CDCl_3$ and TFA solutions were obtained with Varian A-60A (60 MHz), Varian EM 360A (60 MHz), and JEOL JNM-MH-100 (100 MHz) spectrometers. G.c. was performed on Pye Series 104 and PU 4500 instruments equipped with flame-ionisation detectors coupled to an R.E. 541 Venture Servoscribe recorder. Glass columns (2.1 m, 2 mm i.d.) were packed with 10% w/w DEGA (Cambridge Instruments Ltd.) on 80—120 mesh Celite (B.D.H. Ltd.); 5% w/w tris-(2,4-xylyl)-phosphate (Phase Separations Ltd.) on 100—120 mesh Gas Chrom Q (Phase Separations Ltd.); and 20% w/w Polyox 600,000 (Union Carbide Ltd.) on 80—120 mesh Celite.

Chlorination Procedures.—(a) *Reactions in TFA using* N-*chloroammonium salts.* Nitrogen was gently bubbled through a solution containing a measured amount (^{1}H n.m.r. analysis) of *N*-chloroammonium salt in TFA at room temperature to remove any traces of free chlorine. An equivalent quantity of anisole or phenol was then added and the extent of reaction was assessed by ^{1}H n.m.r. spectroscopy. When the reaction had finished the mixture was added dropwise to ice-cooled water and the organic material was extracted into diethyl ether. The ether layer was dried ($MgSO_4$) and analysed by gas chromatography.

(b) *Reaction in TFA with* N-*chloroamines.* The *N*-chloroamine (0.1 g) was added to TFA at −15 °C and the resulting solution was warmed to room temperature before an equimolar quantity of anisole or phenol was added. The procedure then used to monitor, work-up, and analyse the reaction as described above.

(c) *Chlorinations in aqueous sulphuric acid.* A solution of the *N*-chloroammonium salt or *N*-chloroamine was prepared in aqueous sulphuric acid, in place of TFA, and an equivalent amount of anisole or phenol was added. The mixture was then either vigorously stirred or shaken to ensure that the aqueous

acid remained saturated in substrate throughout the reaction. At the end of the reaction (monitored by ^{1}H n.m.r. spectroscopy) the aromatic compounds were extracted into diethyl ether and analysed by g.c.

(d) *Chlorination of anisole with chlorine in TFA.* Anisole was added to TFA which had previously been saturated with chlorine. The reaction was monitored, worked-up and analysed as described above.

(e) *Chlorination of anisole with chlorine and silver trifluoroacetate in TFA or in TFA–TFAA.* Chlorine was gently bubbled through a solution of silver trifluoracetate in TFA. The precipitated silver chloride was filtered off and anisole (equivalent to the amount of silver trifluoracetate) was added to the acidic solution. This reaction was repeated with a 5:1 (v/v) mixture of TFA–TFAA. The products were worked-up and analysed as described above.

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